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Highlights

- Pb, Bi, W, Tl, Sb and As are mobile during subduction and enriched in Antuco magmas
- Behaviour of Se is decoupled from other chalcophiles, degassing on eruption
- Cu and Ag show divergent trends consistent with crystalline sulfide fractionation
- Cu/Ag lower than MORB infers early, deep sulfide fractionation during magma ascent
- Crustal thickness, and hence depth of differentiation control on sulfide saturation

Chalcophile Element Processing Beneath a Continental Arc Stratovolcano

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

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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 Dy_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 SiO₂ 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 H₂O 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 km³ (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 ⁴⁰Ar / ³⁹Ar
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 <<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°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-HNO₃ digestion process, with dry
210 down temperatures set at 65°C to minimise volatile element loss. Solutions were made up to
211 1000-fold dilutions of the original powder weight in a 2% HNO₃ 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 O₂ 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 NH₃ 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 ≤ 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).

243 Antuco samples range from 51.6 to 62.3 wt.% SiO₂ and 1.5 to 6.7 wt.% MgO (anhydrous
 244 values) (**Fig. 3** and **Appendix C, Figs. C1** and **C2**). Titanium dioxide, Fe₂O₃ (as total Fe) and
 245 V display broadly similar trends, all increasing with increasing SiO₂, reaching a maximum of
 246 1.6 wt.%, 10.9 wt.% and ~290 ppm, respectively at ~54-55 wt.% SiO₂, before decreasing
 247 with further increasing SiO₂ (**Fig. 3**). The trends in V, TiO₂ and Fe₂O₃ 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 TiO₂ and Fe₂O₃ at a given SiO₂ (and MgO) compared to Phase 1
 250 samples. Calcium oxide shows a positive correlation with MgO; Al₂O₃ shows a peak in
 251 contents between 3 – 4 wt.% MgO; and K₂O, Na₂O and P₂O₅ 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 SiO₂ (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 SiO₂ and decreasing
 260 MgO (**Figs. 4e** and **C3c**). Three of the ~59 – 62 wt.% SiO₂ (~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 SiO₂ 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 SiO₂ 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 SiO₂ (and decreasing
319 MgO), followed by a sudden drop in Cu, Ag, Se and Cu/Ag at ~60 wt.% SiO₂ (**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 SiO₂ 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 SiO₂ 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 SiO₂ (or decreasing MgO) prior to

365 magnetite fractionation. Broad inflections at Antuco in the trends between TiO_2 , Fe_2O_3 and V
 366 with SiO_2 and MgO indicate the onset of magnetite fractionation in these magmas at ~55
 367 wt.% 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.% 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.% 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 ± 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 Dy_N/Yb_N 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 Dy_N/Yb_N 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:

$$456 \quad C_1 = C_o * (F^{D_o-1})$$

457 where, C_1 is the concentration of an element in the resultant melt, C_o is the concentration of
 458 an element in the source prior to fractional crystallisation, F is the fraction of melt remaining,
 459 and D_o 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 (Kd_{Cu}^{Sul} : 215, Kd_{Ag}^{Sul} : 24) were
 463 those derived experimentally by Li and Audéat (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 TiO_2 , Fe_2O_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.% 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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662

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 (TiO_2 , Fe_2O_3) and Vanadium bivariate plots (vs. SiO_2) of the
680 Antuco samples. Inflections in TiO_2 , Fe_2O_3 and V at ~55 wt.% 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 TiO_2 , Fe_2O_3 and V.

684 Figure 4: Select trace element (Cu, Ag, Se, and S) bivariate plots (vs. SiO_2 , FeO) of the
685 Antuco samples. (a) The continual decrease in Cu contents with increasing 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 SiO_2 , before rapidly decreasing after the onset of magnetite fractionation at
691 ~58 wt.% 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 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 (≥ 30 km)
711 and thin (≤ 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.

