

MIT Open Access Articles

*The importance of H₂O in arc magmas
for the formation of porphyry Cu deposits*

The MIT Faculty has made this article openly available. **Please share** how this access benefits you. Your story matters.

Citation: Bourdin, Hervé and Oliver Jagoutz. "The importance of H₂O in arc magmas for the formation of porphyry Cu deposits." *Ore Geology Reviews* 126 (November 2020): 103744. © 2020 Elsevier B.V.

As Published: <http://dx.doi.org/10.1016/j.oregeorev.2020.103744>

Publisher: Elsevier BV

Persistent URL: <https://hdl.handle.net/1721.1/132668>

Version: Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

Terms of use: Creative Commons Attribution-NonCommercial-NoDerivs License



The importance of H₂O in arc magmas for the formation of porphyry Cu deposits

Hervé Rezeau[†] and Oliver Jagoutz

Department of Earth, Atmospheric, and Planetary Sciences, MIT, Cambridge, USA

[†]Corresponding author: hrezeau@mit.edu

Keywords: Arc magmas; Calc-alkaline and tholeiitic series; Magmatic sulfides; Melt water content; Ore-forming potential; Porphyry copper deposits.

ABSTRACT

Porphyry copper deposits (PCDs) hosted in subvolcanic intrusions at convergent margins are the primary world's copper resources. However, the set of magmatic processes that lead to the generation of ore-bearing magmatic provinces remains unclear. In this paper we review the systematic of Cu evolution during arc magmatic differentiation using new and existing global compilations of whole rock geochemistry data. We trace the Cu evolution from primitive arc magmas through lower crustal plutonic to volcanic rocks. We focus on the well-known tholeiitic and calc-alkaline fractionation sequences, where arc tholeiitic series represents damp primitive melts (<2 wt% H₂O) evolving with iron enrichment, and calc-alkaline series are wet primitive melts (>2 wt% H₂O) that differentiate with iron depletion.

Our study shows that the Cu concentration in primitive arc melts (~80 ppm) is indistinguishable from that of primitive melts formed at mid-ocean ridges (MORBs) implying that Cu is mainly sourced from the mantle wedge in arcs with a limited contribution from the subducted oceanic lithosphere. A global compilation of plutonic rocks whole rock geochemistry (lower crustal cumulates and derivative melts) indicate no systematic difference in Cu concentrations between cumulates associated with tholeiitic or calc-alkaline series. Yet a complementary global compilation of arc volcanic whole rock geochemistry highlights the contrasting behavior of Cu in tholeiitic and calc-alkaline series during magmatic differentiation in arc. In tholeiitic series, Cu shows an incompatible and/or compatible behavior during magma differentiation influenced by the crustal thickness. In calc-alkaline series, Cu is compatible during magma differentiation independently to the crustal thickness. This relates to the timing of sulfide saturation, which is controlled by the

57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112

32 liquid lines of descent (LLD) and/or crustal thickness at redox conditions relevant for arc
33 magmas.

34 We demonstrate that the initial melt H₂O content in primitive arc melts controls the
35 LLD and the volume of remaining melt mass at fluid saturation. We show that the remaining
36 H₂O-saturated melt mass positively correlates with the total mass of Cu transferred into
37 degassing fluids. The mass of extractable Cu ranges from ~3 to ~10 Mt (i.e., large PCD) for
38 calc-alkaline series, and ranges from ~0.3 to ~2.5 Mt for tholeiitic series. The ore-forming
39 potential of calc-alkaline arc magmas is at least ~4 to ~10 times higher relative to tholeiitic
40 arc magmas. Despite the compatible behavior of Cu during magmatic differentiation, we
41 propose that a single stage model for the formation of large economic PCDs (as opposed to
42 multi-stage model for Cu-sulfides storage and remobilization) is most applicable for the calc-
43 alkaline melts. The importance of the initial melt H₂O content ultimately reflects the key role
44 of flux melting associated with wet calc-alkaline series and high ore-forming potential, in
45 opposition to decompression melting associated with damp tholeiitic series.

46
47 **1. Introduction**

48 Porphyry copper deposits (PCDs) formed in arc setting represent ~75% of the global
49 copper resources (Sillitoe, 2010). Large economic PCDs are dominantly associated with
50 volatile-rich and oxidized calc-alkaline sub-volcanic intrusions in continental arcs, although
51 some important ones are also formed in oceanic island arcs (Fig. 1; Kesler et al., 1975; Titley,
52 1975; Solomon, 1990; Richards, 2003, 2011a; Cooke et al., 2005; Sillitoe, 1997, 2010).
53 Magmatic-hydrothermal processes directly associated with the formation of PCDs are
54 reasonably well understood (e.g., Seedorff et al., 2005; Sillitoe, 2010; Kouzmanov and
55 Pokrovski, 2012). In contrast, the role of precursor magmatism (and related source and
56 crustal processes) to generate magmas able to form ore deposits remains less clear (e.g.,
57 Audétat and Simon, 2012; Wilkinson, 2013; Richards, 2015). Specifically, the importance of
58 magmatic sulfide crystallization and saturation of a fluid phase acting as the main Cu
59 scavengers during magmatic differentiation is unclear.

60 Copper is incompatible during magmatic differentiation in thin island arc (<20 km)
61 dominated by tholeiitic series, whereas Cu is compatible during magmatic differentiation in
62 thick continental arc (>30 km) dominated by calc-alkaline series (e.g., Lee et al., 2012;

113
114
115 63 Chiaradia, 2014). Crustal thickness is proposed to have a first-order control on arc magma
116
117 64 differentiation (Miyashiro, 1974; Chiaradia, 2014) and hence the Cu evolution in arc magmas
118
119 65 (Chiaradia, 2014; Lee and Tang, 2020). Furthermore, the different tholeiitic and calc-alkaline
120
121 66 liquid lines of descent (LLD) control the evolution of the melt redox conditions (expressed
122
123 67 in terms of oxygen fugacity, fO_2) in the crust, which in turn impact the solubility of sulfur and
124
125 68 Cu through sulfide immiscibility (e.g., Lee et al., 2012), potentially linked to the onset of
126
127 69 magnetite crystallization (Jenner et al., 2010; Chiaradia, 2014). Alternative views suggest
128
129 70 that the initial H₂O in primitive magma primarily control the LLD (Sisson and Grove, 1993;
130
131 71 Tatsumi and Susuki, 2009; Zimmer et al., 2010; Jagoutz et al., 2011; Müntener and Ulmer,
132
133 72 2018), and high initial melt H₂O contents (>4wt% H₂O) combined with high fO_2 in the
134
135 73 source region are thought to play a major role for the formation of PCDs (Richards, 2003,
136
137 74 2009, 2011a, 2015; Sun et al., 2015, 2017). As a result, endmember models for PCDs
138
139 75 formation in arcs can be grouped in two: (1) multi-stage models envision that early
140
141 76 magmatic Cu-sulfide saturation in the deep arc crust represent a key pre-enrichment step to
142
143 77 the formation of PCDs in continental arc dominated by calc-alkaline series. Subsequent
144
145 78 events within the same or later magmatic cycle remobilize the Cu from these cumulates to
146
147 79 form PCDs in the upper crust (e.g., Lee et al., 2012; Wilkinson, 2013; Chiaradia, 2014);
148
149 80 alternatively (2) single-stage models consider PCDs formed from metal precipitated from
150
151 81 hydrothermal fluids that are exsolved from differentiated mantle-derived, volatile-rich and
152
153 82 oxidized calc-alkaline magmas (e.g., Richards, 2009, 2011a, 2015; Sun et al., 2015, 2017).

148 83 For both endmember models, a wide range of crucial parameters for the formation of
149
150 84 PCDs have been proposed that include the initial metal endowment (McInnes et al., 1999;
151
152 85 Mungall, 2002; Sun et al., 2017; Zheng et al., 2018), the melt water concentration (Richards,
153
154 86 2011a,b; Chiaradia et al., 2012; Loucks, 2014; Chiaradia and Caricchi, 2017), the melt redox
155
156 87 conditions (Lee et al., 2012; Richards et al., 2015; Sun et al., 2015; Lee and Tang, 2020), the
157
158 88 melt metal concentration and/or the melt volume at the time of magmatic fluid saturation
159
160 89 (Cline and Bodnar, 1991; Richards, 2009; Park et al., 2019; Chelle-Michou et al., 2017), the
161
162 90 duration of the precursor magmatism (Rezeau et al., 2016; Chelle-Michou et al., 2017;
163
164 91 Chiaradia and Caricchi, 2017; Richards, 2018) and the overriding plate thickness (i.e.,
165
166
167
168

169
170
171 92 pressure of melt differentiation; Chiaradia, 2014; Matjuschkin et al., 2016; Cox et al., 2019;
172 93 Lee and Tang, 2020).

174 94 The evolution of Cu during arc magma differentiation results from a complex
175 95 interplay of processes occurring in the mantle source region and/or in the crust. Thus, it
176 96 remains unclear which parameter(s) primarily control the ore-forming potential of arc
177 97 magmas. This contribution aims to critically evaluate the role of source- and crustal-related
180 98 magmatic processes related to the ore-forming potential, and examine their respective
181 99 importance. Here, we use a global compilation of arc volcanic and plutonic (cumulates and
184 100 derivative melts) whole rock geochemical analyses to systematically characterize the
186 101 evolution of Cu in arc magmas during magmatic differentiation starting from primitive
187 102 mantle derived arc magmas. Our global compilation aims to evaluate the role of primitive
188 103 magma Cu concentration, initial water content, fO_2 , pressure of melt differentiation and
189 104 different LLD for the formation of economic PCDs in the light of the above mentioned two
192 105 endmember models. Our results emphasize the primary role of the initial melt H₂O content
194 106 regarding the ore-forming potential of arc magmas, whereas the initial melt Cu content is of
195 107 secondary importance. We show that a single stage model can explain the formation of large
197 108 economic PCDs associated with wet calc-alkaline arc series, whereas the multi-stage model
199 109 is applicable form PCD formed from damp tholeiitic arc series. Ultimately, we propose that
200 110 the initial melt H₂O content reflect the importance of the melting regime in the mantle wedge,
202 111 i.e., flux melting in contrast to decompression melting.

204 112

205 113 **2. Copper concentration in primitive arc magmas: implications for the source of Cu**

207 114 ***2.1 Dataset and results***

209 115 Previous studies reported Cu concentration in primitive arc basalts and mid-oceanic
210 116 ridge basalts (MORBs) ranging from ~50 to ~100 ppm (Jenner et al., 2010; Jenner and
212 117 O'Neill, 2012; Lee et al., 2012; Chiaradia, 2014; Richards, 2015). Here, we reevaluate the Cu
213 118 concentration between the different types of primitive arc melts and geodynamic settings.
215 119 We used the primitive arc melts compilation of Schmidt and Jagoutz (2017) with available
216 120 whole rock Cu analyses (n=422) from 20 arcs including intra-oceanic, continental and back-
218 121 arc settings (Supplemental Material Table A1). For this study, we present Cu concentration
220 122 in primitive arc melts using the same classification scheme as Schmidt and Jagoutz (2017),

225
226
227 123 with the exception of primitive depleted tholeiitic andesites which are considered
228
229 124 fractionated melts. Here, they are classified into five types: (1) primitive calc-alkaline basalts
230
231 125 (n=82), (2) primitive tholeiitic basalts (n=50), (3) primitive low-Si basalts (n=64), (4)
232 126 primitive shoshonites (n=78), and (5) primitive high-Mg andesites (n=148) (Fig. 2; Table
233
234 127 A1). For the sake of comparison, we also compiled whole rock Cu analyses (n=58) in
235
236 128 primitive MORBs using the data set of Gale et al. (2013). Primitive MORBs were selected
237 129 based on the same criteria used by Schmidt and Jagoutz (2017) for arc primitive melts, i.e.,
238
239 130 Mg# of 0.65-0.75, Ni concentrations of 150-500 ppm, and Cr concentrations of < 1200 ppm
240
241 131 (Table A1).

242 132 Our global compilation indicates that the Cu concentration of primitive arc melts
243
244 133 range from 35 to 120 ppm with a global average of 78 ± 31 ppm (1σ) for primitive arc basalts
245 134 and of 42 ± 17 ppm for primitive high-Mg andesites (Fig. 2). By comparison, the Cu
246
247 135 concentration in primitive MORBs display a similar range from 50 to 130 ppm, with a global
248
249 136 average of 81 ± 20 ppm (Fig. 2) indistinguishable from primitive arc basalts. Among
250 137 primitive arc basalts, there is no systematics correlation between the Cu concentrations, the
251
252 138 types of primitive melt and/or the geodynamic settings. Only the high-Mg andesites are
253
254 139 characterized by systematically lower Cu concentrations.

255 140

256 141 *2.2 The source of Cu in arc magmas*

258 142 A magmatic origin for Cu in PCDs is widely accepted based on isotopic composition of
259
260 143 hydrothermal and magmatic sulfides, ore-forming fluids, and the genetically related igneous
261
262 144 intrusions (e.g., Hedenquist and Lowenstern, 1994; Rezeau et al., 2016; Zheng et al., 2018).
263 145 However, there is no consensus whether Cu in arc magmas is directly derived from the
264
265 146 mantle wedge/refertilized sub-continental lithospheric mantle (e.g., McInnes et al., 1999;
266 147 Richards, 2009; Hou et al., 2017; Wang et al., 2018; Zheng et al., 2018) or dominantly
267
268 148 inherited from the subducting oceanic lithosphere by slab-related fluid/melt (e.g., Mungall,
269
270 149 2002; Sun et al., 2017).

271 150

273 151 *2.2.1 Mantle-derived vs. slab-related*

274
275
276
277
278
279
280

281
282
283 152 The Cu concentrations in primitive arc basalts range from 50 to 120 ppm, with no
284
285 153 systematics regarding the types of primitive melt and/or the geodynamic settings (Fig. 2).
286
287 154 The range of Cu concentration in primitive arc basalts can be generated after 5 to 30% of
288
289 155 melting of a mantle source having an initial Cu concentration of 30 ppm at fO_2 ranging from
290
291 156 $\Delta FMQ = 0$ to 2 (Lee et al., 2012), which could be reconciled with primitive arc basalts formed
292
293 157 by variable degree of partial melting at different pressure in the mantle wedge (Schmidt and
294
295 158 Jagoutz, 2017). Alternatively, the range of Cu in primitive melts may represent variable input
296
297 160 between incompatible elements and Cu content. Our global compilation lacks of such
298
299 161 systematics as demonstrated by similar average Cu contents (and a comparable range of Cu)
300
301 162 for the different types of primitive basalts characterized by variable involvement of slab-
302
303 163 related fluid and/or melts (Table A1; Schmidt and Jagoutz, 2017). This is consistent with the
304
305 164 limited remobilization of chalcophile elements from subducted sulfide ore deposits during
306
307 165 dehydration of the subducting oceanic lithosphere (Tomkins, 2010; Giacometti et al., 2015).
308
309 166 More importantly, primitive arc basalts and MORBs are characterized by the same global
310
311 167 average Cu concentration of ~80 ppm irrespective of the degree of subduction-related inputs
312
313 168 (Fig. 2). Therefore, our observations are consistent with previous studies (McInnes et al.,
314
315 169 1999; Jenner et al., 2010; Lee et al., 2012; Chiaradia, 2014; Richards, 2015) and strongly
316
317 170 suggest the predominant contribution of Cu from the mantle without necessarily requiring
318
319 171 additional input from slab-related fluids and/or melts.

2.2.2 Refertilization and Cu enrichment via melt-rock reaction

317
318
319 174 In arc setting, Cu and Os isotope studies suggest that Cu enrichment is linked to the
320
321 175 refertilization of the sub-arc mantle through the redistribution of primary sulfides into
322
323 176 sulfide-bearing metasomatic veins by slab-related oxidizing fluids (e.g., McInnes et al., 1999;
324
325 177 Zheng et al., 2018). Our compilation reveals that primitive high-Mg andesites are
326
327 178 characterized by the lowest Cu concentrations (Fig. 2), which are positively correlated with
328
329 179 MgO (Supplemental Figure A1). Primitive high-Mg andesites has been proposed to represent
330
331 180 lower temperature derivatives of primitive calc-alkaline basalts through melt-rock reaction
332
333 181 (also known as refertilization) in the shallow mantle and/or arc lithosphere (Kelemen et

337
338
339 182 [al.,1995; Kelemen et al., 2014; Schmidt and Jagoutz, 2017](#)). Consequently, we suggest that
340
341 183 the low Cu concentrations in primitive high-Mg andesites reflect Cu-sulfide fractionation,
342
343 184 which occur during melt-rock reaction. Such mechanism has been documented in a suite of
344
345 185 MORBs erupted at the Kane Megamullion, where Cu enrichment in the shallow mantle
346
347 186 results from melt-peridotite reaction ([Ciazela et al., 2017](#)). Similarly, melt-rock reaction in
348
349 187 the arc mantle region could represent an additional mechanism for local Cu enrichment in
350
351 188 the sub arc mantle and/or arc lithosphere. We envision that subsequent remelting of these
352
353 189 zones may account for unusually high Cu content in primitive arc basalts.

