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1 **Chalcophile Element Processing Beneath a Continental Arc Stratovolcano**

2 Daniel Cox<sup>\*1</sup>, Sebastian F. L. Watt<sup>1</sup>, Frances E. Jenner<sup>2</sup>, Alan R. Hastie<sup>1</sup>, Samantha J.  
3 Hammond<sup>2</sup>

4

5 <sup>1</sup>School of Geography, Earth and Environmental Sciences, University of Birmingham,  
6 Edgbaston, Birmingham, B15 2TT, U.K.

7 <sup>2</sup>School of Environment, Earth and Ecosystem Sciences, Open University, Walton Hall,  
8 Milton Keynes, MK7 6AA, U.K.

9

10 <sup>\*</sup>Corresponding author: DXC506@student.bham.ac.uk. School of Geography, Earth and  
11 Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT,  
12 U.K.

13

14 **Abstract**

15 The chalcophile elements are important both in terms of their economic value and as potential  
16 tracers of magmatic processes at convergent margins. However, because of analytical  
17 difficulties, comprehensive datasets of chalcophile element concentrations for volcanic rocks  
18 are rare. Here, we present analyses of a near complete suite of chalcophile elements (S, Cu,  
19 Ag, Se, As, Sb, Sn, W, Mo, Pb, Bi, Tl, Zn, Ga, Co) for volcanic rock samples collected from  
20 a typical continental arc stratovolcano in southern Chile (Antuco). Enrichment in Pb, Bi, W,  
21 Tl, Sb and As relative to Parental-MORB indicates that these elements have been mobilised  
22 from the subducting slab into the sub-arc mantle wedge, in contrast to Cu and Ag. Very low  
23 Se concentrations suggest that Se, like S, was lost during co-eruptive degassing of the Antuco

24 magmas. Previous studies on oceanic arcs have demonstrated that as higher  $fO_2$  subduction-  
25 related magmas ascend through the overlying lithosphere, magnetite fractionation may trigger  
26 sulfide fractionation during crystallisation. If such a process is extensive and has a sharp  
27 onset, this would result in a plummet in the Cu, Se and Ag contents of the residual melt. At  
28 Antuco, although a decrease in the  $Fe_2O_{3(T)}$  and  $TiO_2$  concentrations at ~55 wt.%  $SiO_2$  (~3  
29 wt.% MgO) indicates magnetite fractionation, this is not associated with a corresponding  
30 drop in Cu contents. Instead, we observe a general decrease in Cu and a decrease in Cu/Ag  
31 with increasing  $SiO_2$  and decreasing MgO. Furthermore, Cu/Ag in the most primitive Antuco  
32 rocks are lower than the global MORB array, indicating that the melts were sulfide saturated  
33 at an early stage in their crustal evolution. Through modelling fractional crystallisation, we  
34 show that only a minor volume (0.5 – 0.6 vol.%) of fractionating sulfide is needed to produce  
35 divergent trends in Cu and Ag, as observed in the Antuco samples. Our results show that  
36 sulfide fractionation occurred from an early stage during the crustal evolution of Antuco's  
37 magmas. We infer that this was promoted by stalling in the lower crust, which for oxidised  
38 magmas at depths >20 km is within the sulfide stability field. However, elevated  $D_{Y_N/Yb_N}$  of  
39 the Antuco magmas compared to oceanic island arc magmas provides an additional, or  
40 alternate mechanism to inducing sulfide fractionation in the lower crust prior to ascent,  
41 through initial garnet fractionation. Fractional crystallisation within this depth range meant  
42 that later magnetite fractionation had only a minor impact on the partitioning behaviour of the  
43 chalcophile elements. In contrast, arc magmas transiting thinner crust may not experience  
44 sulfide saturation until a later stage in their evolution, induced by magnetite fractionation.  
45 Our results imply that convergent margin crustal thickness, and therefore the depth range of  
46 magmatic differentiation, determines the dominant control on initial magmatic sulfide  
47 saturation and therefore the primary distribution of chalcophile elements. This implies that

48 secondary processes are required to explain the transport and concentration of sulfides and  
49 chalcophile elements at shallower crustal levels.

50

51 Keywords: chalcophile elements, sulfide, saturation, fractionation, continental arc, Antuco

52

### 53 **1. Introduction**

54 The chalcophiles (e.g., Cu, Ag, Se, Pb, Bi) are an important suite of elements both in terms of  
55 their economic value and their potential to investigate magmatic processes active at  
56 convergent margins (Jenner, 2017; Jenner et al., 2010; Noll Jr et al., 1996; Richards, 2009;  
57 Sillitoe, 2010; Wilkinson, 2013). Compared to the bulk continental crust, many of the  
58 economically important chalcophile elements are extremely enriched in porphyry Cu-Au  
59 deposits that are globally associated with convergent margins (Sillitoe, 2010; Wilkinson,  
60 2013). Because primitive subduction-related magmas are not enriched in Cu, Ag, Se or Au  
61 relative to mid-ocean ridge basalt (MORB) magmas, there has been considerable debate  
62 regarding the crustal processes that contribute to the formation of magmatic-hydrothermal ore  
63 deposits (Chiaradia, 2014; Jenner, 2017; Jenner et al., 2010; Lee et al., 2012; Matjuschkin et  
64 al., 2016; Richards, 2009; Wilkinson, 2013). For example, although there is a global  
65 association between porphyry deposits and convergent margins (Sillitoe, 2010), the spatial  
66 distribution of these deposits is sporadic (Sillitoe, 1997) and the remainder of the bulk  
67 continental crust is notably depleted in Cu, Se and Au compared to primitive arc magmas  
68 (Jenner, 2017; Lee et al., 2012). Given that the bulk continental crust has been generated at  
69 convergent margins, these observations suggest that most arc magmas are not predisposed to  
70 fuel the formation of economically viable ore deposits (Jenner, 2017).