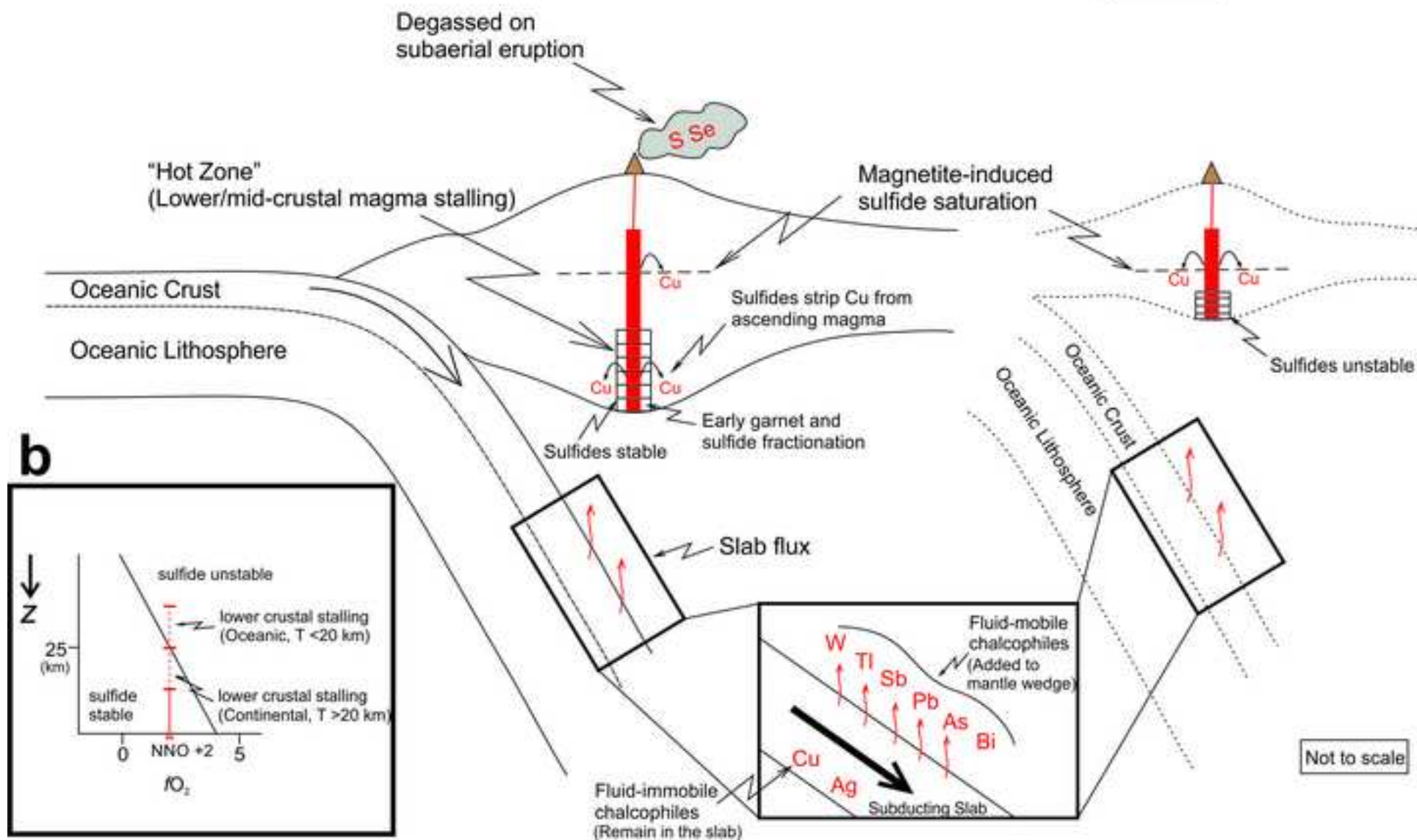
721 Figure 7: Rare Earth Element systematics of the Antuco magmas. Decreasing Dy_N/Yb_N with
722 increasing SiO_2 (a), and a positive correlation between Dy/Dy^* and Dy_N/Yb_N (b) suggest
723 “cryptic amphibole fractionation” from the Antuco magmas (e.g., Davidson et al., 2013,
724 2007). EMBB (J12): 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].