191 **3. Copper concentration in volcanic arc rocks**

192 *3.1 Dataset*

193 It has long been recognized that differentiation of arc magmas dominantly follow
194 either a tholeiitic or calc-alkaline series with minor importance of an alkaline series (e.g.,
195 [Miyashiro, 1974](#)). Global whole rock compilation suggests that the crustal thickness of the
196 overriding plates represents a first-order control on tholeiitic and calc-alkaline
197 differentiation series ([Miyashiro, 1974; Chiaradia, 2014, 2015](#)). Yet, tholeiitic and calc-
198 alkaline arc magmas are documented to coexist along the same arc segment from fore-arc to
199 back-arc (e.g., Cascades, [Baker et al., 1994; Mandler et al., 2014; Kamchatka, Portnyagin et](#)
200 [al., 2007; Izu-Bonin-Mariana, Tatsumi and Susuki, 2009; Brounce et al., 2014; Aleutians,](#)
201 [Zimmer et al., 2010](#)). It has been proposed that the geochemical differences between
202 tholeiitic and calc-alkaline series relate to different LLDs controlled by the initial H₂O content
203 of the primitive arc melt ([Sisson and Grove 1993; Zimmer et al., 2010; Jagoutz et al., 2011;](#)
204 [Melekhova et al., 2013; Müntener and Ulmer, 2018](#)). It has been proposed that primitive arc
205 magmas with high initial H₂O content, that evolve along a calc-alkaline fractionation
206 sequence are related to flux melting in the sub arc mantle ([Grove et al., 2002, 2012; Cervantes](#)
207 [and Wallace, 2003; Jagoutz et al., 2011](#)). Flux melting occurs because the melting point of
208 peridotite is significantly lowered due to the addition of water in the mantle wedge (e.g.,
209 [Grove et al., 2012](#)). The influx of slab-derived hydrous melts/fluids hence produces melts
210 with high initial H₂O. Alternatively, the sub arc mantle can melt due to adiabatic
211 decompression, which produces melts with lower initial H₂O content that evolve along a
212 tholeiitic LLD ([Grove et al., 2002, 2012](#)).

393
394
395 213 Here, we produce a global compilation of whole rock analyses with available Cu of arc
396 214 volcanic rocks from the georoc database (<http://georoc.mpch-mainz.gwdg.de/georoc/>) to
397 215 evaluate the Cu evolution between tholeiitic and calc-alkaline magmatic series along
398 216 individual arc segment. The discrimination between volcanic rock following a calc-alkaline
400 217 (n=9,275) or tholeiitic (n=6,114) differentiation trend is based on the classical FeO/MgO
402 218 versus SiO₂ relationship (Supplemental Figure B1; Miyashiro, 1974). Our global compilation
404 219 includes volcanic rocks from 28 different magmatic arcs for a total of 15,389 entries (Fig. 1,
406 220 3, C1 and D1; Supplementary Table B1). The analyses included in the database fulfilled the
408 221 following criteria: a loss of ignition (LOI) < 2 wt% (if provided), totals of 97-102 wt%, SiO₂
410 222 of 50-70 wt%, MgO of 0.5-10 wt% and FeO/MgO ratio < 15 to avoid any exotic melt
412 223 compositions. Note that we screened and removed analyses from known mineralized
414 224 porphyry district to avoid high Cu concentration influenced by ore-forming hydrothermal
416 225 fluids overprint that are unrelated to the original melt Cu endowment. In the following, all
418 226 the whole rock data have been recalculated on an anhydrous basis.

419 227 420 228 **3.2 Results**

421 229 Our global compilation of volcanic rocks shows a wide range of Cu concentrations.
423 230 For MgO ranging from 0.5 to 10 wt%, most of the Cu data ranges from <10 to ~400 ppm in
424 231 tholeiitic series and from <10 to ~150 ppm in calc-alkaline series (Fig. 3a,d). During magma
426 232 differentiation (i.e., decreasing MgO concentration), the evolution of Cu concentrations in
428 233 tholeiitic and calc-alkaline series differs significantly. In tholeiitic series, the Cu
430 234 concentration increases from the typical primitive arc basalts value of ~80 ppm at 10 wt%
432 235 MgO, to the highest values between 3.5 and 5 wt% MgO with a maximum median Cu
434 236 concentration of ~110 ppm at ~4.2 wt% MgO. This is followed by a decrease of Cu
436 237 concentration down to a median concentration of ~10 ppm at 0.5 wt% MgO (Fig. 3a). FeO_{tot}
438 238 and V concentrations also exhibit the highest values between 3.5 and 5 wt% MgO (Fig. 3b,c).
440 239 In calc-alkaline series, the median Cu concentration steadily decreases from the typical
442 240 primitive arc magma value of ~80 ppm at 10 wt% MgO to ~10 ppm at 0.5 wt% MgO (Fig.
444 241 3d). Both FeO_{tot} and V concentration also mimics the evolution trend of Cu (Fig. 3e, f). This
446 242 suggests an apparent broad correlation between Cu, FeO_{tot} and V for both tholeiitic and calc-
448 243 alkaline series. Based on this correlation, the switch from incompatible to compatible

449
450
451 244 behavior of Cu at MgO ~3-5 wt% is ascribed to the late onset of Fe-oxides crystallization in
452 245 tholeiitic series, whereas the compatible behavior of Cu relates to the early Fe-oxides
453 246 crystallization in calc-alkaline magmas (Jenner et al., 2010; Chiaradia, 2014). In details,
454 247 however, the correlation between the three elements is weak for 17 individual
455 248 representative arc segments characterized by more than 300 whole rock analyses with
456 249 available Cu (Fig. 4a, b; Fig. C1 and D1; Table B1). For calc-alkaline and tholeiitic series, FeO_{tot}
460 250 and V are systematically positively correlated (Fig. 4b). Experiments for tholeiitic and calc-
461 251 alkaline LLDs have demonstrated that the decrease of FeO_{tot} is closely related to the onset of
462 252 crystallization of Fe-Ti-oxides (spinel hercynite, ilmenite, magnetite; Villiger et al., 2004;
463 253 Nandedkar et al., 2014; Ulmer et al., 2018) for which V have a high partition coefficient
464 254 (Kd>>1 up to 130; Luhr and Carmichael, 1980; Latourrette et al. 1991; Canil, 1999). In
465 255 contrast, the evolution of Cu is generally poorly correlated with FeO_{tot} and V (Fig.4a),
466 256 although few arcs display positive correlation (e.g., Izu-Bonin, Aleutians; Fig. C1 and D1).
467 257 Thus, Fe-oxides crystallization may not necessarily have a large effect on Cu depletion.

474 258 We use the Cu concentration at MgO~4 wt% (Cu₄) relative to the initial average Cu
475 259 concentration in primitive arc basalts of ~80 ppm to evaluate the Cu enrichment or depletion
476 260 during magmatic differentiation (Fig. 4c, d). With the exception of one arc segment (Central
477 261 America), calc-alkaline series show a systematic depletion of Cu during magma
478 262 differentiation (Fig. 4c, d), while tholeiitic series are characterized by Cu enrichment and
479 263 depletion during magmatic differentiation (Fig. 4c, d). For tholeiitic series, we observe a
480 264 systematic Cu enrichment in thin arcs (<25 km), which ultimately correlates with the highest
481 265 FeO_{tot} enrichment at MgO~4 wt% (i.e., Fe₄). For tholeiitic series formed in thicker arcs (>25
482 266 km), the Cu depletion dominates. These observations indicate that the evolution of Cu during
483 267 magma differentiation is influenced by the LLD and the pressure of magma differentiation
484 268 that are further discussed below among other parameters.

492 269

493 270 **3. Copper concentration in plutonic rocks and derivative melts**

495 271 Finally, based on the compilation of Jagoutz and Kelemen (2015) and Jagoutz and
496 272 Klein (2018), we produced a compilation of whole rock Cu analyses for lower crustal
497 273 cumulates and their derivative melts from the Kohistan arc in Pakistan, Talkeetna arc in
498 274 Alaska, Sierra Valle Fértil–Sierra Famatina complex in Argentina, Fiordland in New Zealand

505
506
507 275 (Table C1). A complementary whole rock compilation of Cu-bearing cumulates from Chin et
508
509 276 al., 2018 is also included in Table C1, which consist of deep crustal cumulates from Arizona
510
511 277 and Sierra Nevada (Western USA), Bonanza arc (British Columbia), Colombia (North
512
513 278 Volcanic Andean Zone), Kermadec islands (South Pacific Ocean), and Pontides (NE Turkey).
514
515 279 The entire dataset consists in 1606 whole rock major elements analyses, of which 985
516
517 280 include Cu analyses (Table C1).

517 281 Our compilation of lower crust plutons that are cumulates and frozen melt
518
519 282 compositions (Jagoutz, 2010; Jagoutz et al., 2011) is characterized by a range of SiO₂ from 40
520
521 283 to ~76 wt%, Mg# from 0.9 to 0.2, and Cu concentrations from <10 ppm to 250 ppm (Fig. 5,
522
523 284 Table C1). The compiled cumulates are associated with differentiated melt of calc-alkaline
524
525 285 signature (Famatina arc, e.g., Otamendi et al., 2009; Fiordland arc, e.g., Allibone et al., 2009;
526
527 286 Jijal complex in Kohistan arc, e.g., Jagoutz et al., 2011), tholeiitic signature (Chilas complex in
528
529 287 Kohistan arc, e.g., Jagoutz et al., 2011), or overlapping the tholeiitic and calc-alkaline fields
530
531 288 (Talkeetna arc, e.g., Greene et al., 2006). Most of the compiled lower crustal plutons are
532
533 289 characterized by a “Z” shape trend in the Mg# and SiO₂ space, except for the Chilas complex
534
535 290 in Kohistan (Fig. 5a). The different patterns are related to different LLD such as the “Z” shape
536
537 291 represents wet fractionation associated with calc-alkaline series, whereas the others
538
539 292 represent dry fractionation linked to tholeiitic series (Jagoutz, 2010; Jagoutz et al., 2011;
540
541 293 Müntener and Ulmer, 2018). Our global compilation of lower crustal cumulates do not show
542
543 294 any systematics difference in whole rock Cu concentrations between cumulates associated
544
545 295 with calc-alkaline or tholeiitic series (Fig. 5b).

543 297 **4. Discussion**

545 298 When melt reaches sulfide or water saturation during magmatic differentiation Cu is
546
547 299 strongly partitioned into magmatic sulfides and/or the fluid phase. Therefore, we first
548
549 300 discuss the systematic of magmatic sulfide saturation and its role for the different evolutions
550
551 301 of Cu concentration observed between tholeiitic and calc-alkaline magmas (Fig. 3 and 4).
552
553 302 Subsequently, we focus on the initial melt H₂O content and its role for the ore-forming
554
555 303 potential in arc magmas.

556 305 **4.1 Sulfide saturation in arc magmas**

561
562
563 306 Magmatic sulfide minerals are known to be highly efficient Cu scavengers, and
564 307 therefore, it is generally assumed that sulfide saturation plays a crucial role in the ore-
565 308 forming potential of arc magmas. Indeed, magmatic sulfides are ubiquitous in mafic to felsic
566 309 volcanic and plutonic rocks (e.g., Stavast et al., 2006; Lee et al., 2012; Zelenski et al., 2017;
567 310 Georgatou and Chiaradia, 2019). The observed volume of magmatic sulfides in igneous rocks
568 311 range from <0.1 to 0.6 vol% and directly influences the Cu budget during melt differentiation
569 312 (Kiseeva and Wood, 2015; Georgatou et al., 2018; Cox et al., 2019). As copper is a highly
570 313 chalcophile element ($D^{sulfide/melt}_{Cu} \sim 250-1000$; Li and Audétat, 2012), its solubility in
571 314 silicate melt strongly depends on sulfide saturation. Experiments have demonstrated a sharp
572 315 transition from sulfide (S^{2-}) to sulfate (S^{6+}), where sulfide (S^{2-}) is the dominant sulfur species
573 316 in hydrous silicate melts under more reducing conditions (fO_2), whereas sulfate (S^{6+})
574 317 dominates at higher redox conditions (Fig. 6a; Mavrogenes and O'Neill, 1999; O'Neill and
575 318 Mavrogenes, 2002; Jugo, 2009; Jugo et al., 2010; Botcharnikov et al., 2011; Fortin et al., 2015;
576 319 Matjuschkin et al., 2016). Furthermore, higher pressure of differentiation shifts the sulfide-
577 320 sulfate transition towards higher fO_2 (Fig. 6a; Matjuschkin et al., 2016). The sulfur solubility
578 321 in silicate melts strongly correlates with the sulfide-sulfate transition, such as the S solubility
579 322 increases as a function of the fraction of oxidized species in the melt (Fig. 6a; Carroll and
580 323 Rutherford, 1985; Jugo, 2009; Jugo et al., 2010; Botcharnikov et al., 2011; Matjuschkin et al.,
581 324 2016). At convergent margins, the redox conditions in primitive arc basalts and sub-arc
582 325 mantle are on average higher than MORBs, but varies over several log units above the
583 326 fayalite-magnetite-quartz (FMQ) buffer assemblage from $\Delta FMQ \sim 0$ to +4 (Fig. 6a; e.g.,
584 327 Carmichael, 1991; Lee et al., 2010, 2012; Evans et al., 2012; Kelley and Cottrell, 2012;
585 328 Brounce et al., 2014; Bénard et al., 2018; Bucholz and Kelemen, 2019). Furthermore, the
586 329 pressure of differentiation and the volatiles content (H_2O , S) of primitive melt composition
587 330 vary within and among arcs (e.g., Grove et al., 2002; Rowe et al., 2009; Zimmer et al., 2010;
588 331 Wallace and Edmonds, 2011; Brounce et al., 2014; Melekhova et al., 2019). In the following,
589 332 we discuss the importance of sulfide saturation in terms of possible melt evolution paths at
590 333 different pressures of differentiation, LLD, redox conditions, and initial sulfur concentrations
591 334 (Fig. 6a-d) that could explain the Cu evolution in tholeiitic and calc-alkaline differentiation
592 335 series (Fig. 3a, d).

617
618
619 336
620
621 337
622
623 338
624 339
625
626 340
627 341
628 342
629 343
630 344
631 345
632 346
633 347
634 348
635 349
636 350
637 351
638 352
639 353
640 354
641 355
642 356
643 357
644 358
645 359
646 360
647 361
648 362
649 363
650 364
651 365
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672

The effect of variable pressure of differentiation on sulfide saturation

The contrasting Cu evolution trends between tholeiitic and calc-alkaline series could be related to different pressures of differentiation, as at low pressure sulfate stability increases towards lower fO_2 , whereas higher pressure expands the sulfide stability field (Fig. 6a; e.g., Matjuschkin et al., 2016). Here we discuss arc melts with identical initial fO_2 of $\Delta FMQ \sim 1.5$ and sulfur concentration that differentiate at 0.2 GPa and 1 GPa (Figs. 6a, b). As sulfur is highly incompatible during fractional crystallization (e.g., Ripley and Li, 2013), the sulfur concentration increases with $1/F$ (F is the remaining melt mass). At 0.2 GPa, hydrous basaltic melt will reach sulfide saturation at $S \sim 0.5$ wt% (Figs. 6a; Botcharnikov et al., 2011). At higher pressure, the sulfide-sulfate transition shift towards higher fO_2 , and so does the S solubility curve (Matjuschkin et al., 2016). Considering the lack of available experimental data for hydrous basalt at 1 GPa, we shift the experimental sulfur solubility curve obtained at 0.2 GPa and correlate the highest S solubility with the transition of sulfate-only species curve ($S^{6+}/S_{tot} = 1$) at 1 GPa (Figs. 6a). Thus, we can approximate that a hydrous basaltic melt will reach sulfide saturation at $S \sim 0.15$ wt%. Assuming the primitive melt has initially 0.12 wt% S (Fig. 6a; Wallace and Edmonds, 2011; Brounce et al., 2014), the high pressure melt will reach sulfur saturation after $\sim 20\%$ fractionation ($F=0.8$) whereas the low-pressure melt will reach sulfur saturation after 75% differentiation ($F=0.25$) (Fig. 6b, Table D1). If pressure of differentiation is the controlling parameter, then our data would indicate that tholeiitic melts on average fractionate shallower than calc-alkaline melts. This conclusion is supported by the empirical observation that the overriding plate thickness controls the Cu and FeO enrichment in thin island arc (<20 km) relative to Cu and FeO depletion in thick continental arcs (>30 km) (Chiaradia, 2014). This first-order observation would be consistent with the increase of sulfide stability with pressure (Matjuschkin et al., 2016; Cox et al., 2019). Furthermore, our results highlight that thicker crust and hence possible higher pressure of differentiation prevents Cu enrichment during magma differentiation even for tholeiitic series (Fig. 4d). This observation supports the idea that higher pressure lower crustal melt differentiation plays an important role to trigger early sulfide saturation. Yet, calc-alkaline series are characterized by early Cu depletion independently to the crustal thickness

673
674
675 366 suggesting that additional parameters control the timing of sulfide saturation during magma
676
677 367 differentiation in these series.