71 The way in which many chalcophile elements are processed and distributed within a  
72 magmatic system and throughout the continental crust is controlled by the stability of sulfides  
73 (Chiaradia, 2014; Lee et al., 2012; Richards, 2015). The point at which a magma becomes  
74 saturated in a sulfide phase is a function of the temperature, pressure, oxygen fugacity and  
75 composition of the magma (Matjuschkin et al., 2016; Mavrogenes and O'Neill, 1999; O'Neill  
76 and Mavrogenes, 2002; Wallace and Edmonds, 2011). Geochemical studies of volcanic  
77 glasses have demonstrated that the Cu/Ag of MORB magmas remains constant following  
78 sulfide saturation, in contrast to a decreasing post-saturation Cu/Ag in arc-related magmas  
79 (Jenner et al., 2015, 2010). These varying trends have been attributed to differences in the  
80 nature of the fractionating sulfide phase during differentiation of MORB (molten sulfide) and  
81 subduction-related (crystalline sulfide) magmas (Jenner, 2017; Jenner et al., 2010). This  
82 interpretation is supported by experimental studies indicating that Cu and Ag have similar  
83 partition coefficients with respect to molten sulfide, but that Cu is more compatible in  
84 crystalline sulfide than Ag (Li and Audétat, 2015, 2012). During differentiation of oceanic  
85 convergent margin magmas, the decrease in Cu/Ag (marking sulfide saturation and  
86 fractionation of crystalline sulfide) coincides with a sharp decrease in Fe, V, Cu, Ag, S and  
87 Au (reversing the preceding trend of increasing concentrations with increasing SiO<sub>2</sub> and  
88 decreasing MgO), suggesting that magnetite fractionation 'triggers' reduction-related sulfide  
89 saturation (the 'Magnetite Crisis'; Jenner et al., 2010) during the evolution of oceanic arc  
90 magmas (Chiaradia, 2014; Jenner, 2017). Although the 'Magnetite Crisis' potentially controls  
91 sulfide processing and the fate of chalcophile elements during island arc-magmatic evolution,  
92 such a mechanism has not been fully explored within a continental arc.

93 Despite the importance of the chalcophile elements for understanding both mantle and crustal  
94 processes, they are still a relatively under-studied suite of elements. This is partly because  
95 elements such as Se and Ag, which can be used in conjunction with Cu to place constraints

96 on the timing of sulfide saturation (see Jenner, 2017, and references therein), are difficult to  
97 analyse in both natural and experimental materials (Jenner and Arevalo, 2016). Thus, studies  
98 of chalcophile element processing at continental arcs have focussed mainly on whole rock Cu  
99 systematics, arguing that most arc magmas reach sulfide saturation during crustal  
100 differentiation (Chiaradia, 2014; Jenner, 2017; Lee et al., 2012; Richards, 2015). This is  
101 supported by observations of magmatic sulfide inclusions across a broad range of bulk  
102 compositions in Ecuadorian arc volcanic rocks, hosted predominantly in magnetite but also in  
103 silicate phases (Georgatou et al., 2018).

104 Chiaradia (2014) used Cu systematics to argue that magmas erupting through thicker crust  
105 (>30 km) are of calc-alkaline affinity and require smaller proportions of crystallisation to  
106 reach sulfide saturation compared to tholeiitic magmas erupting through thinner crust (<20  
107 km), as a consequence of their higher H<sub>2</sub>O and  $fO_2$ . This would thus influence the timing of  
108 magnetite-triggered sulfide fractionation and the resulting drop in total Fe content and  $fO_2$  of  
109 the evolving magma. However, experimental constraints suggest an alternative explanation  
110 (Matjuschkin et al., 2016), showing that with increased pressure, and therefore depth, the  
111 sulfide stability field shifts to higher  $fO_2$ . In conjunction with this widening of the sulfide  
112 stability field with depth, Jenner (2017) used the Cu deficit and the significantly lower Cu/Ag  
113 of the bulk continental crust compared to mantle-derived melts to argue that continental crust  
114 formation is dominated by the addition of magmas that fractionate high Cu/Ag sulfides at the  
115 base of the continental crust (i.e. in a deep crustal hot zone; cf. Annen et al., 2006), prior to  
116 magma ascent to higher crustal levels.

117 Alternatively, Tang et al. (2018) argue that the Fe-depleting trend (i.e., calc-alkaline series)  
118 observed in magmas erupting through thick crust is attributable to garnet fractionation, from  
119 magmas that have initial  $fO_2$  comparable to MORB. Furthermore, Tang et al. (2018) suggest  
120 that magmas erupting through thick continental crust inherit their high  $fO_2$  (>MORB) as a

121 consequence of this garnet fractionation. However, the limited overlap between the garnet  
122 stability field and the crustal depth range of magmatic differentiation (Alonso-Perez et al.,  
123 2009) suggests that garnet fractionation is unlikely to explain the higher  $fO_2$  of all arc  
124 magmas, particularly those erupted on thinner crust, and high  $fO_2$  compared to MORB  
125 (Matjuschkin et al., 2016) appears to be a ubiquitous characteristic of arc magmas prior to the  
126 earliest stages of their differentiation (Richards, 2015; Kelley and Cottrell, 2012). As the  
127 solubility of S decreases with decreasing total Fe content of a magma, garnet fractionation  
128 would promote sulfide fractionation during magmatic differentiation at high pressures.  
129 Regardless of whether the ‘Magnetite Crisis’, a shift in the sulfide stability field with pressure  
130 (depth), garnet fractionation, or potentially a combination of the above processes are the  
131 ‘trigger’ for sulfide saturation, there is an emerging consensus that most continental arc  
132 volcanic rocks should fractionate sulfide in the lower crust prior to ascent. As a result,  
133 continental arc volcanic rocks should have lower Cu/Ag than primitive arc magmas and the  
134 entire oceanic crust, but there is a lack of reliable Cu/Ag in the literature to test this  
135 hypothesis.

136 Here, we present major and trace element volcanic rock compositions from Antuco Volcano,  
137 Chile, a typical continental arc stratovolcano, in order to characterise chalcophile behaviour  
138 during the generation and subsequent processing of magmas through a continental arc. Bulk  
139 compositions at Antuco span basaltic to andesitic compositions (Lopez-Escobar et al., 1981;  
140 Martínez et al., 2018), and are interpreted to initially stall and crystallise at the base of the  
141 continental crust (~40 km) prior to ascent and shallower crystallisation (~0.9 – 1.5 kbar [~2 –  
142 5 km]; Martínez et al., 2018). This represents an ideal setting to test current models of  
143 chalcophile element processing within a continental arc, which are based on inferences drawn  
144 from oceanic arcs or datasets limited principally to Cu analyses. By generating a novel  
145 dataset that includes a near complete suite of chalcophile elements (S, Cu, Ag, Se, As, Sb, Sn,

146 W, Mo, Pb, Bi, Tl, Zn, Ga, Co), we seek to refine the understanding of the controls of  
147 chalcophile element distribution in continental arcs.

## 148 **2. Tectonic setting and geology of Antuco Volcano**

149 Volcanism in the South American Andes has been divided into four zones, the Northern,  
150 Central, Southern and Austral Volcanic zones, each of which is further divided into several  
151 segments (Stern, 2004). Antuco marks the northernmost point of the central part of the  
152 Southern Volcanic Zone (SVZ, **Fig. 1**) (Hickey-Vargas et al., 2016; Lopez-Escobar et al.,  
153 1995). Antuco is the younger (Pleistocene – Holocene age) of a pair of stratovolcanoes (the  
154 other being the Pleistocene Sierra Velluda Volcano) that form a volcanic complex at 37.2°S  
155 (Lopez-Escobar et al., 1981; Martínez et al., 2018). The Antuco – Sierra Velluda volcanic  
156 complex forms an oblique alignment (50 - 70° E of N) to the main arc (Lopez-Escobar et al.,  
157 1995). Antuco is the smaller of the two stratovolcanoes, with a basal diameter of ~11 km,  
158 rising to 2979 metres above sea level, and an estimated volume of 62 km<sup>3</sup> (Martínez et al.,  
159 2018).