a

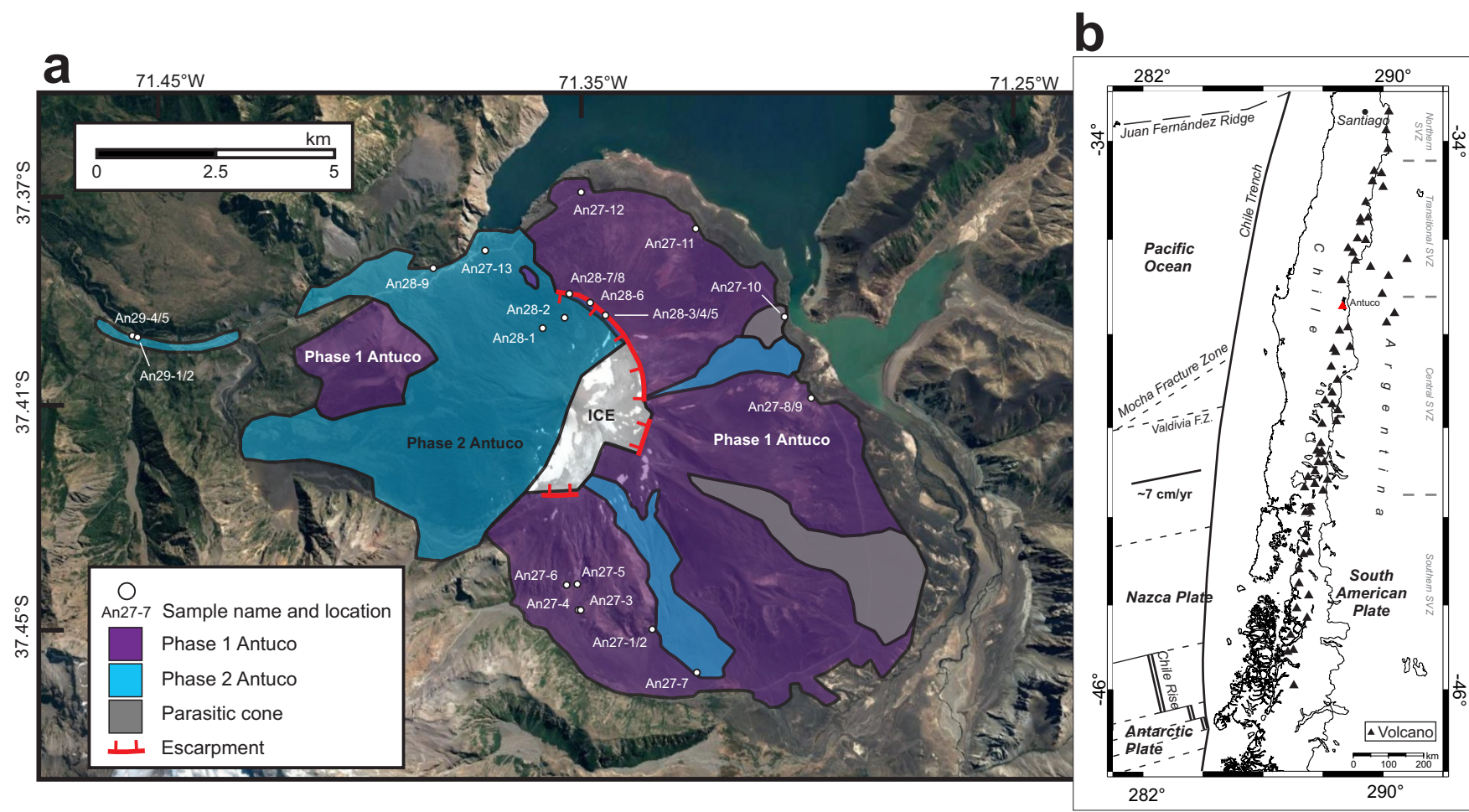
Thick overriding crust (30+ km)

Thinner overriding crust (≤ 20 km)
(IA/BAB?)