678
679 368
680 369 *The importance of different liquid line of descent on sulfide saturation*

681 369
682 370 For a primitive melt that differentiates at a similar initial pressure, fO_2 and S
683 371 concentrations, the contrasting Cu evolution trends could be explained by a progressive
684 371 change of FeO content and redox conditions controlled by the different LLDs (e.g., Lee et al.,
685 372 2012) due to different initial melt H₂O content (e.g., Sisson and Grove, 1993; Villiger et al.,
686 372 2004; Nandedkar et al., 2014). Since the variations of redox conditions are sensitive to the
687 373 melt Fe³⁺/ΣFe ratio, the timing of crystallization of Fe-oxides (i.e., Fe³⁺-bearing minerals) is
688 374 expected to control the redox trajectories in a closed magmatic system, lowering the melt
689 375 Fe³⁺/ΣFe ratio and hence the oxygen fugacity (e.g., Ghiorso and Carmichael, 1987; Ulmer et
690 375 al., 2018). The calc-alkaline series is characterized by an early crystallization of Fe-oxides on
691 376 the LLD compared to the tholeiitic that crystallize Fe-oxide late on the LLD (Sisson and Grove,
692 376 1993). We test the evolution of fO_2 using Rhyolite-MELTS (Gualda et al., 2012) to simulate
693 377 melt crystallization in a thick crust starting from P = 0.8 GPa to 0.15 GPa and in a thin crust
694 377 starting from P = 0.4 GPa to 0.15 GPa for temperatures ranging from ~1220-1350°C (liquidus
695 378 varies as a function of initial melt H₂O content) to ~750-800°C (Table D1). Each computation
696 379 assumes melt differentiation through progressive decompression and cooling followed by
697 379 cooling once the melt reaches 0.15 GPa (Table D1). We use a starting primitive melt
698 380 composition of continental arc calc-alkaline basalt (Schmidt and Jagoutz, 2017) having
699 380 different initial H₂O content of 4 wt%, 1wt% and 0.2 wt% H₂O to account for calc-alkaline
700 381 and tholeiitic LLDs (e.g., Sisson and Grove 1993; Tatsumi and Susuki, 2009; Zimmer et al.,
701 382 2010; Melekhova et al., 2013; Table D1).

702 382
703 383
704 384
705 384
706 385
707 385
708 386 The modelled melt evolution confirms that the onset of crystallization of ferric
709 386 bearing minerals (magnetite) triggers the melt to evolve to lower fO_2 . The onset of magnetite
710 387 fractionation is dependent on the melt H₂O content and occurs at F~0.7 for the calc-alkaline
711 388 series (4 wt% H₂O_{initial}) versus F~0.65-0.4 for the tholeiitic series (1 wt% and 0.2 wt%
712 388 H₂O_{initial}). If both calc-alkaline and tholeiitic melt are S undersaturated at the time of
713 389 magnetite crystallization, the melt evolves toward lower fO_2 as soon as the magnetite
714 390 appears on the LLD to promotes sulfide saturation, which occur at higher melt fraction for
715 390
716 391
717 391
718 392
719 392
720 393
721 394
722 394
723 395
724 395
725 396
726
727
728

729
730
731 397 calc-alkaline magmas compared to tholeiitic ones (Fig. 6c). For tholeiitic series with 1 wt%
732
733 398 $H_2O_{initial}$, magnetite crystallization occurs earlier on the LLD ($F \sim 0.65$) indicative of the
734
735 399 concomitant effect of pressure. Our calculations are consistent with Jenner et al. (2010) and
736
737 400 Chiaradia (2014) suggestion that difference in Cu depletion trends between the calc-alkaline
738
739 401 and tholeiitic differentiation series could be linked to the timing of magnetite crystallization
740
741 402 within the respective LLDs, which is ultimately controlled by the initial H_2O content and the
742
743 403 pressure of differentiation. This interpretation can explain the Cu enrichment and depletion
744
745 404 observed for tholeiitic series in thin arcs (<25 km) and thick arcs (>25 km), while calc-
746
747 405 alkaline series consistently displays Cu depletion irrespective of the crustal thickness (Fig.
748
749 406 4c, d).

408 *The importance of variable initial redox conditions on sulfide saturation*

750
751 409 The importance of the initial fO_2 of the melt is illustrated by the compatible character
752
753 410 of Cu in MORB during differentiation (Jenner and O'Neill, 2012), where the initial fO_2 is ΔFMQ
754
755 411 < 0 and sulfide saturation occurs at low S content (Jugo, 2009; Jugo et al, 2010; Botcharnikov
756
757 412 et al., 2011; Matjuschkin et al., 2016). In comparison to MORBs, arc-related tholeiitic series
758
759 413 are characterized by the early incompatible and compatible character of Cu in thin and thick
760
761 414 arcs, respectively (Fig. 3a and 4c,d). According to the experimental sulfide-sulfate transition
762
763 415 curves at different pressures (0.2-1 GPa, Fig. 6a), the incompatible character of Cu (i.e.
764
765 416 delayed sulfide saturation) in thin arcs could be explained for initial fO_2 conditions of ΔFMQ
766
767 417 > ~ 1 for the primitive arc melt. In contrast, the compatible character of Cu (i.e. early sulfide
768
769 418 saturation) in thick arcs could be explained for initial fO_2 conditions of $\Delta FMQ < \sim 2$ for the
770
771 419 primitive arc melt (Figs. 6a,c). Such range of $\Delta FMQ \sim 1-2$ is consistent with estimates for
772
773 420 tholeiitic and calc-alkaline arc basalts along the Aleutian arc ($\Delta FMQ \sim +0.4-2.1$; Zimmer et al.,
774
775 421 2010) and Mariana arc ($\Delta FMQ \sim +1-1.6$; Brounce et al., 2014), for primitive lower crustal
776
777 422 ultramafic cumulates in the Talkeetna arc ($\Delta FMQ \sim +0.4-2.3$; Bucholz and Kelemen, 2019),
778
779 423 and for sub-arc mantle xenoliths in Kamchatka arc ($\Delta FMQ \sim +1-1.5$; Bénard et al., 2018). If
780
781 424 the initial melt fO_2 controls the different behavior of Cu in arc tholeiitic and calc-alkaline
782
783 425 series in thin arcs, it would imply that the arc tholeiitic series differentiate at higher initial
784
426 fO_2 than calc-alkaline series at the same initial S concentrations (Fig. 6c). Although H_2O itself

785
786
787 427 is a poor oxidant, the oxidation state of arc magmas is mainly affected by the proportion of
788
789 428 subduction-related aqueous components added to the mantle wedge (e.g., Kelley and
790
791 429 Cottrell, 2009), and more specifically to the chemical components associated with the slab-
792
793 430 derived fluids or melts, i.e., Fe³⁺, S⁶⁺, C⁴⁺ (Mungall, 2002; Tomkins and Evans, 2015; Bénard
794
795 431 et al., 2018; Brounce et al., 2019). A positive correlation between H₂O and fO₂ have been
796
797 432 shown from mid-ocean ridges to back-arc tectonic settings (Kelley and Cottrell, 2009;
798
799 433 Zimmer et al., 2010; Brounce et al., 2014), while melt inclusions from primitive arc basalts
800
801 434 from fore-arc to back-arc in the Oregon Cascades do not show any significant differences in
802
803 435 fO₂ between tholeiitic and calc-alkaline melts (Rowe et al., 2009). While the role of slab-
804
805 436 derived fluids or melts for the oxidation of arc magmas remains unclear, there is no evidence
806
807 437 to assume that arc tholeiitic melts have on average higher fO₂ than calc-alkaline melts.
808
809 438 **Consequently, the early sulfide saturation observed for calc-alkaline series in thin arcs**
810
811 439 **should reflect other processes than a systematic difference in fO₂ in primitive melts.**

440 441 *The importance of variable initial sulfur concentrations on sulfide saturation*

812 442 It has been proposed that slab-derived fluids/melts appear to be efficient transfer
813
814 443 agent for the transport of sulfur from slab to mantle wedge (Jégo and Dasgupta, 2014), which
815
816 444 is supported by higher range of S concentrations measured in arc basalts (up to ~0.9 wt%)
817
818 445 compared to MORB (up to ~0.2 wt%; e.g., Jugo et al., 2010; Wallace and Edmonds, 2011). In
819
820 446 this case, fluid flux melting should be characterized by higher contribution of an external
821
822 447 input of S to the mantle wedge via the devolatilization of the subducting oceanic crust
823
824 448 relative to decompression melting. Accordingly, we would expect higher initial S
825
826 449 concentration in calc-alkaline series promoting early sulfide saturation compared to the
827
828 450 tholeiitic series at similar pressure of differentiation and initial fO₂ (Fig. 6d). Positive
829
830 451 correlations between melt H₂O content and S exist in arc magmas (e.g., Johnson et al., 2009;
831
832 452 Zimmer et al., 2010; Kelley and Cottrell, 2012), although it is not systematic (e.g., Wallace,
833
834 453 2005). Furthermore, any apparent positive correlation from melt inclusions studies could be
835
836 454 due to melt degassing (e.g., Wallace and Edmonds, 2011) rather than initial melt conditions.
837
838 455 The relationship between the initial H₂O and S content of primitive arc magmas remains
839
840 456 uncertain.

841
842
843 457
844

845 458 In conclusions, this section highlights the complex interplay of different parameters
846 459 that control sulfide saturation and hence the evolution of melt Cu concentration during
847 460 magmatic differentiation. Based on our compilation (Fig. 3), we propose that the liquid lines
848 461 of descent have a large effect on the timing of sulfide saturation in thin arcs (<25 km),
849 462 whereas the pressure of differentiation becomes the main controlling factor in thicker arcs
850 463 (>25 km). Finally, more chemical data specifically on the sulfur content of arc magmas and
851 464 plutons in combination with experimental studies are needed to better understanding
852 465 sulfide saturation in natural magmatic systems.
853 466

854 467 *4.2 The importance of initial melt H₂O content in arc magmas for the ore-forming potential* 855 468 *of magmas*

856 469 Most of the economic PCDs are preferentially associated with calc-alkaline
857 470 subvolcanic intrusions (Sillitoe, 2010). Yet, our global compilation shows that the average
858 471 melt Cu concentration in calc-alkaline series is systematically lower compared to tholeiitic
859 472 series at a given MgO (Fig. 3a,d). This observation questions the primary importance of melt
860 473 Cu content in the ore-forming potential. In the following, we evaluate the role of the initial
861 474 melt water content and the Cu endowment in magmatic fluids for tholeiitic and calc-alkaline
862 475 series.
863 476

864 477 *4.2.1 Modeling the liquid lines of descent (LLDs)*

865 478 Compelling lines of evidence suggest that the geochemical differences between
866 479 tholeiitic and calc-alkaline series relate to different LLDs controlled by the initial H₂O content
867 480 of the primitive arc melt showing that tholeiitic and calc-alkaline series are best reproduced
868 481 by LLD of an H₂O-poor and H₂O-rich parental melt, respectively (Sisson and Grove 1993;
869 482 Chaussidon and Sobolev, 1996; Villiger et al., 2004; Tatsumi and Susuki, 2009; Zimmer et al.,
870 483 2010; Jagoutz et al., 2011; Melekhova et al., 2013; Brounce et al., 2014; Mandler et al., 2014;
871 484 Nandedkar et al., 2014; Müntener and Ulmer, 2018). We use Rhyolite-MELTS (Gualda et al.,
872 485 2012; Ghiorso and Gualda, 2015) to model LLDs with variable initial melt H₂O content from
873 486 0.2 wt% to 4 wt% representative of the spectrum of tholeiitic to calc-alkaline series
874 487 emplaced at convergent margins (e.g., Sisson and Grove 1993; Tatsumi and Susuki, 2009;
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896

897
898
899 488 Zimmer et al., 2010; Brounce et al., 2014; Melekhova et al., 2013; Mandler et al., 2014). We
900
901 489 used an average primitive melt composition of intra-oceanic tholeiitic basalt and continental
902
903 490 arc calc-alkaline basalt (Table D1; Schmidt and Jagoutz, 2017). Our models simulate melt
904
905 491 differentiation in a thick crust starting from P = 0.8 GPa to 0.15 GPa and in a thin crust
906
907 492 starting from P = 0.4 GPa to 0.15 GPa for temperatures ranging from ~1220-1350°C (liquidus
908
909 493 varies as a function of initial melt H₂O content) to ~750-800°C at ΔFMQ +1 (Table D1). Each
910
911 494 computation assumes melt differentiation through progressive decompression and cooling
912
913 495 followed by cooling once the melt reaches 0.15 GPa (Table D1). The modelled LLDs
914
915 496 reasonably reproduce the tholeiitic and calc-alkaline trends and show that the amplitude of
916
917 497 Fe enrichment decreases as the initial H₂O melt increases (Fig. 7a). Tholeiitic trends are best
918
919 498 reproduced by LLDs resulting from the differentiation of intra-oceanic tholeiitic primitive
920
921 500 basalt with initial 0.2 to 1.5 wt% H₂O, whereas calc-alkaline trends are best reproduced by
922
923 501 LLDs resulting from the differentiation of continental arc calc-alkaline primitive basalt with
924
925 502 initial 2 to 4 wt% H₂O (Fig. 7a). For a given initial melt H₂O content, the absolute Fe
926
927 503 enrichment depends on the initial melt composition, where LLDs resulting from the
928
929 504 differentiation of intra-oceanic tholeiitic primitive basalt show more Fe enrichment
930
931 505 compared to continental arc calc-alkaline primitive basalt. Our results also show that an
932
933 506 increase of the initial pressure of differentiation slightly reduces the amplitude of Fe
934
935 507 enrichment for damp LLDs (Fig. 7a), which is consistent with the broad tendency of having
936
937 508 lower Fe₄ at higher crustal thickness (Fig. 4c). Higher redox conditions (ΔFMQ +2-3)
938
939 509 significantly limit Fe enrichment and therefore obfuscate the effect of H₂O on the LLDs.
940
941 510 Important is that our modeling allows us to quantify the melt composition in respect to the
942
943 511 remaining melt fraction (F), the melt water content and the appearance of the aqueous liquid
944
945 512 phases (i.e., fluid saturation) for the different LLDs. The latter is based on the fluid saturation
946
947 513 model of Ghiorso and Gualda (2015) implemented to Rhyolite-MELT, where thermodynamic
948
949 514 properties of the fluid phase are calculated from the model of Duan and Zhang (2006).

942 514 We also model the evolution of Cu concentration in the melt using the Rayleigh
943 515 fractionation equation:

$$C_1 = C_0 * (F^{D-1}) \quad [1]$$

953
954
955 517 where C_1 is the concentration of Cu in the fractionated melt, C_0 is the Cu concentration
956 518 in the parental melt. F is the remaining melt fraction computed from Rhyolite-MELTS. While
957 519 Cu is incompatible in silicate minerals ($D^{silicates/Cu/melt} < 0.2$; Liu et al., 2014; Hsu et al., 2017),
958 520 it is highly compatible in sulfides ($D^{sulfide/Cu/melt} \sim 250-1000$; Li and Audéat, 2012; Jenner,
959 521 2017). The bulk-partition coefficient (D) of Cu represents an average of partition coefficients
960 522 related to the volume percent of saturated magmatic sulfide and rock-forming minerals.
961 523 Here, we use $D^{sulfide/Cu/melt} = 800$ and $D^{silicates/Cu/melt} = 0.1$, and an average of 0.25 vol% of
962 524 magmatic sulfides (Kiseeva and Wood, 2015; Georgatou et al., 2018) corresponding to a
963 525 bulk-partition coefficient D of 2.1 at sulfide saturation and a D of 0.1 assuming no sulfide
964 526 saturation. For tholeiitic series in thin arc (<25 km), the evolution of the Cu is characterized
965 527 by an initial incompatible behavior followed by a compatible behavior related to late
966 528 magmatic sulfide saturation (Fig. 3a and 4c,d). In this case, we model the incompatible
967 529 behavior of Cu assuming no sulfide saturation with an initial Cu concentration of ~80 ppm
968 530 in the parental melt. The switch from incompatible to compatible behavior of Cu occurs at
969 531 MgO ~4 wt% (Fig. 3a). At this point, we use the melt Cu concentration at MgO ~4 wt% as the
970 532 initial Cu concentration in the parental melt (i.e., C_0 ranging from ~130 to 250 ppm) and we
971 533 assume magmatic sulfide saturation to model the decrease of Cu concentration in tholeiitic
972 534 series (Fig. 7b; Table D1). For tholeiitic series in thick arc (>25 km) and calc-alkaline series,
973 535 we assume an early magmatic sulfides saturation to reproduce the steady decrease of Cu
974 536 concentration (Fig. 7b; Table D1).