160 Volcanism at Antuco has been divided into two phases – Phase 1 and Phase 2 Antuco (**Fig.**  
161 **1a**) – separated by a westward directed, mid-Holocene sector collapse (Lopez-Escobar et al.,  
162 1981; Thiele et al., 1998) dated at 6.2 ka by Lohmar et al. (2005) and 4 ka by Clavero and  
163 Godoy (2010). Recently, Martínez et al. (2018) used a comprehensive dataset of <sup>40</sup>Ar / <sup>39</sup>Ar  
164 dates to further define Early (commencing at 150.4 ka) and Late (~16.3 to 6.2 ka) periods of  
165 volcanism during Phase 1. Phase 1 lavas show a slightly broader compositional range (basalt  
166 to andesite) than Phase 2 lavas (basalt to basaltic andesite) (Lohmar et al., 2005, 1999;  
167 Martínez et al., 2018).

168 Antuco is typical of stratovolcanoes in the SVZ, both in terms of its dimensions (Volker et  
169 al., 2011) and range of erupted compositions, but is also amongst the most isotopically



170 primitive volcanoes in the SVZ (Hickey-Vargas et al., 2016; Hildreth and Moorbath, 1988;  
171 Lohmar et al., 1999). Primitive rock compositions at Antuco indicate a predominantly fluid  
172 enriched, depleted-MORB mantle source, typical of the central SVZ, which has been used as  
173 an endmember to explore additional crustal-derived source enrichment further north in the  
174 SVZ (Holm et al., 2016, 2014). In a global context, the parameters defining this segment of  
175 the SVZ (Syracuse et al., 2010), including a crustal thickness of 40 km (Hickey-Vargas et al.,  
176 2016), suggest that it is a representative continental arc setting. The broad range in lava  
177 compositions and previous interpretations that the Antuco magmas stalled at the base of the  
178 continental crust prior to crystallisation at lower pressures (Martínez et al., 2018), make  
179 volcanic rocks from Antuco ideal for investigating the processing and distribution of the  
180 chalcophile elements during ascent of magmas through the continental crust.

### 181 *2.1. Sample descriptions*

182 The current study made use of twenty-six volcanic rock samples (fifteen Phase 1 and eleven  
183 Phase 2 samples), each from separate lava flows or pyroclastic units, which are thus  
184 considered to represent separate eruptive events and discrete batches of magma. The location  
185 of each sample is highlighted on the map of Antuco in **Fig. 1a**. Petrographically, all samples  
186 have a porphyritic texture. The groundmass is generally cryptocrystalline (crystals too small  
187 to identify) and varies from light grey to dark in colour. Phenocryst phases are dominated by  
188 plagioclase (most common) and olivine, usually comprising *c.* 10 – 20 vol.% (all  
189 phenocrysts) of thin sections (minus vesicles; can be as great as *c.* 40 vol.% and as low as  
190  $\ll 5$  vol.%). Opaques and clinopyroxene phenocrysts are rare. Plagioclase phenocrysts are  
191 mostly subhedral to euhedral laths, and commonly display simple and albite twinning and  
192 oscillatory zoning. Coarse and fine sieve textured plagioclases are common across the  
193 samples. Olivine phenocrysts are usually anhedral (mostly rounded) and fractured.  
194 Glomerocrysts are observed in all sections and comprise plagioclase and/or olivine. Sample

195 A28-6 shows extensive Fe-oxyhydroxide alteration in both phenocryst phases and  
196 groundmass. Brief sample descriptions are provided as Supplementary Data (**Appendix A**).

### 197 **3. Analytical Methods**

198 The major and trace element compositions of the Antuco samples were determined using  
199 whole rock analysis. Weathered material was removed from the samples via hammering. To  
200 avoid metal contamination, samples were crushed using a fly press and powdered in an agate  
201 planetary ball mill. Samples were analysed for major elements using either X-ray  
202 Fluorescence (XRF) at The School of Ocean and Earth Science, National Oceanography  
203 Centre, University of Southampton, U.K., or inductively coupled plasma optical emission  
204 spectrometry (ICP-OES) at The School of Earth and Ocean Sciences, Cardiff University,  
205 Wales, U.K. Replicate XRF analyses were undertaken at The School of Geosciences,  
206 University of Edinburgh, Scotland, U.K. to test analytical precision. The loss on ignition  
207 (LOI) of each sample was measured using  $\sim 1.5 \pm 0.0001$  g of sample powder, baked at  
208  $900^{\circ}\text{C}$ . Acid digestion of sample powders was undertaken at The Open University. 100 mg of  
209 each sample powder was digested in a multi-stage HF-HNO<sub>3</sub> digestion process, with dry  
210 down temperatures set at  $65^{\circ}\text{C}$  to minimise volatile element loss. Solutions were made up to  
211 1000-fold dilutions of the original powder weight in a 2% HNO<sub>3</sub> solution, prior to analysis.  
212 Blanks and International Standard Reference Materials were prepared in the same manner.  
213 Trace elements (except Tm) were analysed using an Agilent 8800 Triple Quadrupole  
214 inductively coupled plasma mass spectrometer (ICP-MS/MS; also referred to as ICP-QQQ) at  
215 The School of Environment, Earth and Ecosystem Sciences, The Open University, U.K.  
216 Lithium, Sc, Co, Ni, Rb, Sr, Y, Zr, Nb, Mo, Sn, Sb, Cs, Ta, W, Tl, Th and U were analysed in  
217 a no gas mode, the REE, S, As, Ba, Hf and Se were analysed in reactive O<sub>2</sub> gas mode, and V,  
218 Cr, Cu, Zn, Ga, Ge, Pb and Bi were analysed in collisional He gas mode. Ag was analysed in  
219 reactive NH<sub>3</sub> gas mode, and an offline correction to remove ZrO interferences was

220 subsequently employed. An online standard (containing Be, Rh, In and Tm) was run at the  
221 same time as samples and unknowns and used to monitor and correct for drift. Thulium was  
222 obtained through ICP-MS analysis at Cardiff University. Data accuracy was assessed using  
223 the International Standard Reference Materials JB1a, JA2, JG1a, BHVO-2 and DNC-1.  
224 Analyses of International Standard Reference Materials fall mostly within 5 % of published  
225 values for all major and trace elements. Exceptions include Se (10 %), Pb (11 %), As (50 %),  
226 W (30%) and Ge (7 %); however, the relative standard deviations of repeat analyses for these  
227 elements are mostly  $\leq 7$  %. We still report values for all these elements, given that  
228 International Standard Reference Material values for the chalcophile elements as a whole are  
229 not as well constrained as other trace elements (Jenner and Arevalo, 2016), with some  
230 chalcophile elements undetermined in some standards [for example, those for As in BHVO-2  
231 are only constrained using a single analytical technique (Jochum et al., 2016)]. No suitable  
232 published values for Ag for the reference materials we used were available, and therefore we  
233 defined values used in our calibration line using standard addition methods. Complete  
234 analyses, including International Standard Reference Materials are provided as  
235 Supplementary Data (**Appendix B, Tables B1 and B2**).