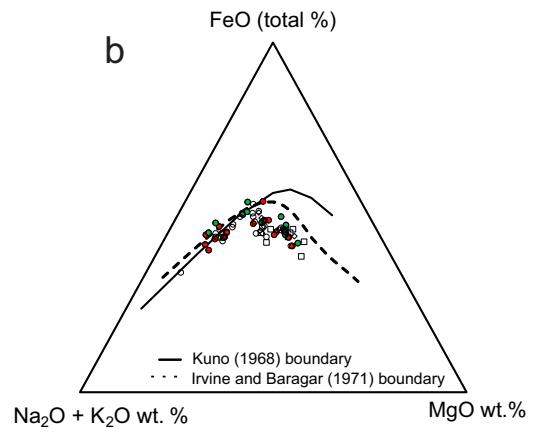
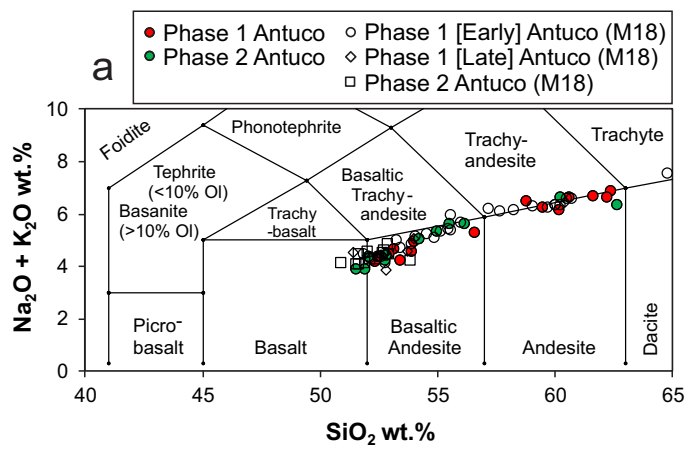
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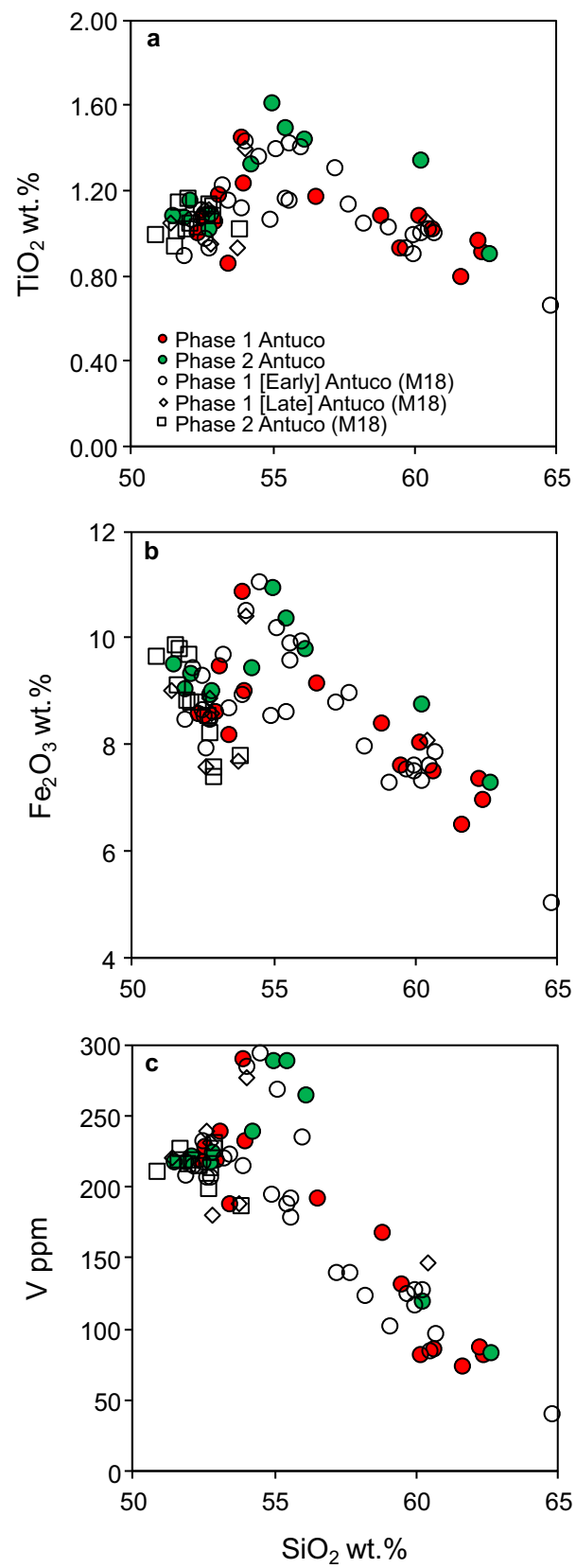