975 537 For melt differentiation starting at $P=4$ kbars, the computed results indicate that the
976 538 magmatic fluid phase saturates at $H_2O=5.7-6.3$ wt%, $F=0.35-0.63$, $P=1.7-2.3$ kbars and Cu
977 539 ~25-50 ppm for the wet series with an initial H_2O content of 2, 2.5, 3, 3.5 and 4 wt%. Damp
978 540 series with an initial H_2O content of 0.5, 1 and 1.5 wt% saturates magmatic fluid at $H_2O=5.4-$
979 541 5.5 wt%, $F=0.09-0.26$, $P=1.5-1.7$ kbars and Cu ~15-30/~5-20 ppm (thin/thick arc model)
980 542 (Figs. 7c,d; Table D1). For melt differentiation starting at $P=8$ kbars, the computed results
981 543 indicate that the magmatic fluid phase saturates at $H_2O=5.5-6.8$ wt%, $F=0.36-0.59$, $P=1.8-2.5$
982 544 kbars and Cu ~25-45 ppm for the wet series, and at $H_2O=5.3-5.4$ wt%, $F=0.11-0.18$, $P=1.5$
983 545 kbars and Cu ~15-20/~10 ppm (thin/thick arc model) for the damp series (Figs. 7c,d; Table
984 546 D1). Independently to the initial pressure of melt differentiation, the wet calc-alkaline LLDs

1009
1010
1011 547 reach fluid saturation at higher melt fraction, melt H₂O content and melt Cu content
1012 compared to damp tholeiitic LLDs (Table D1). Damp melt with initial H₂O content of 0.2 wt%
1013 548
1014 does not reach H₂O saturation, and hence it is not further considered in the next section.
1015 549
1016 550

1017 1018 551 *4.2.2 Assessing the ore-forming potential of tholeiitic vs calc alkaline magmas*

1019 552 The Cu endowment of fluids expelled during degassing of H₂O-saturated melt
1020 primarily depends on the melt H₂O and Cu content together with the volume of melt
1021 553 present at fluid saturation (Cline and Bodnar, 1991; Chelle-Michou et al., 2017). As the mass
1022 of extractable Cu (Mt) correlates with the volume of water-saturated melt (Chelle-Michou et
1023 554 al., 2017) the remaining melt mass (F) of H₂O-saturated melt is a crucial parameter that
1024 555
1025 determine how much total Cu could be extracted from a magmatic system and hence for the
1026 556 formation of economic PCDs. Because of the different initial H₂O content in the primitive
1027 557 magma, the melt mass remaining at H₂O saturation is different for calc-alkaline vs tholeiitic
1028 558 LLD. Our models presented above have shown that the melt mass remaining at fluid
1029 559 saturation for calc-alkaline LLD is ~1.5 to 7 times that of the tholeiitic LLD.
1030 560
1031 561

1032 562 To illustrate this point, we use a simplified approach of Chelle-Michou et al. (2017) to
1033 563 quantify the mass of extractable Cu in fluids expelled during degassing of H₂O-saturated melt
1034 564 and to estimate the relative Cu endowment in expelled fluids between wet calc-alkaline and
1035 565 damp tholeiitic LLD. We estimate the volume of H₂O-saturated melt according to the
1036 566 Rhyolite-MELTS models presented above as it corresponds to the melt fraction at which an
1037 567 initial volume of primitive magma reached H₂O saturation. Here, we use an initial volume of
1038 568 primitive magma of 189 km³ km⁻¹ Myr⁻¹ based on an average arc magma production rate for
1039 569 intra-oceanic arcs (Jicha and Jagoutz, 2015). Once the magma is H₂O-saturated, we calculate
1040 570 the remaining melt fraction of H₂O-saturated melt and the volume of fluids at degassing.
1041 571 Ultimately, the mass of Cu in fluid expelled at degassing corresponds to the volume and
1042 572 density of fluids and the Cu concentration in fluids at degassing. The latter varies according
1043 573 to the melt Cu concentration and the partition coefficient of Cu between the fluid and the
1044 574 melt. The melt Cu concentration is derived from our modelling presented above, while
1045 575 partition coefficients $D_{Cu}^{fluid/melt}$ in the literature range from ~15 to ~300 and strongly
1046 576 depends on the melt salinity, the presence of CO₂, redox conditions, and H₂S content (Zajacz

1065
1066
1067 577 et al., 2008; Tattitch et al., 2015; Tattitch and Blundy, 2017). We use an intermediate value
1068
1069 578 of $D^{fluid/melt}_{Cu} = 140$ (Tattitch and Blundy, 2017). Our calculations yield a range of Cu
1070
1071 579 concentration in fluids range from ~0.03 to ~0.1 wt% (Table D1), which correspond to a
1072
1073 580 lower end estimate when compared to fluid inclusions data ranging from 0.002 to 2 wt% Cu
1074
1075 581 with an average of ~0.26 wt% in PCDs (Kouzmanov and Pokrovski, 2012). Magma degassing
1076
1077 582 occurs periodically during crystallization of H₂O-saturated melt, however the first degassing
1078
1079 583 event accounts for ~50 to 75 wt% of the total fluid expelled with fluids enriched in Cu
1080
1081 584 compared to the latest stages of degassing characterized by negligible amount of fluids (<25
1082
1083 585 wt%) depleted in Cu (Chelle-Michou et al., 2017). For this reason, we consider only a single
1084
1085 586 degassing event, hence providing minimum estimates for the mass of extractable Cu in fluid
1086
1087 587 expelled at degassing. In this simplified approach, we assume fixed parameters (percolation
1088
1089 588 threshold, fluid and melt density, partition coefficient) to assess the role of the initial melt
1090
1091 589 H₂O content and melt Cu concentration at degassing. The reader is referred to the
1092
1093 590 **Supplementary Material A1** and **Table D1** for a detailed description of the calculations.

1090 591 The results indicate a positive correlation between the relative mass of extractable
1091
1092 592 Cu in fluids expelled from H₂O-saturated magmas and the initial melt H₂O content (Fig. 8).
1093
1094 593 The mass of extractable Cu ranges from 2.6 to 9.6 Mt for wet calc-alkaline series modelled
1095
1096 594 with initial melt H₂O between 2 and 4 wt%, whereas calculations for damp tholeiitic series
1097
1098 595 modelled with initial melt H₂O between 0.5 and 1.5 wt% yield ranges from 0.3 to 2.3 Mt for
1099
1100 596 and from 0.2 to 1 Mt for thin and thick arc models, respectively. The corresponding volumes
1101
1102 597 of H₂O-saturated melt required to form PCDs >2 to ~10 Mt Cu (i.e., large to giant deposit)
1103
1104 598 range from 50 to 120 km³, which correspond to reasonable estimates compared to those
1105
1106 599 reported for ore-bearing intrusions (e.g., Cline and Bodnar, 1991; Chelle-Michou et al., 2017;
1107
1108 600 Du and Audétat, 2020). Overall, the ore-forming potential in typical calc-alkaline magmas
1109
1110 601 (initial melt H₂O content of 4 wt%) is ~4-10 times higher relative to damp tholeiitic magmas
1111
1112 602 (initial melt H₂O content of 1.5 wt%), and up to ~20-50 times relative to the dampest
1113
1114 603 tholeiitic magmas (initial melt H₂O content of 0.5 wt%) (Fig. 8). If we assume the same melt
1115
1116 604 Cu content of H₂O-saturated melt, the ore-forming potential in typical calc-alkaline magmas
1117
1118 605 is ~3 to 8 times higher relative to damp tholeiitic magmas (Table D1). Such correlation
1119
1120 606 reflects the crucial importance of the remaining H₂O-saturated melt mass, whereas the melt

1121
1122
1123 607 Cu concentration is of secondary importance. Of course, higher melt Cu content at the time
1124 608 of fluid saturation increases the ore-forming potential of a given LLD, which can be envisioned
1125 609 with high fO_2 (e.g., Richards, 2015) and/or a source enriched in Cu (e.g., Zheng et al., 2018).
1126 610 Ultimately, our results are consistent with Chiaradia (2020a) suggesting that the highest ore-
1127 611 forming potential coincides with an initial H₂O content of 4 wt% in the parental basaltic melt,
1128 612 whereas lower ore-forming potential are modelled for initial melt H₂O content <2 wt% and
1129 613 >6 wt%. Although our modelling primarily aims to evaluate the effect of initial melt H₂O
1130 614 content on the ore-forming potential of arc magmas, we acknowledge that additional
1131 615 parameters including favorable tectonics, long-lived thermal sustainability, magma
1132 616 mingling, and metal precipitation efficiency play a complementary and important role to
1133 617 modulate the size of PCDs (Tosdal and Richards, 2001; Richards, 2003, 2011a; Caricchi et al.,
1134 618 2012; Wilkinson, 2013; Chiaradia and Caricchi, 2017; Chiaradia, 2020b).

1143 619 1144 620 **5. Petrogenetic implications for the formation of giant PCDs**

1145 621 ***5.1 Models of formation for PCDs***

1146 622 In calc-alkaline series, the compatible behavior of Cu during magmatic differentiation
1147 623 (Fig. 3a,d) does not preclude the transfer of significant mass of Cu into the fluids expelled
1148 624 from H₂O-saturated melts to form large economic PCDs in a single stage model (Fig. 9a),
1149 625 where fluid saturation occurs at ~1.5-2.5 kbars with an important volume of fluid-saturated
1150 626 melt at fairly low Cu concentrations of ~25-50 ppm. In contrast, a single stage model for the
1151 627 formation of large economic PCDs associated with damp tholeiitic series is unlikely because
1152 628 fluid saturation occurs late with a small volume of melt remaining and low Cu concentrations
1153 629 (Fig. 9b). Our results are consistent with the fact that large economic PCDs are
1154 630 predominantly associated with subvolcanic fluid-saturated calc-alkaline intrusions
1155 631 emplaced at ~2 kb (Richards, 2003; Sillitoe, 2010), whereas tholeiitic series are barren in
1156 632 the main arc (e.g., Kesler et al., 1977) and/or associated with shallow and smaller epithermal
1157 633 Cu-Au deposits associated with bi-modal suites in rift-related setting (e.g., Sillitoe and
1158 634 Hedenquist, 2003). In the case of the successive emplacement of damp tholeiitic series
1159 635 followed by wet calc-alkaline series, Cu-sulfide segregated in tholeiitic crustal cumulates
1160 636 could represent an additional source of Cu if remelting of lower crustal cumulates occurs
1161 637 during a subsequent hydrous magmatic event (Fig. 9c). Of course, Cu-sulfide segregated in

1177
1178
1179 638 lower crustal cumulates formed from hydrous melts could equally be remobilized during a
1180
1181 639 subsequent hydrous magmatic event (Fig. 9c; Richards, 2009, 2011a, 2015; Lee et al., 2012;
1182
1183 640 Chiaradia, 2014; Hou et al., 2015). This scenario would increase the ore-forming potential
1184 641 and lead to the formation of large PCDs consistent with a multi-stage model that could occur
1185
1186 642 in both subduction-related and post-subduction settings. In conclusions, we suggest that
1187
1188 643 both scenarios are likely to occur in accretionary orogens, however, Cu-sulfide segregation
1189 644 and remobilization does not appear to be a prerequisite to form economic large PCDs in
1190
1191 645 subduction-related setting.
1192
1193 646

1194 647 *5.2 Source vs. crustal processes*

1195
1196 648 The importance of the melt H₂O content has long been recognized since large
1197 649 economic PCDs are predominantly associated with subvolcanic calc-alkaline intrusions
1198
1199 650 characterized by high Sr/Y and La/Yb ratios ascribed to the early crystallization of
1200
1201 651 amphibole in the deep crust (\pm garnet at high pressure) (Richards, 2011b; Chiaradia et al.,
1202 652 2012; Loucks, 2014). Furthermore, these ratios positively correlate with arc crustal
1203
1204 653 thickness (Chiaradia, 2015; Profeta et al., 2015; Lieu and Stern, 2019), which ultimately
1205 654 correlates with tholeiitic and calc-alkaline differentiation series at the global scale
1206
1207 655 (Miyashiro, 1974; Chiaradia, 2014). It has been proposed that the crustal thickness
1208
1209 656 primarily controls the association of large PCDs, calc-alkaline magmas and thicker arc with
1210
1211 657 a limited role for the composition of the mantle source (e.g., Chiaradia, 2014). Yet, at the arc
1212 658 scale, tholeiitic and calc-alkaline arc magmas are temporally and spatially related from fore-
1213
1214 659 arc to back-arc and the different LLDs are controlled by the initial H₂O content of the
1215 660 primitive arc melt independently to the pressure of differentiation (Fig. 7a; Sisson and Grove
1216
1217 661 1993; Baker et al., 1994; Villiger et al., 2004; Tatsumi and Susuki, 2009; Zimmer et al., 2010;
1218 662 Melekhova et al., 2013; Brounce et al., 2014; Mandler et al., 2014; Nandedkar et al., 2014;
1219
1220 663 Ulmer et al., 2018). Here, we suggest that the importance of the initial melt H₂O content in
1221
1222 664 the ore forming potential of arc magmas reflects the primary role of flux melting in the
1223 665 mantle source associated with wet calc-alkaline series, in opposition to decompression
1224
1225 666 melting associated with damp tholeiitic series (Fig. 9; Grove et al., 2002; Cervantes and
1226
1227 667 Wallace, 2003; Jagoutz et al., 2011). The first order relationship between calc-alkaline
1228
1229
1230
1231
1232

1233
1234
1235 668 magmas and crustal thicknesses (Miyashiro, 1974; Chiaradia, 2014) illustrates that the
1236
1237 669 crustal thickness controls the height of the mantle column and influences the relative
1238
1239 670 importance of decompression melting versus flux melting (Grove et al., 2002; Jagoutz et al.,
1240 671 2011; Karlstrom et al. 2014; Turner and Langmuir, 2015). This makes intuitively sense as a
1241
1242 672 thicker crust reduces the mantle wedge thickness and hence is associated with a shorter
1243
1244 673 melting column, reducing the capability of the mantle to decompress. At the arc scale, the
1245 674 preferential association of PCDs with the episode of crustal thickening (e.g., Cooke et al.,
1246 675 2005) would be consistent with a shorter melting column and the dominance of flux melting
1248 676 regimes during internal tectonic and magmatic cycles. In conclusions, the role of flux melting
1249
1250 677 at a given arc location remains of primary importance for the ore-forming potential in arc
1251
1252 678 magmas and the formation of economic PCDs.

1253 679

1255 680 6. Conclusions

1256 681 In this study, we reviewed the Cu concentrations in primitive arc melts, plutonic rocks
1257
1258 682 and derivative melts, and volcanic rocks to discuss the role of mantle source and crustal
1259
1260 683 magmatic processes to generate fertile magmatism associated with large economic PCDs.
1261 684 The compilation of primitive arc melt does not indicate any particular Cu endowment for a
1262
1263 685 specific type of primitive arc melt and/or geodynamic setting. Our results are consistent with
1264
1265 686 previous studies (Lee et al., 2012) showing an average Cu concentration in different types of
1266 687 primitive arc basalts similar to MORBs (~80 ppm) indicative of the predominant
1267
1268 688 contribution of Cu from the mantle wedge and limited slab-related fluid/melts input. This
1269
1270 689 suggests that the initial Cu endowment in the primitive arc melt is unlikely to represent a
1271 690 crucial prerequisite to form large economic PCDs. Our global compilation of plutonic rocks
1272
1273 691 illustrates that Cu-rich arc (> 100 ppm) cumulates are associated with both calc-alkaline and
1274 692 tholeiitic series. In contrast, our global compilation of volcanic rocks documents
1275
1276 693 systematically different Cu evolution during magma differentiation in calc-alkaline and
1277
1278 694 tholeiitic series for each arc. The contrasting evolution of Cu in tholeiitic and calc-alkaline
1279 695 systematically correlates with FeO_{tot} and V, which is consistent with previous studies
1280
1281 696 suggesting that the different timing of magmatic sulfide saturation relates to the onset of Fe-
1282
1283 697 oxides crystallization on the respective LLDs (Jenner et al., 2010; Chiaradia, 2014).
1284 698 Additional parameters (pressure of magma differentiation, LLDs, $f\text{O}_2$, and/or sulfur

1289
1290
1291
1292
1293
1294
1295
1296
1297
1298
1299
1300
1301
1302
1303
1304
1305
1306
1307
1308
1309
1310
1311
1312
1313
1314
1315
1316
1317
1318
1319
1320
1321
1322
1323
1324
1325
1326
1327
1328
1329
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1340
1341
1342
1343
1344

699 concentration) may locally play a role and account for the large range of Cu concentration
700 observed in the compiled data. Although the average Cu concentrations during melt
701 differentiation is systematically higher for tholeiitic series compared to calc-alkaline series,
702 we propose that the melt Cu concentrations have minor implications for the ore-forming
703 potential of arc magmas. Instead, we demonstrate that the initial melt H₂O content in
704 primitive arc melts controls the LLD and the volume of remaining melt mass at fluid
705 saturation. We showed that the melt mass remaining is a key parameter for calculating the
706 total mass of Cu transferred into exsolving hydrothermal fluids. We propose that the single
707 stage model for the formation of large economic PCDs is most applicable for melts from the
708 calc-alkaline series. The importance of the initial melt H₂O content ultimately reflects the key
709 role of flux melting associated with wet calc-alkaline series and high ore-forming potential,
710 in opposition to decompression melting associated with damp tholeiitic series.

Acknowledgments

713 H. R. acknowledges the support by the Swiss National Foundation through the early post-doc
714 mobility research grant P2GEP2_178008. The work of O. J and H. R. was supported by
715 National Science Foundation under grant number EAR-1552202. The authors are grateful
716 for the active discussions during group meetings at MIT that contribute to shape our ideas.
717 The authors thank the reviewers for their insightful comments that helped to clarify and
718 improve the manuscript.

Disclosure Statement

721 No potential conflict of interest was reported by the authors.

FIGURE CAPTION

724 **Fig. 1:** World map showing the distribution of arc magmatism and porphyry copper deposits.
725 The location of calc-alkaline and tholeiitic magmatism compiled in this study is from the
726 Georoc database (<http://georoc.mpch-mainz.gwdg.de/georoc/>). The location of porphyry
727 copper deposits and the deposit size are from [Singer et al. \(2005\)](#). Phanerozoic felsic
728 magmatism is after [Jagoutz and Klein \(2018\)](#). The location of active margins is from [Hayes
729 et al. \(2018\)](#).

1345
1346
1347
1348
1349
1350
1351
1352
1353
1354
1355
1356
1357
1358
1359
1360
1361
1362
1363
1364
1365
1366
1367
1368
1369
1370
1371
1372
1373
1374
1375
1376
1377
1378
1379
1380
1381
1382
1383
1384
1385
1386
1387
1388
1389
1390
1391
1392
1393
1394
1395
1396
1397
1398
1399
1400

730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758

Fig. 2: Compilation of Cu concentrations in primitive arc melts and mid-oceanic ridge basalts (MORBs). (a) Whisker plot showing the Cu concentrations in primitive arc melt based on variable tectonic settings using the classification scheme of Schmidt and Jagoutz (2017). The ranges of Cu values for primitive MORBs are compiled from Gale et al. (2013). (b) Average Cu concentration and associated uncertainties (1 SD) for primitive arc basalts (blue), primitive arc high-Mg andesites (orange), and primitive MORBs (grey). (c) Histogram showing the distribution of Cu concentrations for primitive arc basalts, primitive arc high-Mg andesites (HMA), and primitive MORBs. Abbreviations in (a): C for continental arc, IO for Intra-oceanic arc, and BAB for back-arc basin.