#### 236 **4. Geochemical Results**

237 In terms of classification, both Phase 1 and Phase 2 samples span a similar range on a total  
238 alkali against silica (TAS) plot (**Fig. 2a**). Phase 1 samples range from basalt to andesite, with  
239 Phase 2 samples ranging from basaltic-andesite to andesite; however, two samples, one from  
240 each phase, classify as trachy-andesite. The majority of samples plot in the calc-alkaline field  
241 on an AFM (alkali – FeO – MgO) ternary plot (**Fig. 2b**) following the boundaries of Kuno  
242 (1968) and Irvine and Baragar (1971).

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243 Antuco samples range from 51.6 to 62.3 wt.% SiO<sub>2</sub> and 1.5 to 6.7 wt.% MgO (anhydrous  
244 values) (**Fig. 3** and **Appendix C, Figs. C1** and **C2**). Titanium dioxide, Fe<sub>2</sub>O<sub>3</sub> (as total Fe) and  
245 V display broadly similar trends, all increasing with increasing SiO<sub>2</sub>, reaching a maximum of  
246 1.6 wt.%, 10.9 wt.% and ~290 ppm, respectively at ~54-55 wt.% SiO<sub>2</sub>, before decreasing  
247 with further increasing SiO<sub>2</sub> (**Fig. 3**). The trends in V, TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> are also seen when  
248 plotted against MgO, reaching a maximum at ~3 wt.% MgO (**Fig. C1**). Many of the Phase 2  
249 samples have higher TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> at a given SiO<sub>2</sub> (and MgO) compared to Phase 1  
250 samples. Calcium oxide shows a positive correlation with MgO; Al<sub>2</sub>O<sub>3</sub> shows a peak in  
251 contents between 3 – 4 wt.% MgO; and K<sub>2</sub>O, Na<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub> show negative correlations  
252 (**Fig. C2**). Manganese oxide shows no correlation with MgO (**Fig. C2**). Our data are  
253 consistent with the major element data discussed in detail by Martínez et al. (2018), in the  
254 most recent study of Antuco (**Figs. 2, 3, C1** and **C2**).

255 Most of the chalcophile elements (excluding Cu and Se) show negative correlations with  
256 MgO across the Antuco sample set (**Fig. C3** and **C4**). Phase 1 samples show a broad overall  
257 decrease in Cu with increasing SiO<sub>2</sub> (and decreasing MgO), which follows the trend defined  
258 by sulfide saturated lava samples from Ecuador (Georgatou et al., 2018) (**Figs. 4a** and **C3a**).  
259 Additionally, Phase 1 samples show a decrease in Cu/Ag with increasing SiO<sub>2</sub> and decreasing  
260 MgO (**Figs. 4e** and **C3c**). Three of the ~59 – 62 wt.% SiO<sub>2</sub> (~1.5 – 2.5 wt.% MgO) Phase 1  
261 samples have considerably lower Cu contents (5.4 – 25.0 ppm) and Cu/Ag (124 – 691)  
262 compared to other samples with a comparable SiO<sub>2</sub> and MgO (48.6 – 58.9 ppm Cu and 771 –  
263 1497 Cu/Ag). The Cu contents of Phase 2 samples remain approximately constant with  
264 increasing SiO<sub>2</sub> and decreasing MgO (**Figs. 4a** and **C3a**).

265 At a given MgO, the most primitive (highest MgO) Antuco samples have higher Pb, Tl, Sb,  
266 As and similar Bi and W compared to the MORB array (**Fig. C4**). The contents of Mo, Sn,  
267 Cu and Ag of the most primitive Antuco samples are comparable to MORB (**Figs. C3** and

268 **C4).** The S and Se contents of the Antuco samples are considerably lower than the MORB  
269 array (**Fig. 4b** and **d**). On a Parental-MORB normalised plot (**Fig. 5a**), the Antuco samples  
270 display negative Nb-Ta anomalies (barring one showing only a negative Nb anomaly)  
271 compared to neighbouring elements. Samples also show substantial peaks (15 – 100 times  
272 Parental-MORB) in W, Tl, As, Pb, Sb and Bi relative to the REE.

## 273 **5. Discussion**

### 274 *5.1. Subduction mobile chalcophile elements*

275 In order to distinguish which of the chalcophile elements are mobile during subduction,  
276 Jenner (2017) normalised samples to Parental-MORB (calculated), which represents an  
277 undifferentiated melt composition, approximating that of the bulk oceanic crust, and can  
278 therefore be used to constrain the relative differences in elemental fluxes at convergent  
279 margins compared to at MOR. On a Parental-MORB normalised plot (**Fig. 5a**), the Antuco  
280 samples display geochemical signatures typical of a volcano situated above a subduction zone  
281 (e.g., Pearce et al., 2005); enrichments in mobile large ion lithophile elements (LILE)  
282 compared to the moderately mobile REE, and enrichments of the moderately mobile REE  
283 compared to the high field strength elements (HFSE). All Antuco samples display  
284 enrichments in chalcophile elements W, Tl, As, Pb, Sb and Bi (**Fig. 5a**) compared to the REE  
285 and the HFSE, demonstrating that W, Tl, As, Pb, Sb and Bi are mobile during subduction. By  
286 comparison, other chalcophile elements (Mo, Sn, Zn, Ga, Co) appear to be immobile during  
287 subduction. These findings are in general agreement with previous geochemical studies  
288 regarding the relative mobility of chalcophile elements during the petrogenesis of convergent  
289 margin magmas (Jenner, 2017; Noll Jr et al., 1996). Parental-MORB-like Cu and Ag contents  
290 of the most primitive Antuco samples indicate that neither Cu nor Ag were mobilised in a  
291 slab flux to the mantle wedge during subduction, and were thus sourced from the mantle

292 wedge. The minor difference in enrichment of Ag relative to Cu (**Fig. 5a**) is likely a result of  
293 early sulfide fractionation from the Antuco magmas, preferentially removing Cu (over Ag).