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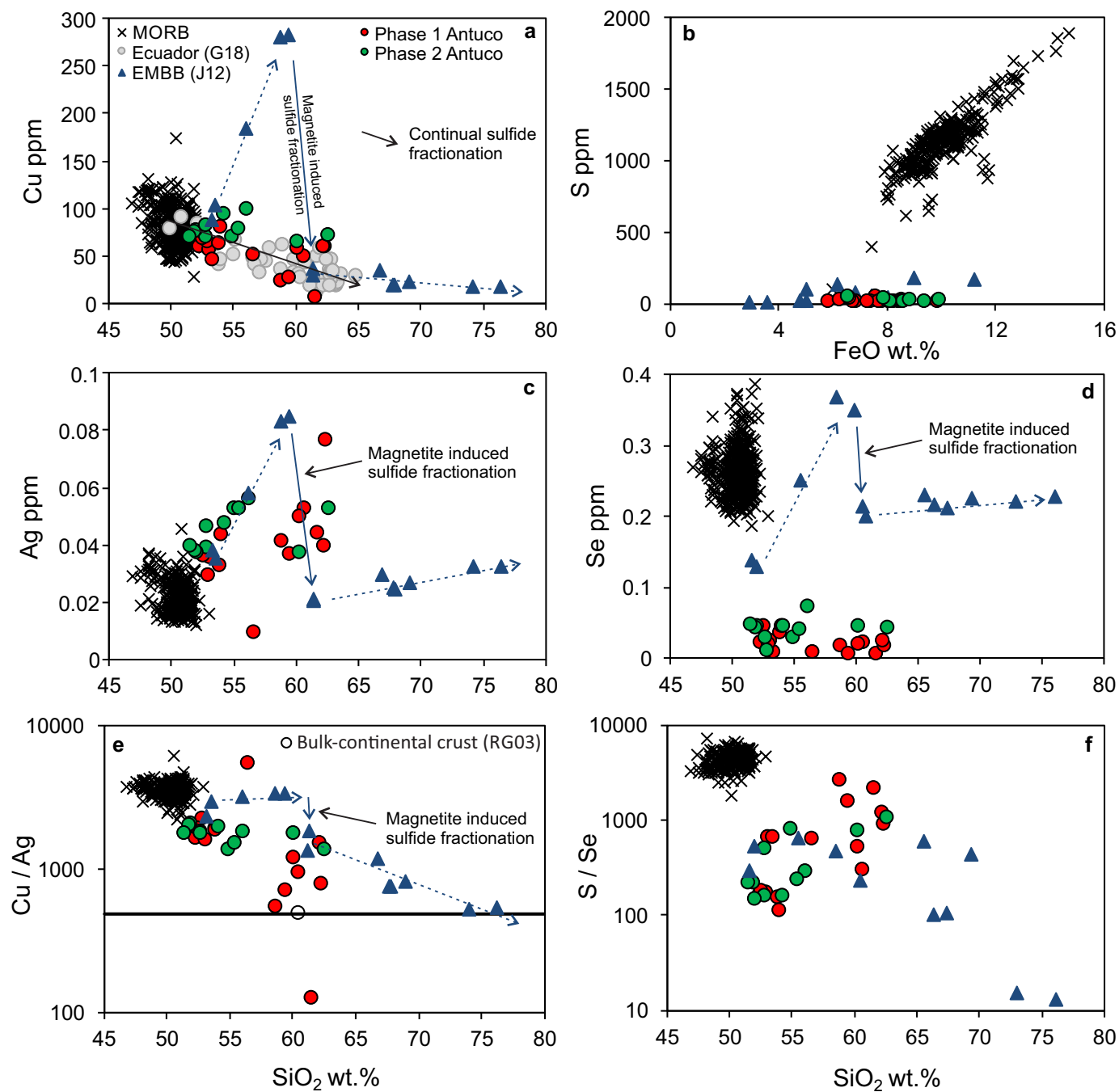
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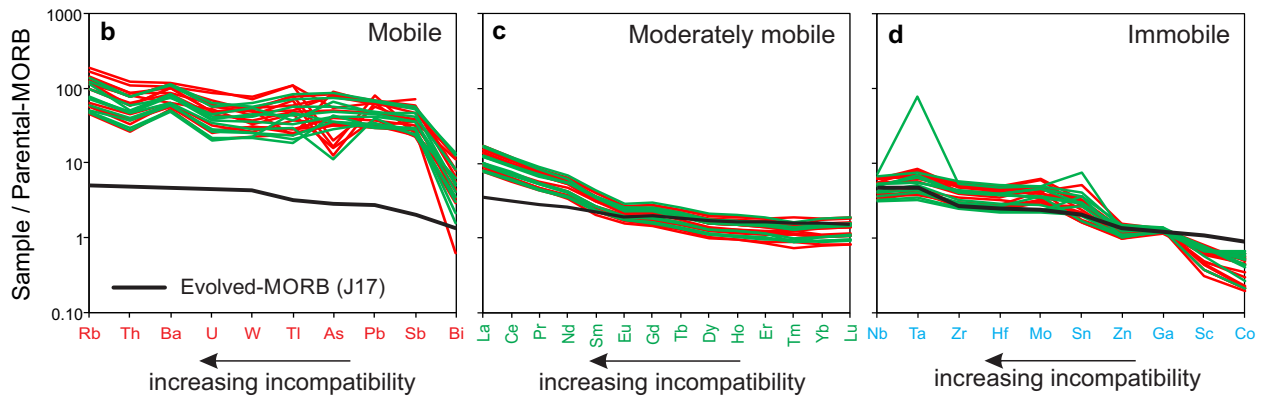