Fig. 3: Plots of Cu, FeO_{tot} and V versus MgO for volcanic rocks of 28 arcs. (a–c) Tholeiitic rocks (n=6,114) (d–f) Calc-alkaline rocks (n=9,275). Median values for each compiled arc are also plotted at every MgO = 0.5 wt% for tholeiitic series (dark red circle) and calc-alkaline series (light blue circle) (see details in Fig. C1). Median values of Cu, FeO_{tot} and V for every MgO = 0.5 wt% are shown for the global compilation of tholeiitic and calc-alkaline series (yellow diamond). The average Cu concentration and associated uncertainties (1 SD) for primitive arc basalts (black bar) is shown in (a) and (d).

Fig. 4: Geochemical relationships between Cu, FeO_{tot}, V and crustal thicknesses for 17 volcanic arcs with representative whole rock geochemical data set (n>300). (a) Cu versus FeO_{tot}. (b) V versus FeO_{tot}. (c) Cu₄ versus Fe₄, where Cu₄ and Fe₄ correspond to the average of median values and associated uncertainties (1 SD) of Cu and Fe between MgO = 3 and MgO = 5 wt% (see Table B1). Circles and squares represent thin (<25 km) and thick arc (>25 km). (d) Cu₄ versus crustal thickness. References for crustal thicknesses and associated uncertainties (1 SD) are available in Table B1. The average Cu concentration and associated uncertainties (1 SD) for primitive arc basalts (black bar) is shown in (c) and (d).

1401
1402
1403
1404
1405
1406
1407
1408
1409
1410
1411
1412
1413
1414
1415
1416
1417
1418
1419
1420
1421
1422
1423
1424
1425
1426
1427
1428
1429
1430
1431
1432
1433
1434
1435
1436
1437
1438
1439
1440
1441
1442
1443
1444
1445
1446
1447
1448
1449
1450
1451
1452
1453
1454
1455
1456

Fig. 5: (a) Plots of Mg# (molar Mg/(Mg+Fe)) versus SiO₂ for compiled whole-rock compositions of plutonic rocks for four crustal sections (Famatina, Fjordland, Kohistan and Talkeetna; Jagoutz and Kelemen, 2015; Jagoutz and Klein, 2018 and references therein) together with other cumulates xenoliths from the Bonanza arc, Sierra Nevada, Arizona, Eastern Pontides and Kermadec (Chin et al., 2018 and references therein). Red dots are used for the Chilas complex in Kohistan arc as it represents a damp tholeiitic fractionation, whereas dots with different shades of blue represent plutonic rocks and cumulates xenoliths associated with wet calc-alkaline fractionation (Jagoutz et al., 2011; Jagoutz and Klein, 2018). (b) Histogram showing the density of Cu concentrations for the four crustal sections and other cumulates xenoliths. See discussion for details and the full data set and references in Table C1.

Fig. 6: Sulfur speciation in melt and sulfur solubility as a function of oxygen fugacity, expressed log units relative to the fayalite-magnetite-quartz buffer (ΔFMQ). (a) The different black curves illustrates the changes in S₆₊/S_{tot} in hydrous silicate melts with pressure from Jugo et al., (2010), Botcharnikov et al., (2011) and Matjuschkin et al. (2016). The brown line represents the sulfur solubility curve at sulfide and sulfate saturation at 0.2 GPa after Botcharnikov et al. (2011), whereas the brown dotted line represents an hypothetical similar sulfur solubility curve at higher pressure of 1 GPa. The upper inset indicates the redox ranges for mid-ocean ridge basalt (MORB), sub-arc mantle and arc basalts from Ballhaus (1993), Carmichael (1991), Parkinson and Arculus (1999), Arai and Ishimaru (2008), Wallace and Edmons (2011), Evans et al., (2012) and Bénard et al., (2018). We report a range of sulfur concentrations (orange whisker plot with a median values of 0.12 wt%) measured in olivine-hosted melt inclusions for arc-related basalts and basalt-andesites compiled from the Georoc database (n=456). (b-e) Sulfur solubility curves simplified from Figure 6a to illustrate the effect of different parameters on sulfide saturation, including (b) variable pressure of differentiation, (c) different liquid line of descent, (d) variable initial redox conditions, and (e) variable initial sulfur content [S]_i. In (b) and (c), the values of F and the timing of

magnetite is quantified in [Table D1](#). The different scenarios are also discussed in details in the section 4.1 of the manuscript.

Fig. 7: Computed melt composition, melt Cu concentration, melt H₂O content, melt fraction (F), during magmatic differentiation for wet (2 to 4 wt% H₂O - blue) and damp (0.2 to 1.5 wt% H₂O - red) at $\Delta\text{FMQ} = 1$ for variable starting pressure of differentiation (i.e., 8-1.5 kbars (dotted lines) and 4-1.5 kbars (plain lines)) using Rhyolite-MELTS ([Gualda et al., 2012](#)). (a) Computed melt evolution of FeO_{tot} versus MgO. For damp LLDs, the highest and lowest Fe enrichment at MgO ~4-5 wt% corresponds to initial H₂O of 0.2 and 1.5 wt%, respectively. The black line corresponds to modelled LLD with initial H₂O of 1 wt% at $\Delta\text{FMQ} = 1$ from [Zimmer et al. \(2010\)](#), showing the effect of the initial primitive melt composition for the Fe enrichment. Shaded dots are single data and median data per arc from our global compilation of tholeiitic and calc-alkaline volcanic rocks in [Figure 3b,e](#). (b) Evolution of the Cu concentration versus MgO in wet, damp and dry melt modelled using Rayleigh fractionation assuming 0.25 vol.% sulfide ($D_{\text{Cu}}^{\text{sulfide/melt}} = 800$) and 99.75 vol.% silicate ($D_{\text{Cu}}^{\text{silicate/melt}} = 0.1$). Shaded dots are single data and median data per arc from our global compilation of tholeiitic and calc-alkaline volcanic rocks in [Figure 3a,d](#). The steady depletion assumes early sulfide saturation to simulate the trends observed in all calc-alkaline series and some tholeiitic series in thick arcs (>25 km). In contrast, the early enrichment in Cu followed by a sharp depletion simulates late sulfide saturation at MgO ~4 wt% to reproduce the evolution of Cu concentration displayed by tholeiitic series in thin arcs (<25 km). (c, d) Rhyolite-MELTS computed melt H₂O content versus the remaining melt mass (F) and pressure (P). See text for detailed discussion and [Table D1](#) for full data sets.

Fig. 8: Relationship between the initial melt H₂O content and the ore-forming potential for the different liquid lines of descents modelled in Figure 7. The ore-forming potential is expressed as the relative Cu endowment in fluid expelled at degassing of a H₂O-saturated magma normalized to damp tholeiitic melts modelled with an initial H₂O content of 0.5 wt% (circles) and 1.5 wt% (squares) according to the variable pressure of differentiation from 4 to 1.5 kbars (4 kb – filled symbol) from 8 to 1.5 kbars (8 kb – empty symbol). The different

1513
1514
1515 818 colors reflect melt Cu content at H₂O saturation in tholeiitic series assuming late sulfide
1516 819 saturation in thin arc (grey) and early sulfide saturation in thick arc (yellow). Details of the
1517 820 calculation is provided in [Table D1](#) and [Supplementary Material A1](#). See text for discussion.
1518
1519
1520 821

1521
1522 822 **Fig. 9:** Conceptual cartoon of the single-stage and multi-stage models for the formation of
1523 823 porphyry Cu deposits (PCDs). (a) The single stage model assumes the formation of large
1524 824 economic PCDs associated with the generation of wet calc-alkaline melts, where flux melting
1525 825 is predominant in the main arc. (b) The single stage model assumes the formation of barren
1526 826 upper crustal intrusions associated with the generation of damp tholeiitic melts, where
1527 827 decompression melting is predominant in the main arc. (c) The multi-stage model assumes
1528 828 the remobilization of Cu-sulfide sequestered in crustal cumulates during a later hydrous and
1529 829 oxidized magmatic event in the main arc, which may result in the formation of large PCDs.
1530
1531
1532
1533
1534

1535 830
1536 831 **Fig. A1:** Plots of Cu versus MgO for primitive arc basalts and primitive high-Mg Andesites
1537 832 using the classification scheme of [Schmidt and Jagoutz \(2017\)](#).
1538
1539
1540 833

1541 834 **Fig. B1:** Classification of tholeiitic and calc-alkaline volcanic rocks (n=15,389) based on the
1542 835 FeO/MgO versus SiO₂ after [Miyashiro \(1974\)](#).
1543
1544
1545 836

1546 837 **Fig. C1:** Plots of Cu, FeO_{tot} and V versus MgO for calc-alkaline and tholeiitic volcanic rocks for
1547 838 each compiled arc. Median Cu, FeO_{tot} and V values for each arc are plotted at every MgO = 0.5
1548 839 wt%.
1549
1550

1551 840
1552 841 **Fig. D1:** Plots of Cu and V versus FeO_{tot} for calc-alkaline and tholeiitic volcanic rocks for each
1553 842 compiled arc.
1554
1555

1556 843 1557 844 REFERENCES

1559 845 Allibone, A. H., Jongens, R., Scott, J. M., Tulloch, A. J., Turnbull, I. M., Cooper, A. F., Powell, N. G., Ladley, E. B., King,
1560 846 R. P., Rattenbury, M. S., 2009. Plutonic rocks of the Median Batholith in eastern and central Fiordland, New
1561 847 Zealand. Field relations, geochemistry, correlation, and nomenclature: *New Zeal. J. of Geol. Geop.* 52, 101–
1562 848 148.
1563
1564
1565
1566
1567
1568

1569
1570
1571 849 Arai, S., Ishimaru, S., 2008. Insights into petrological characteristics of the lithosphere of mantle wedge beneath
1572 arcs through peridotite xenoliths: a review. *J. Petrol.* 49, 665-695.
1573 850
1574 851 Parkinson, I. J., Arculus, R. J., 1999. The redox state of subduction zones: insights from arc-peridotites. *Chem.*
1575 852 *Geol.* 160, 409-423.
1576
1577 853 Audétat, A., Simon, A. C., 2012. Magmatic Controls on Porphyry Copper Genesis. In *Geology and Genesis of Major*
1578 854 *Copper Deposits and Districts of the World: A Tribute to Richard H. Sillitoe*, eds. Jeffrey W. Hedenquist,
1579 855 Michael Harris, Francisco Camus. Society of Economic Geologists, Special Publication 16, 553-572.
1580
1581 856 Baker, M. B., Grove, T. L., Price, R., 1994. Primitive basalts and andesites from the Mt. Shasta region, N. California:
1582 857 products of varying melt fraction and water content. *Contrib Mineral Petrol.* 118, 111-129.
1583 858
1584 Ballhaus, C., 1993. Redox states of lithospheric and asthenospheric upper mantle. *Contrib Mineral Petrol.* 114,
1585 859 331-348.
1586 860 Bénéard, A., Klimm, K., Woodland, A. B., Arculus, R. J., Wilke, M., Botcharnikov, R. E., Shimizu, N., Nebel, O., Rivard,
1587 861 C., Ionov, D. A., 2018. Oxidising agents in sub-arc mantle melts link slab devolatilisation and arc magmas.
1588 *Nat. Commun.* 9, 3500.
1589 862
1590 863 Botcharnikov, R. E., Linnen, R. L., Wilke, M., Holtz, F., Jugo, P. J., and Berndt, J., 2011. High gold concentrations in
1591 864 sulphide-bearing magma under oxidizing conditions. *Nat. Geo.* 4, 112-115.
1592
1593 865 Brounce, M. N., Kelley, K. A., and Cottrell, E., 2014. Variations in $Fe^{3+}/\Sigma Fe$ of Mariana Arc basalts and mantle
1594 866 wedge fO_2 . *J. Petrol.* 55, 2513-2536.
1595
1596 867 Brounce, M., Cottrell, E., and Kelley, K. A., 2019. The redox budget of the Mariana subduction zone. *Earth Planet.*
1597 868 *Sci. Lett.* 528, 115859.
1598 869
1599 Bucholz, C. E., Kelemen, P. B., 2019. Oxygen fugacity at the base of the Talkeetna arc, Alaska. *Contrib Mineral*
1600 870 *Petrol.* 174, 79.
1601 871
1602 872 Canil, D., 1999. Vanadium partitioning between orthopyroxene, spinel and silicate melt and the redox states of
1603 mantle source regions for primary magmas *Geochim. Cosmochim. Acta* 63, 557-572.
1604 873
1605 874 Carmichael, I. S., 1991. The redox states of basic and silicic magmas: a reflection of their source regions?. *Contrib*
1606 *Mineral Petrol.* 106, 129-141.
1607 875
1608 876 Caricchi, L., Simpson, G., Schaltegger, U., 2014. Zircons reveal magma fluxes in the Earth's crust. *Nature* 511,
1609 877 457-461.
1610
1611 878 Cervantes, P., and Wallace, P. J., 2003. Role of H₂O in subduction-zone magmatism: new insights from melt
1612 879 inclusions in high-Mg basalts from central Mexico. *Geology* 31, 235-238.
1613 880
1614 881 Chelle-Michou, C., Rottier, B., Caricchi, L., Simpson, G., 2017. Tempo of magma degassing and the genesis of
1615 porphyry copper deposits. *Sci. Rep.* 7, 40566.
1616 882
1617 883 Chiaradia, M., 2014. Copper enrichment in arc magmas controlled by overriding plate *Nat. Geo.* 7, 43-46.
1618
1619 884 Chiaradia, M., 2015. Crustal thickness control on Sr/Y signatures of recent arc magmas: an Earth scale
1620 885 perspective. *Sci. Rep.* 5, 8115.
1621
1622 Chiaradia, M., 2020a. How much water in basaltic melts parental to porphyry copper deposits?. *Frontiers in*
1623 *Earth Sciences*, 8, 313.
1624

1625
1626
1627 886 Chiaradia, M., 2020b. Gold endowments of porphyry deposits controlled by precipitation efficiency. *Nat.*
1628 887 *Commun.* 11, 1-10.
1630 888 Chiaradia, M., Caricchi, L., 2017. Stochastic modelling of deep magmatic controls on porphyry copper deposit
1631 889 endowment. *Sci. Rep.* 7, 44523.
1632
1633 890 Chiaradia, M., Ulianov, A., Kouzmanov, K., Beate, B., 2012. Why large porphyry Cu deposits like high Sr/Y
1634 891 magmas? *Sci. Rep.* 2, 685.
1635 892 Chin, E.J., Shimizu, K., Bybee, G.M., Erdman, M.E., 2018. On the development of the calc-alkaline and tholeiitic
1636 893 magma series: a deep crustal cumulate perspective. *Earth Planet. Sci. Lett.* 482, 277–287.
1638 894 Ciazela, J., Dick, H. J., Koepke, J., Pieterek, B., Muszynski, A., Botcharnikov, R., Kuhn, T., 2017. Thin crust and
1639 895 exposed mantle control sulfide differentiation in slow-spreading ridge magmas. *Geology* 45, 935-938.
1640
1641 896 Cline, J. S., Bodnar, R. J., 1991. Can economic porphyry copper mineralization be generated by a typical
1642 897 calc-alkaline melt?. *J. Geophys. Res. Solid Earth* 96(B5), 8113-8126.
1643 898 Cooke, D. R., Hollings, P., Walshe, J. L., 2005. Giant porphyry deposits: characteristics, distribution, and tectonic
1644 899 controls. *Econ. Geol.* 100, 801-818.
1646 900 Cox, D., Watt, S. F., Jenner, F. E., Hastie, A. R., Hammond, S. J., 2019. Chalcophile element processing beneath a
1647 901 continental arc stratovolcano. *Earth Planet. Sci. Lett.* 522, 1-11.
1649 902 Du, J., Audétat, A., 2020. Early sulfide saturation is not detrimental to porphyry Cu-Au formation. *Geology*, 48,
1650 903 519-524
1651 904 Duan, Z., Zhang, Z., 2006. Equation of state of the H₂O, CO₂, and H₂O–CO₂ systems up to 10 GPa and 2573.15 K:
1652 905 molecular dynamics simulations with ab initio potential surface. *Geochim Cosmochim Acta* 70:2311–2324
1653 906 Evans, K. A., Elburg, M. A., Kamenetsky, V. S., 2012. Oxidation state of subarc mantle. *Geology* 40, 783-786.
1654 907 Fliedner, M. M., Klemperer, S. L., 1999. Structure of an island-arc: Wide-angle seismic studies in the eastern
1657 908 Aleutian Islands, Alaska. *Journal of Geophysical Research: Solid Earth*, 104(B5), 10667-10694.
1658 909 Fortin, M. A., Riddle, J., Desjardins-Langlais, Y., Baker, D. R., 2015. The effect of water on the sulfur concentration
1659 910 at sulfide saturation (SCSS) in natural melts. *Geochim Cosmochim Acta* 160, 100-116.
1661 911 Gale, A., Dalton, C. A., Langmuir, C. H., Su, Y., Schilling, J. G., 2013. The mean composition of ocean ridge basalts.
1662 912 *Geochem Geophys Geosyst.* 14, 489-518.
1663 913 Georgatou, A., Chiaradia, M., 2019. Magmatic sulphides in high-K calc-alkaline to shoshonitic and alkaline rocks.
1665 914 *Solid Earth.* <https://doi.org/10.5194/se-2019-106>
1666 915 Georgatou, A., Chiaradia, M., Rezeau, H., Wälle, M., 2018. Magmatic sulphides in Quaternary Ecuadorian arc
1667 916 magmas. *Lithos* 296, 580-599.
1669 917 Ghiorso, M. S., Carmichael, I. S., 1987. Modeling magmatic systems; petrologic applications. *Rev Mineral*
1670 918 *Geochem*, 17, 467-499.
1671 919 Ghiorso, M. S., Gualda, G. A., 2015. An H₂O–CO₂ mixed fluid saturation model compatible with rhyolite-MELTS.
1672 920 *Contrib Mineral Petrol.*, 169, 1-30.
1673 921 Duan Z, Zhang Z (2006) Equation of state of the H₂O, CO₂, and H₂O–CO₂ systems up to 10 GPa and 2573.15 K:
1674 922 molecular dynamics simulations with ab initio potential surface. *Geochim Cosmochim Acta* 70:2311–2324
1675
1676
1677
1678
1679
1680