294 When plotted in isolation, the mobile (i.e., Rb, Th, Ba, U, W, Tl, As, Pb, Sb and Bi, **Fig. 5b**),  
295 moderately mobile (i.e., REE, **Fig. 5c**) and immobile (i.e., HFSE, Mo, Sn Zn, Ga, Sc and Co,  
296 **Fig. 5d**) elements show relatively smooth patterns. Additionally, each group of elements  
297 shows a slight increase in Parental-MORB normalised values with increasing incompatibility  
298 of the element during differentiation of the oceanic crust. Detailed work on the partitioning of  
299 chalcophile and siderophile elements during the differentiation of mantle-derived melts  
300 (MORB and subduction-related volcanic rocks) conducted by Jenner (2017) has shown that  
301 the majority of chalcophile and siderophile elements are incompatible during differentiation  
302 (e.g., As, Sb, Tl, Pb, W, Bi). As such, these elements are preferentially enriched in the upper  
303 oceanic crust (e.g., Evolved-MORB [at ~7 wt.% MgO]) compared to the bulk (Parental-  
304 MORB) and lower oceanic crust, and are therefore more likely to be fluxed into the sub-arc  
305 mantle wedge during arc magma genesis, relative to Cu and Ag, which are compatible and  
306 reside in the lower oceanic crust (Jenner, 2017). Hence, the slight increase in the magnitude  
307 of the enrichments of the mobile elements in the Antuco samples, which mimics the upper  
308 oceanic crustal distributions of elements, suggests that the mobile elements have been added  
309 from the subducting slab to the mantle wedge source of the Antuco magmas in roughly the  
310 same proportions as their distributions in the upper oceanic crust.

### 311 *5.2. Degassing of S and Se*

312 Sulfur is commonly degassed from magmatic systems during magma ascent and/or during  
313 subaerial eruption, and consequently, determining the pre-degassing S content of magmas is  
314 challenging (Jenner et al., 2010; Wallace and Edmonds, 2011). Previous studies have  
315 demonstrated the use of Se, Cu and Ag for reconstructing the pre-eruptive S contents (i.e.,

316 melt inclusion contents of S) of magmatic systems (Jenner et al., 2015, 2010). For example,  
317 during differentiation of backarc basin magmas from the Eastern Manus Basin, the initial  
318 increase in FeO, Cu, Ag and Se, but constant Cu/Ag with increasing SiO<sub>2</sub> (and decreasing  
319 MgO), followed by a sudden drop in Cu, Ag, Se and Cu/Ag at ~60 wt.% SiO<sub>2</sub> (**Fig. 4**), has  
320 been attributed to magnetite-triggered sulfide fractionation rather than Cu, Se and Ag  
321 degassing (Jenner et al., 2015, 2012, 2010). As S is an essential ingredient required for  
322 fractionation of sulfides, and also because melt inclusions from the same suite have sufficient  
323 S for the melts to be considered sulfide saturated, S degassing of the Eastern Manus Basin  
324 and other backarc basin magmas is considered to take place during eruption rather than  
325 differentiation (Jenner et al., 2015, 2010). Evidence for sulfide fractionation prior to S  
326 degassing has also been demonstrated by the presence of magmatic sulfides in convergent  
327 margin magmas (Georgatou et al., 2018; Zelenski et al., 2018), such as those from Ecuador,  
328 which show a similar range in Cu versus SiO<sub>2</sub> systematics to the Antuco samples (**Fig. 4a**).  
329 However, the behaviour of Cu, Ag and Se in the Manus Basin was investigated using glass  
330 samples erupted beneath a significant (>1600 m) water column. Thus, it is important to re-  
331 assess the behaviour of the chalcophile elements during subaerial eruptions.

332 Unlike Cu, Ag, Pb, Tl, Sb, Bi, W, Sn and As, which have contents that are comparable to or  
333 higher than MORB at Antuco, the behaviour of Se appears to be decoupled from the rest of  
334 the chalcophile elements, except S. The very low S and Se concentrations – considerably  
335 lower than Parental-MORB (**Fig. 5a**), the MORB array (**Fig. 4**) and Eastern Manus Backarc  
336 Basin samples (**Fig. 4b, d** and **C3d**) – suggests that both S and Se were degassed from the  
337 melts, during either differentiation and/or eruption. Observations of Se enrichment in  
338 volcanic plumes at Mt Etna (Floor and Román-Ross, 2012) support this interpretation. The  
339 S/Se of the Antuco samples are similar to those observed in the Eastern Manus Backarc basin  
340 suite, but are considerably lower than MORB (**Fig. 4f**), indicating that S was more volatile

341 than Se during degassing. Interestingly, the three samples that have the highest S/Se (i.e., the  
 342 least degassed samples, approaching MORB values) have the lowest Cu contents and Cu/Ag,  
 343 suggesting that sulfur degassing cannot explain the trend to low Cu with increasing evolution  
 344 of the Antuco samples. Given that sulfide fractionation requires the presence of S in the melt,  
 345 we consider that the degassing of S (and Se) must have predominantly taken place during  
 346 eruption rather than during differentiation.

347 *5.3. Crustal processing of the chalcophile elements*

348 Many of the chalcophile elements either have such low sulfide-silicate melt partition  
 349 coefficients ( $D^{\text{sulf-sil}}$ ) that they cannot be used to assess whether a melt has fractionated sulfide  
 350 (e.g., As, Tl, Sb, Mo, Pb, Bi), and/or they show ‘mixed affinities’ (e.g., In, Ga, Sn, Zn, Cd),  
 351 because their bulk partitioning is controlled by a combination of silicate, oxide and sulfide  
 352 minerals (Jenner, 2017). Only a few of the chalcophile elements (e.g., Cu, Ag, Se, Au) are  
 353 sufficiently compatible in sulfide phases to be of use for demonstrating sulfide fractionation  
 354 from an evolving melt. For example, unlike the incompatible elements (e.g., As, Pb, Sb and  
 355 Tl) which show a steep increase in contents with decreasing MgO (**Fig. C4**), the contents of  
 356 Cu and Ag of the Antuco samples remain approximately constant and/or show a subtle  
 357 decrease with increasing SiO<sub>2</sub> and decreasing MgO (**Figs. 4** and **C3**). Thus, like lava samples  
 358 from Ecuador (Georgatou et al., 2018), the full compositional range of Antuco’s magmas  
 359 have been affected by sulfide fractionation. Given the potentially limited depth range of  
 360 sulfide stability in the lower crust (Matjuschkin et al., 2016), this suggests that much of the  
 361 compositional diversity of these magmas was acquired at lower crustal levels (consistent with  
 362 “hot zone” models; e.g., Annen et al., 2006).