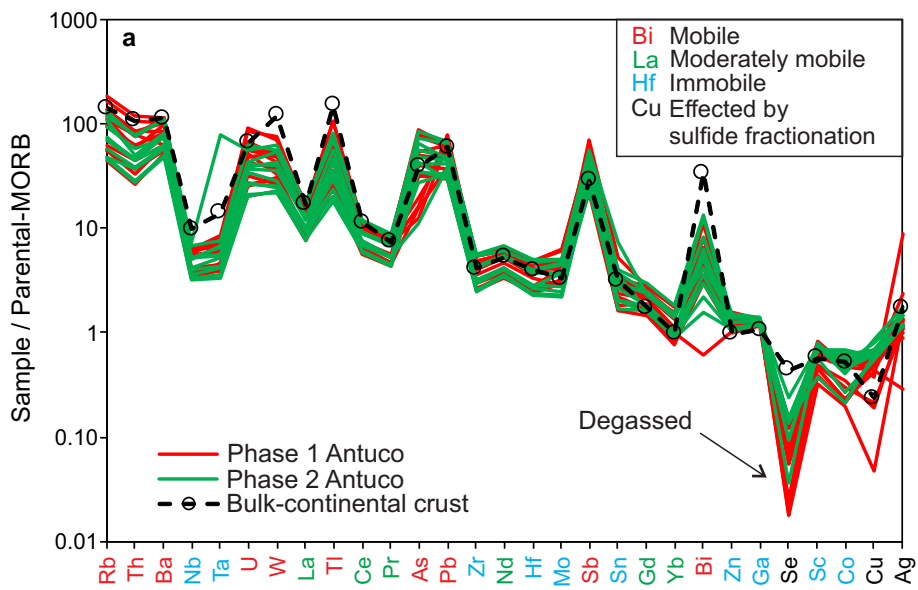
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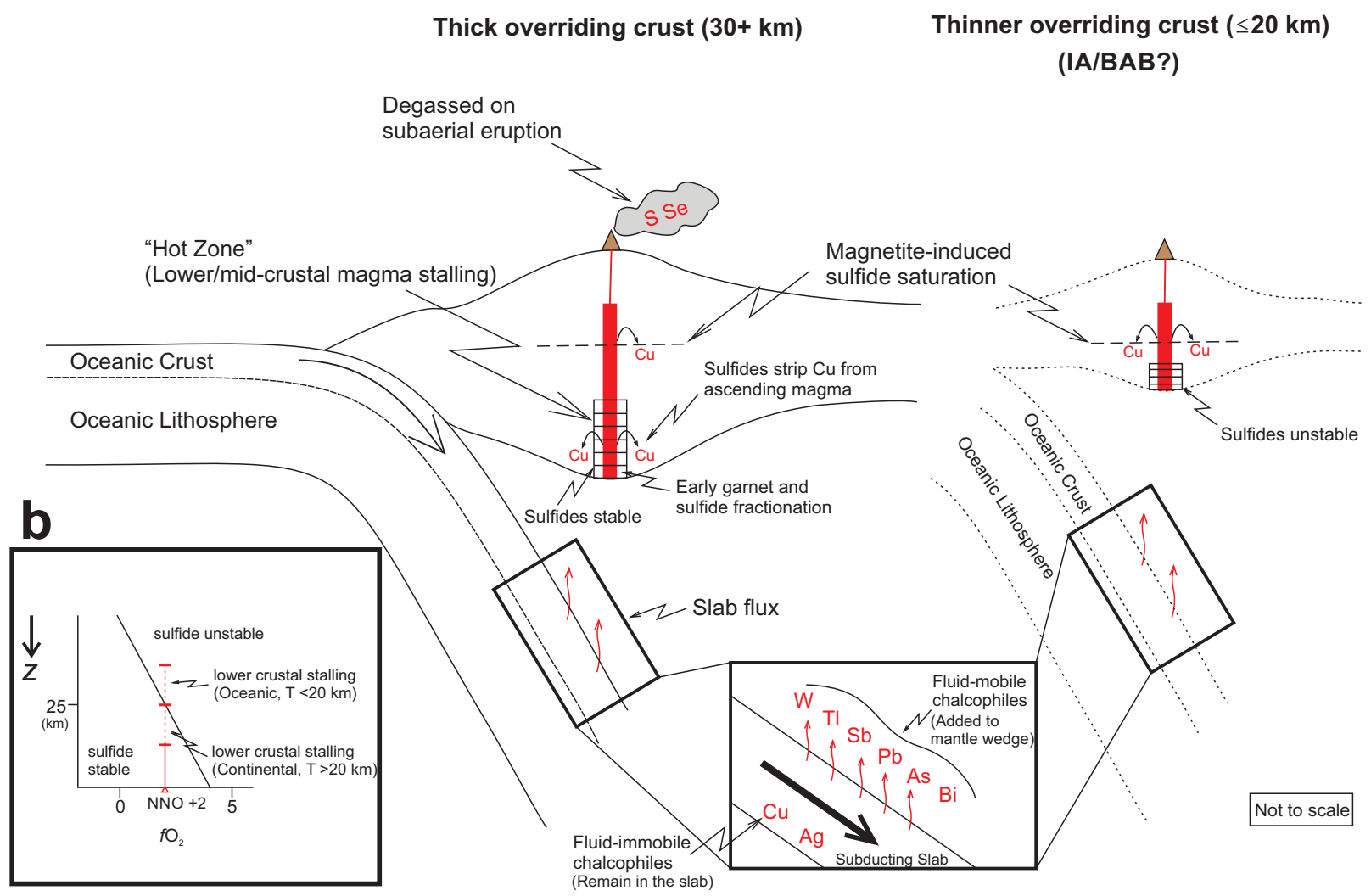
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