1681
1682
1683 923 Giacometti, F., Evans, K. A., Rebay, G., Cliff, J., Tomkins, A. G., Rossetti, P., Vaggelli, G., Adams, D. T. (2014). Sulfur
1684 924 isotope evolution in sulfide ores from Western Alps: Assessing the influence of subduction-related
1685 925 metamorphism. *Geochem Geophys Geosyst* 15, 3808-3829.
1686 926
1687 926 Greene, A. R., DeBari, S. M., Kelemen, P. B., Blusztajn, J., Clift, P. D., 2006. A detailed geochemical study of island
1688 927 arc crust: the Talkeetna arc section, south-central Alaska. *J Petrol*, 47, 1051-1093.
1689 927
1690 928 Grove, T., Parman, S., Bowring, S., Price, R., Baker, M., 2002. The role of an H₂O-rich fluid component in the
1691 929 generation of primitive basaltic andesites and andesites from the Mt. Shasta region, N California. *Contrib*
1692 930 *Mineral Petrol.* 142, 375-396.
1693 930
1694 931 Grove, T. L., Till, C. B., Krawczynski, M. J., 2012. The role of H₂O in subduction zone magmatism. *Annu. Rev. Earth*
1695 932 *Planet. Sci*, 40, 413-439.
1696 932
1697 933 Gualda, A.R., Ghiorso, M.S., Lemons, R. V., Tamara L., Carley, T. L., 2012. Rhyolite-MELTS: a Modified Calibration
1698 934 of MELTS Optimized for Silica-rich, Fluid-bearing Magmatic Systems, *J Petrol.* 53, 875-890.
1699 935
1700 935 Hayes, G. P., Moore, G. L., Portner, D. E., Hearne, M., Flamme, H., Furtney, M., Smoczyk, G. M., 2018. Slab2, a
1701 936 comprehensive subduction zone geometry model. *Science* 362, 58-61.
1702 937
1703 937 Hedenquist, J.W., Lowenstern, J.B., 1994. The role of magmas in the formation of hydrothermal ore deposits.
1704 938 *Nature* 370, 519.
1705 939
1706 939 Hou, Z., Yang, Z., Lu, Y., Kemp, A., Zheng, Y., Li, Q., Tang, J., Yang, Z. and Duan, L., 2015. A genetic linkage between
1707 940 subduction-and collision-related porphyry Cu deposits in continental collision zones. *Geology* 43, 247-
1708 941 250.
1709 942
1710 942 Hsu, Y. J., Zajacz, Z., Ulmer, P., Heinrich, C. A., 2017. Copper partitioning between silicate melts and amphibole:
1711 943 Experimental insight into magma evolution leading to porphyry copper ore formation. *Chem. Geol.* 448,
1712 944 151-163.
1713 945
1714 945 Jagoutz, O. E., 2010. Construction of the granitoid crust of an island arc. Part II: a quantitative petrogenetic
1715 946 model. *Contrib Mineral Petrol.* 160, 359-381.
1716 947
1717 947 Jagoutz, O., Klein, B., 2018. On the importance of crystallization-differentiation for the generation of SiO₂-rich
1718 948 melts and the compositional build-up of arc (and continental) crust. *Am. J. Sci*, 318, 29-63.
1719 949
1720 949 Jagoutz, O., Kelemen, P. B., 2015. Role of arc processes in the formation of continental crust. *Annu. Rev. Earth*
1721 950 *Planet. Sci*, 43, 363-404.
1722 951
1723 951 Jagoutz, O., Müntener, O., Schmidt, M. W., Burg, J. P., 2011. The roles of flux-and decompression melting and
1724 952 their respective fractionation lines for continental crust formation: Evidence from the Kohistan arc. *Earth*
1725 953 *Planet Sc Lett.* 303, 25-36.
1726 954
1727 954 Jégo, S., Dasgupta, R., 2014. The fate of sulfur during fluid-present melting of subducting basaltic crust at
1728 955 variable oxygen fugacity. *J. Petrol.* 55, 1019-1050.
1729 956
1730 956 Jenner, F. E., 2017. Cumulate causes for the low contents of sulfide-loving elements in the continental crust. *Nat.*
1731 957 *Geo.* 10, 524-529.
1732 958
1733 958 Jenner, F. E., O'Neill, H. S. C., 2012. Analysis of 60 elements in 616 ocean floor basaltic glasses. *Geochem,*
1734 959 *Geophys, Geosyst.* 13.
1735
1736

1737
1738
1739 960 Jenner, F.E., O'Neill, H.S.C., Arculus, R.J., Mavrogenes, J.A., 2010. The magnetite crisis in the evolution of arc-
1740 related magmas and the initial concentration of Au, Ag and Cu. *J. Petrol.* 51, 2445–2464.
1741 961
1742 962 Jicha, B. R., Jagoutz, O., 2015. Magma production rates for intraoceanic arcs. *Elements* 11, 105-111.
1743 963 Johnson, E. R., Wallace, P. J., Delgado Granados, H., Manea, V. C., Kent, A. J., Bindeman, I. N., and Donegan, C. S.,
1744 964 2009. Subduction-related volatile recycling and magma generation beneath Central Mexico: insights from
1746 965 melt inclusions, oxygen isotopes and geodynamic models. *J. Petrol.* 50, 1729-1764.
1747 966 Jugo, P. J., 2009. Sulfur content at sulfide saturation in oxidized magmas. *Geology* 37, 415-418.
1748 967 Jugo, P.J., Wilke, M., Botcharnikov, R.E., 2010. Sulfur K-edge XANES analysis of natural and synthetic basaltic
1750 968 glasses: implications for S speciation and S content as function of oxygen fugacity. *Geochim. Cosmochim.*
1751 969 *Acta* 74, 5926–5938
1752 970 Karlstrom, L., Lee, C.T., Manga, M., 2014. The role of magmatically driven lithospheric thickening on arc front
1754 971 migration. *Geochem. Geophys. Geosyst.* 15, 2655–2675.
1755 972 Kelemen, P. B., Shimizu, N., Salters, V. J. M., 1995. Formation of harzburgite by pervasive melt/rock reaction
1756 973 in the upper mantle, *Nature* 358, 635–641.
1758 974 Kelemen, P., Hanghøj, B., K., Greene, A. R., 2014. One view of the geochemistry of subduction-related magmatic
1759 975 arcs, with an emphasis on primitive andesite and lower crust. In *The Crust, Treatise on Geochemistry*,
1761 976 edited by H. D. Holland and K. K. Turekian, pp. 669–701, Elsevier-Pergamon, Oxford, U. K.
1762 977 Kelley, K.A., Cottrell, E., 2009. Water and the oxidation state of subduction zone magmas. *Science* 325, 605–607
1763 978 Kelley, K. A., Cottrell, E., 2012. The influence of magmatic differentiation on the oxidation state of Fe in a basaltic
1765 979 arc magma. *Earth Planet. Sci.* 329, 109-121.
1766 980 Kesler, S.E., Jones, L.M., Walker, R.L., 1975, Intrusive rocks associates with porphyry copper mineralization in
1767 981 island arc areas. *Econ. Geol.* 70, 515-526.
1769 982 Kesler, S. E., Sutter, J. F., Issigonis, M. J., Jones, L. M., Walker, R. L., 1977. Evolution of porphyry copper
1770 983 mineralization in an oceanic island arc; Panama. *Econ. Geol.* 72, 1142-1153.
1771 984 Kiseeva, E. S., Wood, B. J., 2015. The effects of composition and temperature on chalcophile and lithophile
1773 985 element partitioning into magmatic sulphides. *Earth Planet. Sci.* 424, 280-294.
1774 986 Kouzmanov, K., Pokrovski, G. S., 2012. Hydrothermal controls on metal distribution in porphyry Cu(–Au–Mo)
1776 987 systems. In *Geology and Genesis of Major Copper Deposits and Districts of the World: A Tribute to Richard*
1777 988 *H. Sillitoe*, eds. Jeffrey W. Hedenquist, Michael Harris, Francisco Camus. Society of Economic Geologists,
1778 989 *Special Publication* 16, 573–618.
1780 990 La Tourrette, T. Z., Burnett, D. S., and Bacon, C. R., 1991. Uranium and minor-element partitioning in Fe-Ti oxides
1781 991 and zircon from partially melted granodiorite, Crater Lake, Oregon. *Geochim. Cosmochim. Acta* 55, 457-
1782 992 469.
1783 993 Lee, C. T. A., Tang, M., 2020. How to make porphyry copper deposits. *Earth Planet. Sci.* 529, 115868.
1784 994 Lee, C. T. A., Luffi, P., Le Roux, V., Dasgupta, R., Albaréde, F., Leeman, W. P., 2010. The redox state of arc mantle
1785 995 using Zn/Fe systematics. *Nature* 468, 681-685.
1786
1787
1788
1789
1790
1791
1792

1793
1794
1795 996 Lee, C.-T.A., Luffi, P., Chin, E.J., Bouchet, R., Dasgupta, R., Morton, D.M., Le Roux, V., Yin, Q.-z., Jin, D., 2012. Copper
1796 997 systematics in arc magmas and implications for crust–mantle differentiation. *Science* 336, 64–68.
1798 998 Li, Y., Audétat, A., 2012. Partitioning of V, Mn, Co, Ni, Cu, Zn, As, Mo, Ag, Sn, Sb, W, Au, Pb, and Bi between sulfide
1799 999 phases and hydrous basanite melt at upper mantle conditions. *Earth Planet. Sci. Lett.* 355–356, 327–340.
1800 1000 Lieu, W. K., Stern, R. J., 2019. The robustness of Sr/Y and La/Yb as proxies for crust thickness in modern arcs.
1801 1001 *Geosphere* 15, 621-641.
1803 1002 Liu, X., Xiong, X., Audétat, A., Li, Y., Song, M., Li, L., Sun, W., Ding, X., 2014. Partitioning of copper between olivine,
1804 1003 orthopyroxene, clinopyroxene, spinel, garnet and silicate melts at upper mantle conditions. *Geochim.*
1805 1004 *Cosmochim. Acta* 125, 1–22.
1806 1005 Loucks, R., 2014. Distinctive composition of copper–ore-forming arc magmas. *Aust. J. Earth Sci.* 61, 5–16.
1807 1006 Luhr, J. F., Carmichael, I. S., 1980. The colima volcanic complex, Mexico. *Contrib Mineral Petrol.* 71, 343-372.
1808 1007 Mandler, B. E., Donnelly-Nolan, J. M., Grove, T. L., 2014. Straddling the tholeiitic/calc-alkaline transition: the
1809 1008 effects of modest amounts of water on magmatic differentiation at Newberry Volcano, Oregon. *Contrib*
1810 1009 *Mineral Petrol.* 168, 1066.
1811 1010 Matjuschkin, V., Blundy, J.D., Brooker, R.A., 2016. The effect of pressure on sulphur speciation in mid-to deep-
1812 1011 crustal arc magmas and implications for the formation of porphyry copper deposits. *Contrib. Mineral.*
1813 1012 *Petrol.* 171, 66.
1814 1013 Mavrogenes, J. A., O'Neill, H. S. C., 1999. The relative effects of pressure, temperature and oxygen fugacity on
1815 1014 the solubility of sulfide in mafic magmas. *Geochim Cosmochim Acta* 63, 1173-1180.
1816 1015 McInnes, B. I., McBride, J. S., Evans, N. J., Lambert, D. D., Andrew, A. S., 1999. Osmium isotope constraints on ore
1817 1016 metal recycling in subduction zones. *Science* 286, 512-516.
1818 1017 Melekhova, E., Annen, C., Blundy, J., 2013. Compositional gaps in igneous rock suites controlled by magma
1819 1018 system heat and water content. *Nat. Geo.* 6, 385.
1820 1019 Melekhova, E., Schlaphorst, D., Blundy, J., Kendall, J. M., Connolly, C., McCarthy, A., Arculus, R., 2019. Lateral
1821 1020 variation in crustal structure along the Lesser Antilles arc from petrology of crustal xenoliths and seismic
1822 1021 receiver functions. *Earth Planet. Sci.* 516, 12-24.
1823 1022 Miyashiro, A., 1974. Volcanic rock series in island arcs and active continental margins. *Am. J. Sci.* 274, 321–355.
1824 1023 Mungall, J. E., 2002. Roasting the mantle: Slab melting and the genesis of major Au and Au-rich Cu deposits.
1825 1024 *Geology* 30, 915-918.
1826 1025 Müntener, O., Ulmer, P., 2018. Arc crust formation and differentiation constrained by experimental petrology.
1827 1026 *Am. J. Sci.* 318, 64-89.
1828 1027 Nandedkar, R. H., Ulmer, P., and Müntener, O., 2014. Fractional crystallization of primitive, hydrous arc
1829 1028 magmas: an experimental study at 0.7 GPa. *Contrib Mineral Petrol.* 167, 1015.
1830 1029 O'Neill, H. S. C., Mavrogenes, J. A., 2002. The sulfide capacity and the sulfur content at sulfide saturation of
1831 1030 silicate melts at 1400 C and 1 bar. *J. Petrol.* 43, 1049-1087.
1832
1833
1834
1835
1836
1837
1838
1839
1840
1841
1842
1843
1844
1845
1846
1847
1848

1849
1850
1851 1031 Otamendi, J. E., Vujovich, G. I., de la Rosa, J. D., Tibaldi, A. M., Castro, A., Martino, R. D., and Pinotti, L. P., 2009.
1852
1853 1032 Geology and petrology of a deep crustal zone from the Famatinian paleo-arc, Sierras de Valle Fértil and La
1854 1033 Huerta, San Juan, Argentina. *J. S. Am. Earth Sci.* 27, 258-279.
1855 1034 Park, J. W., Campbell, I. H., Malaviarachchi, S. P., Cocker, H., Hao, H., & Kay, S. M., 2019. Chalcophile element
1856
1857 1035 fertility and the formation of porphyry Cu±Au deposits. *Min. Dep.* 54, 657-670.
1858 1036 Portnyagin, M., Hoernle, K., Plechov, P., Mironov, N., and Khubunaya, S., 2007. Constraints on mantle melting
1859 1037 and composition and nature of slab components in volcanic arcs from volatiles (H₂O, S, Cl, F) and trace
1860
1861 1038 elements in melt inclusions from the Kamchatka Arc. *Earth Planet. Sci.* 255, 53-69.
1862 1039 Profeta, L., Ducea, M. N., Chapman, J. B., Paterson, S. R., Gonzales, S. M. H., Kirsch, M., Petrescu, L., and DeCelles,
1863 1040 P. G., 2015. Quantifying crustal thickness over time in magmatic arcs. *Sci. Rep.* 5, 17786.
1864
1865 1041 Rezeau, H., Moritz, R., Wotzlaw, J. F., Tayan, R., Melkonyan, R., Ulianov, A., Selby, D., d'Abzac, F. X., Stern, R. A.,
1866 1042 2016. Temporal and genetic link between incremental pluton assembly and pulsed porphyry Cu-Mo
1867
1868 1043 formation in accretionary orogens. *Geology* 44, 627-630.
1869 1044 Richards, J. P., 2003. Tectono-magmatic precursors for porphyry Cu-(Mo-Au) deposit formation. *Econ. Geol.* 98,
1870 1045 1515-1533.
1871
1872 1046 Richards, J.P., 2009. Postsubduction porphyry Cu–Au and epithermal Au deposits: products of remelting of
1873 1047 subduction-modified lithosphere. *Geology* 37, 247–250.
1874 1048 Richards, J. P., 2011a. Magmatic to hydrothermal metal fluxes in convergent and collided margins. *Ore Geol.*
1875 1049 *Rev.* 40, 1-26.
1876
1877 1050 Richards, J. P., 2011b. High Sr/Y arc magmas and porphyry Cu±Mo±Au deposits: just add water. *Econ. Geol.* 106,
1878 1051 1075-1081.
1879
1880 1052 Richards, J. P., 2015. The oxidation state, and sulfur and Cu contents of arc magmas: implications for
1881 1053 metallogeny. *Lithos* 233, 27-45.
1882 1054 Richards, J. P., 2018. A shake-up in the porphyry world?. *Econ. Geol.* 113, 1225-1233.
1883
1884 1055 Ripley, E. M., Li, C., 2013. Sulfide saturation in mafic magmas: Is external sulfur required for magmatic Ni-Cu-
1885 1056 (PGE) ore genesis?. *Econ. Geol.*, 108, 45-58.
1886
1887 1057 Rowe, M. C., Kent, A. J., Nielsen, R. L., 2009. Subduction influence on oxygen fugacity and trace and volatile
1888 1058 elements in basalts across the Cascade Volcanic Arc. *J. Petrol.* 50, 61-91.
1889 1059 Schmidt, M. W., Jagoutz, O. 2017. The global systematics of primitive arc melts. *Geochem Geophys Geosyst*, 18,
1890 1060 2817-2854.
1891
1892 1061 Seedorff, E., J. H. Dilles, J. M. Proffett, M. T. Einaudi, L. Zurcher, W. J. A. Stavast, D. A. Johnson, and M. D. Barton,
1893 1062 2005, Porphyry deposits: characteristics and origin of hypogene features. *Economic Geology* 100th
1894 1063 Anniversary Volume, eds. Jeffrey W. Hedenquist, John F. H. Thompson, Richard J. Goldfarb, Jeremy P.
1895 1064 Richards
1896
1897 1065 Sillitoe, R.H., 2010. Porphyry copper systems. *Econ. Geol.* 105, 3–41.
1898
1899 1066 Sillitoe, R. H., 1997. Characteristics and controls of the largest porphyry copper-gold and epithermal gold
1900 1067 deposits in the circum-Pacific region, *Aust. J. Earth Sci.* 44, 373-388.
1901
1902
1903
1904