363 Unlike samples from the Eastern Manus Backarc Basin, neither the Antuco nor the Ecuador  
 364 samples show an initial increase in Cu with increasing SiO<sub>2</sub> (or decreasing MgO) prior to



365 magnetite fractionation. Broad inflections at Antuco in the trends between  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and V  
366 with  $\text{SiO}_2$  and MgO indicate the onset of magnetite fractionation in these magmas at ~55  
367 wt.%  $\text{SiO}_2$  (~3 wt.% MgO) (**Figs. 3** and **C1**). However, this does not correspond with a drop  
368 in Cu contents for any Phase 2 samples or for the majority of Phase 1 samples (**Figs. 4a** and  
369 **C3a**). A similar pattern is observed in Cu data presented by Martínez et al. (2018); some, but  
370 not all Early/Late Antuco samples (Phase 1 Antuco) display a drop in Cu contents post-55  
371 wt.%  $\text{SiO}_2$  (or post-3 wt.% MgO), but this drop is not observed in the post-collapse samples  
372 (Phase 2 Antuco). These systematics suggest that magnetite fractionation did not play a  
373 strong control on Cu partitioning in the Antuco magmas, because the melts were already  
374 sulfide saturated before magnetite saturation. A minor impact of magnetite fractionation on  
375 the proportion of sulfide fractionation is, however, suggested by the scatter to lower Cu/Ag of  
376 some of the Phase 1 samples at ~55 wt.%  $\text{SiO}_2$  and ~3 wt.% MgO (**Figs. 4e** and **C3c**).

377 The indistinguishable Cu/Ag of MORB, oceanic island basalts, oceanic plateau basalts,  
378 primitive convergent margin magmas and mantle xenoliths has been attributed to the  
379 presence of sulfide melt in the mantle source region at each tectonic setting (Jenner, 2017;  
380 Jenner et al., 2015, 2012, 2010; Wang et al., 2018). With the exception of one sample with a  
381 Cu/Ag of 5416, the Cu/Ag of the Antuco samples are all lower than the global MORB array  
382 (**Figs. 4e** and **C3c**), even in the most primitive Antuco magmas. This may indicate that minor  
383 amounts of Cu were removed from the parental Antuco melts at an early stage in their  
384 evolution. Cu/Ag patterns across the full Antuco sample set suggest fractionation of Cu from  
385 Ag throughout the crustal differentiation of these magmas, which is consistent with  
386 crystalline, rather than a sulfide melt, fractionation (Jenner et al., 2010; Li and Audétat,  
387 2012). Some of the most evolved Antuco samples (lowest MgO) have Cu/Ag approaching  
388 that of the bulk-continental crust (**Figs. 4e** and **C3c**). It is unlikely that an early fractionating  
389 phase, such as olivine, could cause such a drop in Cu/Ag from mantle values, given the

390 incompatibility of Cu and Ag in potential fractionating silicate phases (Jenner, 2017; Lee et  
391 al., 2012). We therefore suggest that sulfide fractionation began in the lower crust and at a  
392 very early stage in the evolution of Antuco's parental magmas, prior to ascent and low-  
393 pressure fractional crystallisation (**Fig. 6**). This is consistent with initial stalling and  
394 crystallisation at the base of the continental crust prior to ascent to higher crustal levels (e.g.,  
395 Annen et al., 2006). Lower crustal sulfide saturation is likely a result of the increased stability  
396 of crystalline sulfides at depth (Matjuschkin et al., 2016) (**Fig. 6b**). Fractionation of  
397 crystalline sulfide at the base of the continental crust (cf. Jenner, 2017) contrasts with  
398 observations in thinner, oceanic island arc/backarc settings, where Cu and Ag systematics  
399 suggest that mantle-derived melts are sulfide undersaturated until the point of magnetite  
400 fractionation, and only fractionate sulfide after this point in their evolution (e.g., Eastern  
401 Manus Basin; Chiaradia, 2014; Jenner et al., 2012, 2010) (**Fig. 6**).

402 Consequently, for oxidised parental arc magmas (e.g.,  $fO_2$  of  $\sim NNO +2$ ; Matjuschkin et al.,  
403 2016; cf. Kelley and Cottrell, 2012; Richards, 2015), sulfides would likely be stable during  
404 stalling and subsequent differentiation in 'deep crustal hot zones' (Annen et al., 2006) where  
405 the crust is  $\geq \sim 20$  km (i.e., mid- to lower continental crust) (**Fig. 6b**). In contrast, on stalling  
406 at shallower crustal levels (i.e.,  $< 20$  km), approximating that of the lower crust of oceanic  
407 island arcs, oxidised magmas would not be within the field of sulfide stability (Matjuschkin  
408 et al., 2016) (**Fig. 6b**), and would thus retain their chalcophiles until their first point of sulfide  
409 fractionation was initiated by magnetite fractionation and a  $fO_2$ -related drop in S solubility.  
410 Through this mechanism, the 'Magnetite Crisis' plays a more dominant control on the fate of  
411 the chalcophile elements in thinner, oceanic arcs than it does in arcs built on thicker crust.  
412 Crustal thickness thus exerts a fundamental control on chalcophile element distribution via its  
413 influence on initial depths of magmatic differentiation, and the stability of sulfide at these  
414 depths.

415 Recently, Tang et al. (2018) used an inverse correlation between  $[Dy/Yb]_N$  and  $FeO_T/MgO$  of  
 416 global arc magmas to argue that garnet fractionation results in the simultaneous Fe depletion  
 417 and increase in  $fO_2$  of magmas, from initial  $fO_2$  values comparable to MORB, during early  
 418 differentiation of continental arc magmas. As a consequence, because the solubility of sulfur  
 419 decreases with decreasing  $FeO_T$ , if primitive magmas intruding the lower continental crust  
 420 were fractionating garnet, this would be expected to induce sulfide fractionation (and would  
 421 also be a mechanism to increase  $fO_2$  of the residual magma). As such, this provides an  
 422 additional mechanism for deep-crustal sulfide fractionation, distinct from pressure-related  
 423 effects on the sulfide stability field (e.g., Matjuschkin et al., 2016).

424 A direct comparison cannot be made between our data from Antuco and the trend observed  
 425 between  $[Dy/Yb]_N$  and  $FeO_T/MgO$  presented by Tang et al. (2018), as the  $FeO_T$  values  
 426 presented for global arc magmas are for intermediate compositions (i.e.,  $4 \pm 1$  wt.% MgO)  
 427 only, highlighting garnet fractionation-induced Fe depletion. However, REE systematics  
 428 presented by Davidson et al. (2013, 2007) demonstrate the difference between amphibole and  
 429 garnet fractionation; amphibole fractionation will result in a decrease in Dy/Yb with  
 430 increasing  $SiO_2$ , whereas garnet fractionation will result in an increase in Dy/Yb with  
 431 increasing  $SiO_2$ . Thus, the decrease in  $Dy_N/Yb_N$  with increasing  $SiO_2$ , and positive correlation  
 432 between  $Dy/Dy^*$  and  $Dy_N/Yb_N$  of the Antuco suite is consistent with amphibole, not garnet  
 433 fractionation (**Fig. 7**). The absence of amphibole phenocrysts in the Antuco samples further  
 434 supports Davidson et al.'s (2007) interpretation that these REE ratios imply “cryptic  
 435 amphibole fractionation”.