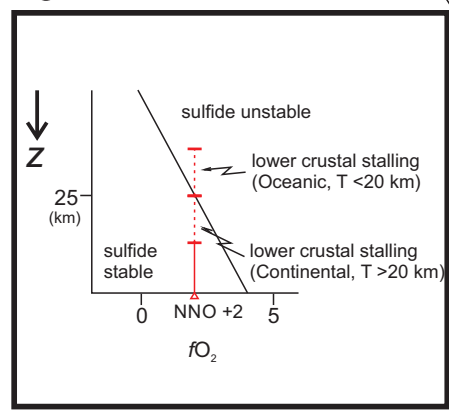
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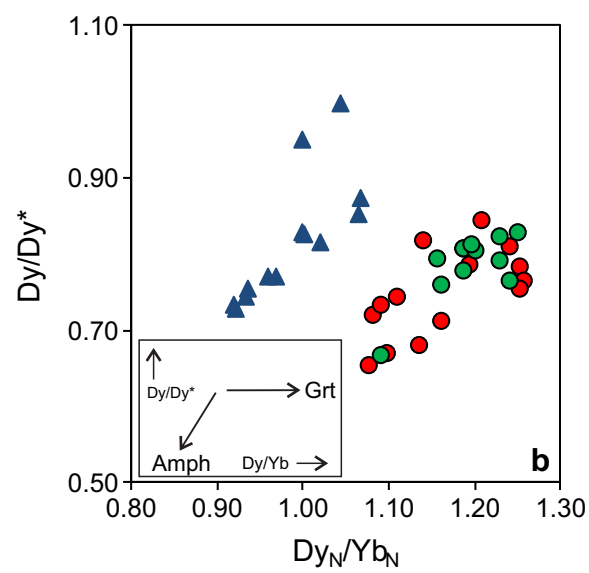
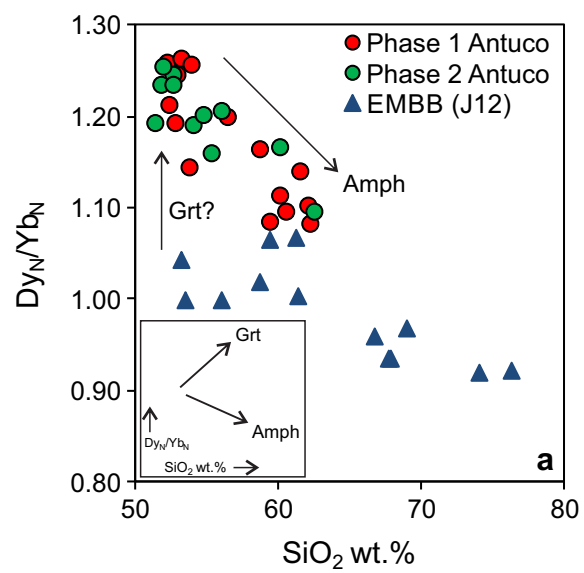