1905
1906
1907 1068 Sillitoe, R.H., Hedenquist, J.W., 2003. Linkages between volcanotectonic settings, ore-fluid compositions, and
1908 1069 epithermal precious metal deposits. SEG Special Publication 10, 315–343.
1910 1070 Singer, D. A., Berger, V. I., Menzie, W. D., Berger, B. R., 2005. Porphyry copper deposit density. *Econ. Geol.* 100,
1911 1071 491-514.
1912
1913 1072 Sisson, T. W., Grove, T. L., 1993. Experimental investigations of the role of H₂O in calc-alkaline differentiation
1914 1073 and subduction zone magmatism. *Contrib Mineral Petrol.* 113, 143-166.
1915 1074 Sobolev, A. V., and Chaussidon, M., 1996. H₂O concentrations in primary melts from supra-subduction zones
1916 1075 and mid-ocean ridges: implications for H₂O storage and recycling in the mantle. *Earth Planet. Sci. Lett.*
1918 1076 137, 45-55.
1919 1077 Solomon, M., 1990. Subduction, arc reversal, and the origin of porphyry copper-gold deposits in island arcs.
1920 1078 *Geology* 18, 630-633.
1922 1079 Stavast, W. J., Keith, J. D., Christiansen, E. H., Dorais, M. J., Tingey, D., Larocque, A., Evans, N., 2006. The fate of
1923 1080 magmatic sulfides during intrusion or eruption, Bingham and Tintic districts, Utah. *Econ. Geol.* 101, 329-
1924 1081 345.
1925 1081
1926 1082 Sun, W., Wang, J. T., Zhang, L. P., Zhang, C. C., Li, H., Ling, M. X., Ding, X., Li, C-y., Liang, H. Y., 2017. The formation
1927 1083 of porphyry copper deposits. *Acta Geochim*, 36, 9-15.
1928 1083
1929 1084 Sun, W., Huang, R. F., Li, H., Hu, Y. B., Zhang, C. C., Sun, S. J., Zhang, L-p., Ding, X., Li, C.Y., Zartman, R.E., Ling, M. X.,
1930 1085 2015. Porphyry deposits and oxidized magmas. *Ore Geol. Rev.* 65, 97-131.
1931 1085
1932 1086 Tatsumi, Y., and Suzuki, T., 2009. Tholeiitic vs calc-alkalic differentiation and evolution of arc crust: constraints
1933 1087 from melting experiments on a basalt from the Izu-Bonin-Mariana Arc. *J. Petrol.* 50, 1575-1603.
1934 1088 Tattitch, B. C., and Blundy, J. D., 2017. Cu-Mo partitioning between felsic melts and saline-aqueous fluids as a
1935 1088 function of X NaC_l, f O₂, and f S₂. *Am. Mineral* 102, 1987-2006.
1936 1089
1937 1090 Tattitch, B. C., Candela, P. A., Piccoli, P. M., Bodnar, R. J., 2015. Copper partitioning between felsic melt and H₂O-
1938 1091 CO₂ bearing saline fluids. *Geochim Cosmochim Acta* 148, 81-99.
1939 1091
1940 1092 Titley, S.R., 1975, Geological characteristics and environment of some porphyry copper occurrences in the
1941 1093 southwestern Pacific. *Econ. Geol.* 70, 499-514.
1942 1093
1943 1094 Tomkins, A. G., 2010. Windows of metamorphic sulfur liberation in the crust: Implications for gold deposit
1944 1095 genesis. *Geochim Cosmochim Acta* 74, 3246-3259.
1945 1096 Tomkins, A. G., and Evans, K. A., 2015. Separate zones of sulfate and sulfide release from subducted mafic
1946 1096 oceanic crust. *Earth Planet. Sci.* 428, 73-83.
1947 1097
1948 1098 Tosdal, R.M., Richards, J.P., 2001. Magmatic and structural controls on the development of porphyry Cu ± Mo ±
1949 1099 Au deposits: *Rev. Econ. Geol.* 14, p. 157–181.
1950 1099
1951 1100 Turner, S. J., and Langmuir, C. H., 2015. What processes control the chemical compositions of arc front
1952 1101 stratovolcanoes?. *Geochem Geophys Geosyst*, 16, 1865-1893.
1953 1102 Ulmer, P., Kaegi, R., and Müntener, O., 2018. Experimentally derived intermediate to silica-rich arc magmas by
1954 1102 fractional and equilibrium crystallization at 1.0 GPa: An evaluation of phase relationships, compositions,
1955 1103 liquid lines of descent and oxygen fugacity. *J. Petrol.* 59, 11-58.
1956 1104
1957
1958
1959
1960

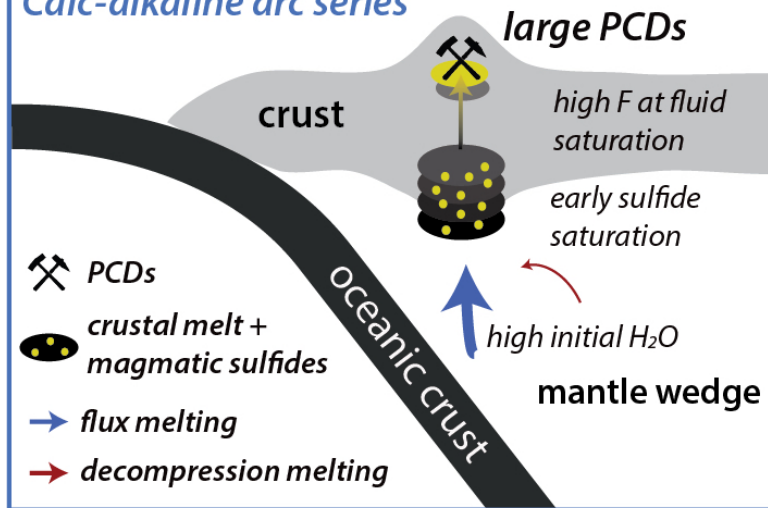
1961
1962
1963 1105 Vasseur, J., and Wadsworth, F. B., 2017. Sphere models for pore geometry and fluid permeability in
1964 1106 heterogeneous magmas. *Bull. Volcanol.* 79, 77.
1966 1107 Villiger, S., Ulmer, P., Müntener, O., and Thompson, A. B., 2004. The liquid line of descent of anhydrous, mantle-
1967 1108 derived, tholeiitic liquids by fractional and equilibrium crystallization—an experimental study at 1.0 GPa.
1968 1109 *J. Petrol.* 45, 2369-2388.
1970 1110 Wallace, P. J., 2005. Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion
1971 1111 and volcanic gas data. *J Volcanol Geoth Res* 140, 217-240.
1972 1112 Wallace, P. J., and Edmonds, M., 2011. The sulfur budget in magmas: evidence from melt inclusions, submarine
1973 1113 glasses, and volcanic gas emissions. *Rev Mineral Geochem*, 73, 215-246.
1974 1114 Walsh, S. D., and Saar, M. O. 2008. Magma yield stress and permeability: Insights from multiphase percolation
1975 1115 theory. . *Volcanol. Geotherm. Res.* 177, 1011-1019.
1978 1116 Wang, R., Weinberg, R. F., Collins, W. J., Richards, J. P., and Zhu, D. C., 2018. Origin of postcollisional magmas and
1979 1117 formation of porphyry Cu deposits in southern Tibet. *Earth Sci. Rev.* 181, 122-143.
1981 1118 Wilkinson, J.J., 2013. Triggers for the formation of porphyry ore deposits in magmatic arcs. *Nat. Geosci.* 6, 917.
1982 1119 Zajacz, Z., Halter, W. E., Pettke, T., and Guillong, M., 2008. Determination of fluid/melt partition coefficients by
1983 1120 LA-ICPMS analysis of co-existing fluid and silicate melt inclusions: controls on element partitioning.
1984 1121 *Geochim Cosmochim Acta* 72, 2169-2197.
1986 1122 Zelenski, M., Kamenetsky, V. S., Mavrogenes, J. A., Danyushevsky, L. V., Matveev, D., Gurenko, A. A. 2017.
1987 1123 Platinum-group elements and gold in sulfide melts from modern arc basalt (Tolbachik volcano,
1988 1124 Kamchatka). *Lithos* 290, 172-188.
1990 1125 Zellmer, G. F., 2008. Some first-order observations on magma transfer from mantle wedge to upper crust at
1991 1126 volcanic arcs. *Geological Society, London, Special Publications*, 304, 15-31.
1993 1127 Zimmer, M. M., Plank, T., Hauri, E. H., Yogodzinski, G. M., Stelling, P., Larsen, J., Singer, B., Jicha, B., Mandeville, C.,
1994 1128 and Nye, C. J., 2010. The role of water in generating the calc-alkaline trend: new volatile data for Aleutian
1995 1129 magmas and a new tholeiitic index. *J. Petrol.* 51, 2411-2444.
1997 1130 Zheng, Y. C., Liu, S. A., Wu, C. D., Griffin, W. L., Li, Z. Q., Xu, B., Yang, Z. M., Hou, Z-Q., O'Reilly, S. Y., 2018. Cu isotopes
1998 1131 reveal initial Cu enrichment in sources of giant porphyry deposits in a collisional setting. *Geology* 47, 135-
1999 1132 138.
2000 1133
2001 1134
2002 1135
2003 1136
2004 1137
2005 1138
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016

1
2
3 **HIGHLIGHTS**
4

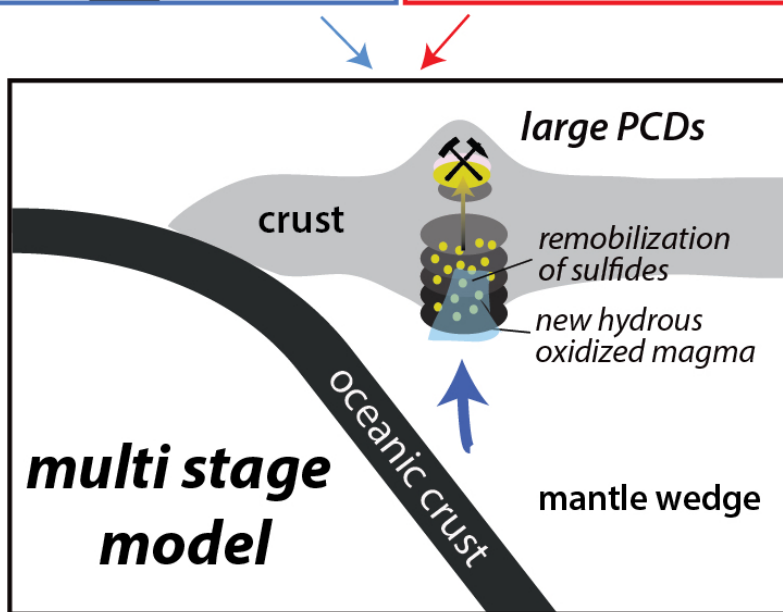
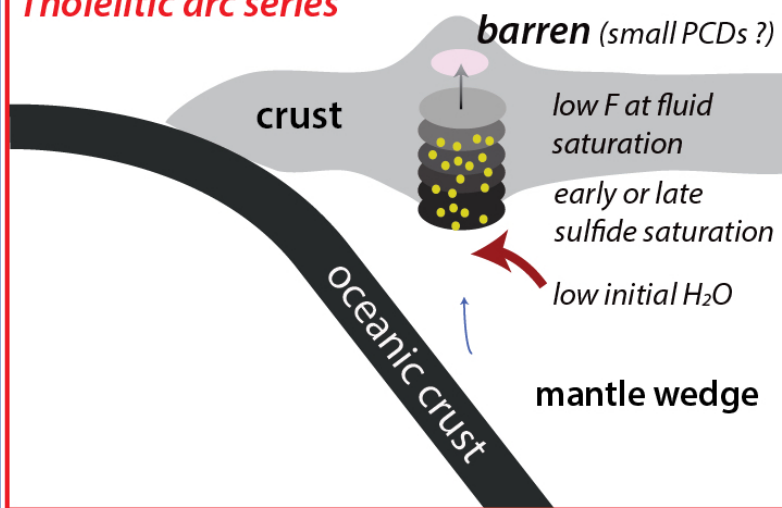
- 5 • Copper (Cu) concentration in primitive arc basalts mainly derived from mantle wedge
- 6
- 7 • Different evolution of melt Cu concentration in calc-alkaline and tholeiitic magmas
- 8
- 9 • Large porphyry copper deposits mostly controlled by initial H₂O melt content in arc
- 10 magmas
- 11
- 12
- 13 • Flux melting in the mantle wedge plays a key role for the ore-forming potential in arc
- 14 settings.
- 15
- 16
- 17
- 18
- 19
- 20
- 21
- 22
- 23
- 24
- 25
- 26
- 27
- 28
- 29
- 30
- 31
- 32
- 33
- 34
- 35
- 36
- 37
- 38
- 39
- 40
- 41
- 42
- 43
- 44
- 45
- 46
- 47
- 48
- 49
- 50
- 51
- 52
- 53
- 54
- 55
- 56

single stage models

Calc-alkaline arc series



Tholeiitic arc series



The importance of H₂O in arc magmas for the formation of porphyry Cu deposits

Hervé Rezeau[†] and Oliver Jagoutz

Department of Earth, Atmospheric, and Planetary Sciences, MIT, Cambridge, USA

[†]Corresponding author: hrezeau@mit.edu

Keywords: Arc magmas; Calc-alkaline and tholeiitic series; Magmatic sulfides; Melt water content; Ore-forming potential; Porphyry copper deposits.

ABSTRACT

Porphyry copper deposits (PCDs) hosted in subvolcanic intrusions at convergent margins are the primary world's copper resources. However, the set of magmatic processes that lead to the generation of ore-bearing magmatic provinces remains unclear. In this paper we review the systematic of Cu evolution during arc magmatic differentiation using new and existing global compilations of whole rock geochemistry data. We trace the Cu evolution from primitive arc magmas through lower crustal plutonic to volcanic rocks. We focus on the well-known tholeiitic and calc-alkaline fractionation sequences, where arc tholeiitic series represents damp primitive melts (<2 wt% H₂O) evolving with iron enrichment, and calc-alkaline series are wet primitive melts (>2 wt% H₂O) that differentiate with iron depletion.

Our study shows that the Cu concentration in primitive arc melts (~80 ppm) is indistinguishable from that of primitive melts formed at mid-ocean ridges (MORBs) implying that Cu is mainly sourced from the mantle wedge in arcs with a limited contribution from the subducted oceanic lithosphere. A global compilation of plutonic rocks whole rock geochemistry (lower crustal cumulates and derivative melts) indicate no systematic difference in Cu concentrations between cumulates associated with tholeiitic or calc-alkaline series. Yet a complementary global compilation of arc volcanic whole rock geochemistry highlights the contrasting behavior of Cu in tholeiitic and calc-alkaline series during magmatic differentiation in arc. In tholeiitic series, Cu shows an incompatible and/or compatible behavior during magma differentiation influenced by the crustal thickness. In calc-alkaline series, Cu is compatible during magma differentiation independently to the crustal thickness. This relates to the timing of sulfide saturation, which is controlled by the

57
58
59 32 liquid lines of descent (LLD) and/or crustal thickness at redox conditions relevant for arc
60 33 magmas.

61
62 34 We demonstrate that the initial melt H₂O content in primitive arc melts controls the
63 35 LLD and the volume of remaining melt mass at fluid saturation. We show that the remaining
64 36 H₂O-saturated melt mass positively correlates with the total mass of Cu transferred into
65 37 degassing fluids. The mass of extractable Cu ranges from ~3 to ~10 Mt (i.e., large PCD) for
66 38 calc-alkaline series, and ranges from ~0.3 to ~2.5 Mt for tholeiitic series. The ore-forming
67 39 potential of calc-alkaline arc magmas is at least ~4 to ~10 times higher relative to tholeiitic
68 40 arc magmas. Despite the compatible behavior of Cu during magmatic differentiation, we
69 41 propose that a single stage model for the formation of large economic PCDs (as opposed to
70 42 multi-stage model for Cu-sulfides storage and remobilization) is most applicable for the calc-
71 43 alkaline melts. The importance of the initial melt H₂O content ultimately reflects the key role
72 44 of flux melting associated with wet calc-alkaline series and high ore-forming potential, in
73 45 opposition to decompression melting associated with damp tholeiitic series.