436 Despite arguing that at Antuco the magmas have been affected by amphibole, rather than  
 437 garnet fractionation, we do not discount Tang et al.'s (2018) suggestion that the crystallising  
 438 assemblage from arc magmas is likely to transition from magnetite to garnet fractionation if  
 439 the crust becomes sufficiently thick. Indeed, the noticeably higher  $Dy_N/Yb_N$  of the most

440 primitive Antuco samples compared to the Eastern Manus Backarc Basin suite is consistent  
 441 with the fractionation of garnet (**Fig. 7**). Thus, the high  $D_{YbN}/D_{DyN}$  and low Cu/Ag of the  
 442 Antuco suite could indicate that garnet and sulfide were fractionated from the most primitive  
 443 Antuco magmas (during the earliest or deepest stages of magmatic differentiation), prior to  
 444 ascent. Additionally, a minor initial decrease in  $Fe_2O_3$  with increasing  $SiO_2$  (**Fig. 3b**) supports  
 445 an initial stage of garnet fractionation.

446 However, the degree of garnet fractionation from the Antuco magmas appears minimal  
 447 (based on the  $D_{YbN}/D_{DyN}$  trends supporting a predominance of amphibole fractionation). As  
 448 such, we still call upon the effect of pressure on the sulfide stability field (Matjuschkin et al.,  
 449 2016) to achieve sulfide saturation in the lower continental crust and explain the overall  
 450 Cu/Ag trends at Antuco, which is a satisfactory explanation especially if convergent margin  
 451 magmas have a higher initial  $fO_2$  compared to MORB or are driven to a higher  $fO_2$  as a  
 452 consequence of garnet fractionation.

453 To place constraints on the proportion of sulfide fractionation required to explain the Cu and  
 454 Ag systematics of the Antuco magmas, we have used the following fractional crystallisation  
 455 equation:

$$456 \quad C_1 = C_0 * (F^{D_0-1})$$

457 where,  $C_1$  is the concentration of an element in the resultant melt,  $C_0$  is the concentration of  
 458 an element in the source prior to fractional crystallisation,  $F$  is the fraction of melt remaining,  
 459 and  $D_0$  is the bulk-partition coefficient of an element prior to fractional crystallisation.

460 Starting compositions used for Cu (68.9 ppm) and Ag (0.04 ppm) are those of the most  
 461 primitive (highest MgO wt.%) Antuco sample (An27-7). Partition coefficients used for Cu  
 462 and Ag in crystalline (monosulfide solid solution) sulfides ( $K_{Cu}^{Sul}$ : 215,  $K_{Ag}^{Sul}$ : 24) were  
 463 those derived experimentally by Li and Audétat (2012) (average of experiments LY15 and

464 LY17) and are chosen as they are determined under conditions that best replicated a  
465 subduction zone setting (i.e., oxidised). Available partition coefficients for Cu and Ag in  
466 plagioclase and olivine show them both to be very low at  $\ll 0.1$  (Adam and Green, 2006;  
467 Ewart et al., 1973; Lee et al., 2012). As such, both plagioclase and olivine were grouped as  
468 one in the modelling calculations. For full details on the modelling parameters, see **Table 1**.

469 With only a minor volume (0.5 to 0.6 vol.%) of sulfide fractionation, broadly flat to slightly  
470 decreasing Cu and increasing Ag trends can be produced (**Figs. 8a** and **C5**). Consequently, as  
471 a result of the divergent trends in Cu and Ag, a continual decrease in Cu/Ag is also produced  
472 (**Fig. 8b**). These trends match those seen in Cu and Ag at Antuco and supports our conclusion  
473 that the Antuco magmas have been affected by a small degree (~0.5 vol.%) of sulfide  
474 fractionation throughout their petrogenesis.

## 475 **6. Conclusion**

476 The near complete suite of chalcophile elements were analysed in twenty-six volcanic rock  
477 samples from Antuco Volcano, Chile, which were used to investigate their processing and  
478 distribution within the magmatic system of a typical continental arc stratovolcano.  
479 Enrichments in W, Tl, As, Pb, Sb and Bi in the Antuco volcanic rocks suggest these  
480 chalcophile elements were mobilised during subduction. Additionally, the relative  
481 enrichments of these chalcophile elements indicate that the flux of elements from the oceanic  
482 crust to the mantle wedge is determined by their prior concentration in the subducting upper  
483 oceanic crust. Cu and Ag concentrations similar to the global MORB array suggest that  
484 neither Cu nor Ag were mobilised during subduction, and that Mo, Sn, Zn, Ga and Co were  
485 also immobile. Very low Se and S concentrations relative to the global MORB array reflect  
486 low-pressure degassing of these elements during eruption, preventing the reconstruction of Se  
487 systematics from subaerial volcanic rocks.

488 Inflections in the  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and V concentrations, and a corresponding (minor) drop in Cu  
489 contents and Cu/Ag of some Phase 1 Antuco samples at ~55 wt.%  $\text{SiO}_2$  and ~3 wt.% MgO,  
490 suggests that magnetite fractionation occurred during the crustal evolution of these magmas.  
491 However, in contrast to oceanic arc magmas, there is no strong correspondence between  
492 magnetite and sulfide fractionation. Mostly flat Cu and Ag trends indicate that the Antuco  
493 melts were already sulfide saturated from a very early stage in their crustal history, and well  
494 before magnetite fractionation. Fractionation of Cu from Ag (i.e., a decreasing Cu/Ag ratio  
495 throughout the evolutionary trend) suggests that the fractionating sulfide phase was  
496 crystalline and can be explained by 0.5 to 0.6% of fractionating sulfide during crustal  
497 differentiation. The low Cu/Ag of the most primitive Antuco samples compared to the global  
498 MORB array suggest an early, high-pressure stage of sulfide fractionation from the Antuco  
499 magmas. This implies that sulfide fractionation began at the base of the continental crust, in  
500 primitive magmas, and that sulfide is stable at lower crustal pressures in continental arcs,  
501 which is the predominant depth range of magmatic differentiation. As such, sulfide  
502 fractionation was not strongly influenced by magnetite fractionation, as is more likely the  
503 case in thinner, oceanic arcs. In oceanic arcs, the initial depth range of magmatic  
504 differentiation may be outside the field of sulfide stability, and magnetite thus acts as a  
505 dominant control on sulfide fractionation. We have shown that crustal thickness plays an  
506 important role in controlling the differentiation of continental arc magmas and the resulting  
507 distribution of the chalcophile elements in the arc crust. Beneath continental arcs, these  
508 processes would lead to the formation of a theoretical chalcophile-rich reservoir at or near the  
509 base of the continental crust that could be tapped to fuel ore deposit formation.