b



Figure

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Figure

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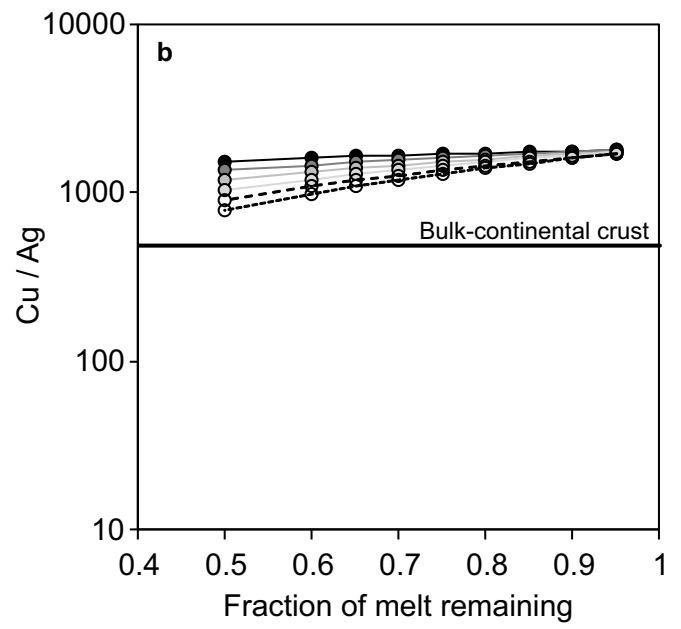
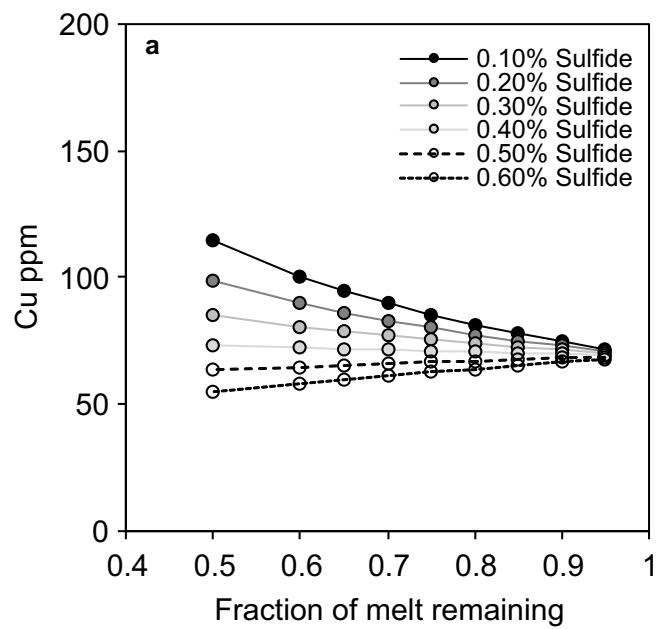


Table 1 Fractional crystallisation modelling parameters

	Plagioclase / Olivine	Sulphide
Mineral proportion	0.994	0.006
Kd	Cu	Ag
Plagioclase / Olivine	0.05	0.001
Sulphide (crystalline)	215	24
Do	1.340	0.145
Co (An27-7)	68.923	0.038

Kd: Partition coefficient for a particular element in a mineral, Do: Bulk-distribution coefficient of a particular element prior to fractional crystallisation, Co: Concentration of a particular element in the source.