510

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522

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### 663 **Figure Captions**

664 Figure 1: (a) Simplified geological map of Antuco Volcano, Chile. Sample locations  
665 highlighted with filled circles. Geological map adapted after Martínez et al. (2018). Base  
666 image from Google Earth (2018). (b) Location map of Antuco Volcano, highlighting its  
667 location at the northern end of the Central Southern Volcanic Zone. The reader is referred to  
668 the online version of this article for interpretation of the figure(s) in colour.

669 Figure 2: (a) Total-alkali-silica (TAS) plot of the Antuco samples. Antuco Phase 1 samples of  
670 the current study range in composition from basalt to andesite, with one classifying as a  
671 trachy-andesite. Antuco Phase 2 samples of the current study have a slightly narrower

672 compositional range from basaltic andesite to andesite, again with one classifying as a trachy-  
673 andesite. Also plotted are samples analysed by Martínez et al. (2018) from Antuco (M18),  
674 which display very similar compositional ranges to the current study. Classification fields as  
675 of Le Bas et al. (1986). (b) Alkali-iron-magnesium (AFM) ternary plot of the Antuco  
676 samples. The majority of both Phase 1 and 2 samples plot in the calc-alkaline field. Ternary  
677 plot constructed in TernPlot (Marshall, 1996), using the boundary lines of Kuno (1968) and  
678 Irvine and Baragar (1971).

679 Figure 3: Select major element ( $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ) and Vanadium bivariate plots (vs.  $\text{SiO}_2$ ) of the  
680 Antuco samples. Inflections in  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and V at ~55 wt.%  $\text{SiO}_2$  highlight the onset of  
681 magnetite fractionation in the Antuco magmas. Also plotted are samples from Antuco  
682 analysed by Martínez et al. (2018) (M18). Samples from M18 display similar concentration  
683 ranges and show inflections in  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and V.

684 Figure 4: Select trace element (Cu, Ag, Se, and S) bivariate plots (vs.  $\text{SiO}_2$ , FeO) of the  
685 Antuco samples. (a) The continual decrease in Cu contents with increasing  $\text{SiO}_2$  shown by  
686 Phase 1 samples (and Early Antuco samples of M18) is similar to that seen in Cu data from  
687 sulfide saturated Ecuadorian volcanoes [data from Georgatou et al., 2018 (G18)]. (a, c, d, e)  
688 The trends seen in Cu at Antuco and in Ecuadorian volcanoes are different to that seen in data  
689 from the Eastern Manus Backarc Basin (EMBB), where Cu (and Ag, Se) contents increase  
690 with increasing  $\text{SiO}_2$ , before rapidly decreasing after the onset of magnetite fractionation at  
691 ~58 wt.%  $\text{SiO}_2$  [data from Jenner et al., 2012 (J12)]. (b, d, f) The S and Se contents of the  
692 Antuco samples are considerably lower than the Global (Pacific and Atlantic) MORB array  
693 [data from Jenner and O'Neill, 2012], suggesting they were both degassed from the Antuco  
694 magmas. This is unlike that seen in Se data from the Eastern Manus Backarc Basin (EMBB),  
695 where Se contents increase then decrease with increasing  $\text{SiO}_2$ , attributed to magnetite

696 induced sulfide fractionation [data from Jenner et al., 2012 (J12)]. Bulk continental crust  
697 composition from Rudnick and Gao (2003) (RG03).

698 Figure 5: Parental-MORB normalised (values from Jenner, 2017) multi-element plots. (a)  
699 Complete multi-element plot of Antuco samples compared to the bulk-continental crust [data  
700 from Rudnick and Gao, 2003]. Element ordering reflects increasing incompatibility (from  
701 right to left) of the elements during low-pressure differentiation of MORB (see Jenner, 2017).  
702 Isolated mobile (b), moderately mobile (c) and immobile (d) Parental-MORB normalised  
703 multi-element plots show that the mobile chalcophile elements are considerably more  
704 enriched in the Antuco magmas compared to the REE and HFSE. Additionally, the relatively  
705 unfractionated patterns displayed by the Parental-MORB normalised mobile chalcophile  
706 elements, together with the slight increase in values with increasing incompatibility during  
707 MORB differentiation, indicates that these elements were added into the mantle wedge in  
708 roughly similar proportions as they are found in the upper oceanic crust [i.e., pattern  
709 comparable to Evolved-MORB, as presented by Jenner (2017) (J17)].

710 Figure 6: (a) Schematic illustration comparing the processing of Cu beneath thick ( $\geq 30$  km)  
711 and thin ( $\leq 20$  km) overriding crust at convergent margins. Fluid mobile chalcophile elements  
712 (W, Tl, Sb, Pb, As, Bi) are added to the mantle wedge via a slab flux, whereas the immobile  
713 chalcophile elements (Cu, Ag) are retained in the lower oceanic crust. Thicker overriding  
714 (continental) crust promotes early sulfide fractionation from the Antuco magmas (and  
715 removal of Cu from the ascending magma) due to the increased stability of sulfides at higher  
716  $fO_2$  with increased pressure (and therefore depth) (**inset b**; adapted after Matjuschkin et al.,  
717 2016). The thinner nature of the overriding crust at island arcs (IA) and backarc basins (BAB)  
718 means sulfides are less likely to be stable at the base of the crust and therefore do not  
719 fractionate, allowing Cu contents to increase as magmas ascends prior to magnetite induced  
720 sulfide fractionation.

721 Figure 7: Rare Earth Element systematics of the Antuco magmas. Decreasing  $D_{Y_N/Yb_N}$  with  
722 increasing  $SiO_2$  (a), and a positive correlation between  $Dy/Dy^*$  and  $D_{Y_N/Yb_N}$  (b) suggest  
723 “cryptic amphibole fractionation” from the Antuco magmas (e.g., Davidson et al., 2013,  
724 2007). EMBB (J12): Eastern Manus Backarc Basin (data from Jenner et al., 2012).  
725 Normalising values from Sun and McDonough (1989). Grt: garnet; Amph: amphibole.

726 Figure 8: Trace element modelling of fractional crystallisation. Minimal sulfide fractionation  
727 (0.5 – 0.6 vol.%) is required to produce divergent trends in Cu (a) and Ag (**Appendix C, Fig.**  
728 **C5**) and Cu/Ag approaching that of the bulk continental crust (b), as observed in the Antuco  
729 samples. Starting Cu and Ag compositions used were those of the most primitive (highest  
730 MgO wt.%) Antuco sample (An27-7). The composition of the bulk continental crust is  
731 plotted for comparison [data from Rudnick and Gao, 2003].