82 46

83 47 1. Introduction

84 48 Porphyry copper deposits (PCDs) formed in arc setting represent ~75% of the global
85 49 copper resources (Sillitoe, 2010). Large economic PCDs are dominantly associated with
86 50 volatile-rich and oxidized calc-alkaline sub-volcanic intrusions in continental arcs, although
87 51 some important ones are also formed in oceanic island arcs (Fig. 1; Kesler et al., 1975; Titley,
88 52 1975; Solomon, 1990; Richards, 2003, 2011a; Cooke et al., 2005; Sillitoe, 1997, 2010).
89 53 Magmatic-hydrothermal processes directly associated with the formation of PCDs are
90 54 reasonably well understood (e.g., Seedorff et al., 2005; Sillitoe, 2010; Kouzmanov and
91 55 Pokrovski, 2012). In contrast, the role of precursor magmatism (and related source and
92 56 crustal processes) to generate magmas able to form ore deposits remains less clear (e.g.,
93 57 Audétat and Simon, 2012; Wilkinson, 2013; Richards, 2015). Specifically, the importance of
94 58 magmatic sulfide crystallization and saturation of a fluid phase acting as the main Cu
95 59 scavengers during magmatic differentiation is unclear.

100 60 Copper is incompatible during magmatic differentiation in thin island arc (<20 km)
101 61 dominated by tholeiitic series, whereas Cu is compatible during magmatic differentiation in
102 62 thick continental arc (>30 km) dominated by calc-alkaline series (e.g., Lee et al., 2012;

113
114
115 63 Chiaradia, 2014). Crustal thickness is proposed to have a first-order control on arc magma
116
117 64 differentiation (Miyashiro, 1974; Chiaradia, 2014) and hence the Cu evolution in arc magmas
118
119 65 (Chiaradia, 2014; Lee and Tang, 2020). Furthermore, the different tholeiitic and calc-alkaline
120
121 66 liquid lines of descent (LLD) control the evolution of the melt redox conditions (expressed
122
123 67 in terms of oxygen fugacity, fO_2) in the crust, which in turn impact the solubility of sulfur and
124
125 68 Cu through sulfide immiscibility (e.g., Lee et al., 2012), potentially linked to the onset of
126
127 69 magnetite crystallization (Jenner et al., 2010; Chiaradia, 2014). Alternative views suggest
128
129 70 that the initial H₂O in primitive magma primarily control the LLD (Sisson and Grove, 1993;
130
131 71 Tatsumi and Susuki, 2009; Zimmer et al., 2010; Jagoutz et al., 2011; Müntener and Ulmer,
132
133 72 2018), and high initial melt H₂O contents (>4wt% H₂O) combined with high fO_2 in the
134
135 73 source region are thought to play a major role for the formation of PCDs (Richards, 2003,
136
137 74 2009, 2011a, 2015; Sun et al., 2015, 2017). As a result, endmember models for PCDs
138
139 75 formation in arcs can be grouped in two: (1) multi-stage models envision that early
140
141 76 magmatic Cu-sulfide saturation in the deep arc crust represent a key pre-enrichment step to
142
143 77 the formation of PCDs in continental arc dominated by calc-alkaline series. Subsequent
144
145 78 events within the same or later magmatic cycle remobilize the Cu from these cumulates to
146
147 79 form PCDs in the upper crust (e.g., Lee et al., 2012; Wilkinson, 2013; Chiaradia, 2014);
148
149 80 alternatively (2) single-stage models consider PCDs formed from metal precipitated from
150
151 81 hydrothermal fluids that are exsolved from differentiated mantle-derived, volatile-rich and
152
153 82 oxidized calc-alkaline magmas (e.g., Richards, 2009, 2011a, 2015; Sun et al., 2015, 2017).

148 83 For both endmember models, a wide range of crucial parameters for the formation of
149
150 84 PCDs have been proposed that include the initial metal endowment (McInnes et al., 1999;
151
152 85 Mungall, 2002; Sun et al., 2017; Zheng et al., 2018), the melt water concentration (Richards,
153
154 86 2011a,b; Chiaradia et al., 2012; Loucks, 2014; Chiaradia and Caricchi, 2017), the melt redox
155
156 87 conditions (Lee et al., 2012; Richards et al., 2015; Sun et al., 2015; Lee and Tang, 2020), the
157
158 88 melt metal concentration and/or the melt volume at the time of magmatic fluid saturation
159
160 89 (Cline and Bodnar, 1991; Richards, 2009; Park et al., 2019; Chelle-Michou et al., 2017), the
161
162 90 duration of the precursor magmatism (Rezeau et al., 2016; Chelle-Michou et al., 2017;
163
164 91 Chiaradia and Caricchi, 2017; Richards, 2018) and the overriding plate thickness (i.e.,
165
166
167
168

169
170
171 92 pressure of melt differentiation; Chiaradia, 2014; Matjuschkin et al., 2016; Cox et al., 2019;
172 93 Lee and Tang, 2020).

174 94 The evolution of Cu during arc magma differentiation results from a complex
175 95 interplay of processes occurring in the mantle source region and/or in the crust. Thus, it
176 96 remains unclear which parameter(s) primarily control the ore-forming potential of arc
177 97 magmas. This contribution aims to critically evaluate the role of source- and crustal-related
180 98 magmatic processes related to the ore-forming potential, and examine their respective
181 99 importance. Here, we use a global compilation of arc volcanic and plutonic (cumulates and
184 100 derivative melts) whole rock geochemical analyses to systematically characterize the
186 101 evolution of Cu in arc magmas during magmatic differentiation starting from primitive
187 102 mantle derived arc magmas. Our global compilation aims to evaluate the role of primitive
189 103 magma Cu concentration, initial water content, fO_2 , pressure of melt differentiation and
190 104 different LLD for the formation of economic PCDs in the light of the above mentioned two
192 105 endmember models. Our results emphasize the primary role of the initial melt H₂O content
194 106 regarding the ore-forming potential of arc magmas, whereas the initial melt Cu content is of
195 107 secondary importance. We show that a single stage model can explain the formation of large
197 108 economic PCDs associated with wet calc-alkaline arc series, whereas the multi-stage model
199 109 is applicable form PCD formed from damp tholeiitic arc series. Ultimately, we propose that
200 110 the initial melt H₂O content reflect the importance of the melting regime in the mantle wedge,
202 111 i.e., flux melting in contrast to decompression melting.

204 112

205 113 **2. Copper concentration in primitive arc magmas: implications for the source of Cu**

207 114 ***2.1 Dataset and results***

209 115 Previous studies reported Cu concentration in primitive arc basalts and mid-oceanic
210 116 ridge basalts (MORBs) ranging from ~50 to ~100 ppm (Jenner et al., 2010; Jenner and
212 117 O'Neill, 2012; Lee et al., 2012; Chiaradia, 2014; Richards, 2015). Here, we reevaluate the Cu
213 118 concentration between the different types of primitive arc melts and geodynamic settings.
215 119 We used the primitive arc melts compilation of Schmidt and Jagoutz (2017) with available
216 120 whole rock Cu analyses (n=422) from 20 arcs including intra-oceanic, continental and back-
218 121 arc settings (Supplemental Material Table A1). For this study, we present Cu concentration
220 122 in primitive arc melts using the same classification scheme as Schmidt and Jagoutz (2017),

225
226
227 123 with the exception of primitive depleted tholeiitic andesites which are considered
228
229 124 fractionated melts. Here, they are classified into five types: (1) primitive calc-alkaline basalts
230
231 125 (n=82), (2) primitive tholeiitic basalts (n=50), (3) primitive low-Si basalts (n=64), (4)
232 126 primitive shoshonites (n=78), and (5) primitive high-Mg andesites (n=148) (Fig. 2; Table
233
234 127 A1). For the sake of comparison, we also compiled whole rock Cu analyses (n=58) in
235
236 128 primitive MORBs using the data set of Gale et al. (2013). Primitive MORBs were selected
237 129 based on the same criteria used by Schmidt and Jagoutz (2017) for arc primitive melts, i.e.,
238
239 130 Mg# of 0.65-0.75, Ni concentrations of 150-500 ppm, and Cr concentrations of < 1200 ppm
240
241 131 (Table A1).

242 132 Our global compilation indicates that the Cu concentration of primitive arc melts
243
244 133 range from 35 to 120 ppm with a global average of 78 ± 31 ppm (1σ) for primitive arc basalts
245 134 and of 42 ± 17 ppm for primitive high-Mg andesites (Fig. 2). By comparison, the Cu
246
247 135 concentration in primitive MORBs display a similar range from 50 to 130 ppm, with a global
248
249 136 average of 81 ± 20 ppm (Fig. 2) indistinguishable from primitive arc basalts. Among
250 137 primitive arc basalts, there is no systematics correlation between the Cu concentrations, the
251
252 138 types of primitive melt and/or the geodynamic settings. Only the high-Mg andesites are
253
254 139 characterized by systematically lower Cu concentrations.

255 140

256 141 *2.2 The source of Cu in arc magmas*

258 142 A magmatic origin for Cu in PCDs is widely accepted based on isotopic composition of
259
260 143 hydrothermal and magmatic sulfides, ore-forming fluids, and the genetically related igneous
261
262 144 intrusions (e.g., Hedenquist and Lowenstern, 1994; Rezeau et al., 2016; Zheng et al., 2018).
263 145 However, there is no consensus whether Cu in arc magmas is directly derived from the
264
265 146 mantle wedge/refertilized sub-continental lithospheric mantle (e.g., McInnes et al., 1999;
266 147 Richards, 2009; Hou et al., 2017; Wang et al., 2018; Zheng et al., 2018) or dominantly
267
268 148 inherited from the subducting oceanic lithosphere by slab-related fluid/melt (e.g., Mungall,
269
270 149 2002; Sun et al., 2017).

271 150

273 151 *2.2.1 Mantle-derived vs. slab-related*

274
275
276
277
278
279
280

281
282
283 152 The Cu concentrations in primitive arc basalts range from 50 to 120 ppm, with no
284
285 153 systematics regarding the types of primitive melt and/or the geodynamic settings (Fig. 2).
286
287 154 The range of Cu concentration in primitive arc basalts can be generated after 5 to 30% of
288
289 155 melting of a mantle source having an initial Cu concentration of 30 ppm at fO_2 ranging from
290
291 156 $\Delta FMQ = 0$ to 2 (Lee et al., 2012), which could be reconciled with primitive arc basalts formed
292
293 157 by variable degree of partial melting at different pressure in the mantle wedge (Schmidt and
294
295 158 Jagoutz, 2017). Alternatively, the range of Cu in primitive melts may represent variable input
296
297 160 between incompatible elements and Cu content. Our global compilation lacks of such
298
299 161 systematics as demonstrated by similar average Cu contents (and a comparable range of Cu)
300
301 162 for the different types of primitive basalts characterized by variable involvement of slab-
302
303 163 related fluid and/or melts (Table A1; Schmidt and Jagoutz, 2017). This is consistent with the
304
305 165 limited remobilization of chalcophile elements from subducted sulfide ore deposits during
306
307 166 dehydration of the subducting oceanic lithosphere (Tomkins, 2010; Giacometti et al., 2015).
308
309 167 More importantly, primitive arc basalts and MORBs are characterized by the same global
310
311 168 average Cu concentration of ~80 ppm irrespective of the degree of subduction-related inputs
312
313 170 (Fig. 2). Therefore, our observations are consistent with previous studies (McInnes et al.,
314
315 171 1999; Jenner et al., 2010; Lee et al., 2012; Chiaradia, 2014; Richards, 2015) and strongly
316
317 172 suggest the predominant contribution of Cu from the mantle without necessarily requiring
318
319 174 additional input from slab-related fluids and/or melts.

2.2.2 Refertilization and Cu enrichment via melt-rock reaction

319 174 In arc setting, Cu and Os isotope studies suggest that Cu enrichment is linked to the
320
321 175 refertilization of the sub-arc mantle through the redistribution of primary sulfides into
322
323 176 sulfide-bearing metasomatic veins by slab-related oxidizing fluids (e.g., McInnes et al., 1999;
324
325 177 Zheng et al., 2018). Our compilation reveals that primitive high-Mg andesites are
326
327 178 characterized by the lowest Cu concentrations (Fig. 2), which are positively correlated with
328
329 179 MgO (Supplemental Figure A1). Primitive high-Mg andesites has been proposed to represent
330
331 181 lower temperature derivatives of primitive calc-alkaline basalts through melt-rock reaction
332
333
334
335
336

337
338
339 182 [al.,1995; Kelemen et al., 2014; Schmidt and Jagoutz, 2017](#)). Consequently, we suggest that
340
341 183 the low Cu concentrations in primitive high-Mg andesites reflect Cu-sulfide fractionation,
342
343 184 which occur during melt-rock reaction. Such mechanism has been documented in a suite of
344
345 185 MORBs erupted at the Kane Megamullion, where Cu enrichment in the shallow mantle
346
347 186 results from melt-peridotite reaction ([Ciazela et al., 2017](#)). Similarly, melt-rock reaction in
348
349 187 the arc mantle region could represent an additional mechanism for local Cu enrichment in
350
351 188 the sub arc mantle and/or arc lithosphere. We envision that subsequent remelting of these
352
353 189 zones may account for unusually high Cu content in primitive arc basalts.

191 **3. Copper concentration in volcanic arc rocks**

192 ***3.1 Dataset***

193 It has long been recognized that differentiation of arc magmas dominantly follow
194 either a tholeiitic or calc-alkaline series with minor importance of an alkaline series (e.g.,
195 [Miyashiro, 1974](#)). Global whole rock compilation suggests that the crustal thickness of the
196 overriding plates represents a first-order control on tholeiitic and calc-alkaline
197 differentiation series ([Miyashiro, 1974; Chiaradia, 2014, 2015](#)). Yet, tholeiitic and calc-
198 alkaline arc magmas are documented to coexist along the same arc segment from fore-arc to
199 back-arc (e.g., Cascades, [Baker et al., 1994; Mandler et al., 2014; Kamchatka, Portnyagin et](#)
200 [al., 2007; Izu-Bonin-Mariana, Tatsumi and Susuki, 2009; Brounce et al., 2014; Aleutians,](#)
201 [Zimmer et al., 2010](#)). It has been proposed that the geochemical differences between
202 tholeiitic and calc-alkaline series relate to different LLDs controlled by the initial H₂O content
203 of the primitive arc melt ([Sisson and Grove 1993; Zimmer et al., 2010; Jagoutz et al., 2011;](#)
204 [Melekhova et al., 2013; Müntener and Ulmer, 2018](#)). It has been proposed that primitive arc
205 magmas with high initial H₂O content, that evolve along a calc-alkaline fractionation
206 sequence are related to flux melting in the sub arc mantle ([Grove et al., 2002, 2012; Cervantes](#)
207 [and Wallace, 2003; Jagoutz et al., 2011](#)). Flux melting occurs because the melting point of
208 peridotite is significantly lowered due to the addition of water in the mantle wedge (e.g.,
209 [Grove et al., 2012](#)). The influx of slab-derived hydrous melts/fluids hence produces melts
210 with high initial H₂O. Alternatively, the sub arc mantle can melt due to adiabatic
211 decompression, which produces melts with lower initial H₂O content that evolve along a
212 tholeiitic LLD ([Grove et al., 2002, 2012](#)).

393
394
395 213 Here, we produce a global compilation of whole rock analyses with available Cu of arc
396 214 volcanic rocks from the georoc database (<http://georoc.mpch-mainz.gwdg.de/georoc/>) to
397 215 evaluate the Cu evolution between tholeiitic and calc-alkaline magmatic series along
398 216 individual arc segment. The discrimination between volcanic rock following a calc-alkaline
400 217 (n=9,275) or tholeiitic (n=6,114) differentiation trend is based on the classical FeO/MgO
402 218 versus SiO₂ relationship (Supplemental Figure B1; Miyashiro, 1974). Our global compilation
404 219 includes volcanic rocks from 28 different magmatic arcs for a total of 15,389 entries (Figs. 1,
405 220 3, C1 and D1; Supplementary Table B1). The analyses included in the database fulfilled the
407 221 following criteria: a loss of ignition (LOI) < 2 wt% (if provided), totals of 97-102 wt%, SiO₂
409 222 of 50-70 wt%, MgO of 0.5-10 wt% and FeO/MgO ratio < 15 to avoid any exotic melt
411 223 compositions. Note that we screened and removed analyses from known mineralized
413 224 porphyry district to avoid high Cu concentration influenced by ore-forming hydrothermal
415 225 fluids overprint that are unrelated to the original melt Cu endowment. In the following, all
416 226 the whole rock data have been recalculated on an anhydrous basis.

418 227 419 228 **3.2 Results**

421 229 Our global compilation of volcanic rocks shows a wide range of Cu concentrations.
423 230 For MgO ranging from 0.5 to 10 wt%, most of the Cu data ranges from <10 to ~400 ppm in
424 231 tholeiitic series and from <10 to ~150 ppm in calc-alkaline series (Fig. 3a,d). During magma
426 232 differentiation (i.e., decreasing MgO concentration), the evolution of Cu concentrations in
428 233 tholeiitic and calc-alkaline series differs significantly. In tholeiitic series, the Cu
429 234 concentration increases from the typical primitive arc basalts value of ~80 ppm at 10 wt%
431 235 MgO, to the highest values between 3.5 and 5 wt% MgO with a maximum median Cu
432 236 concentration of ~110 ppm at ~4.2 wt% MgO. This is followed by a decrease of Cu
434 237 concentration down to a median concentration of ~10 ppm at 0.5 wt% MgO (Fig. 3a). FeO_{tot}
436 238 and V concentrations also exhibit the highest values between 3.5 and 5 wt% MgO (Fig. 3b,c).
437 239 In calc-alkaline series, the median Cu concentration steadily decreases from the typical
439 240 primitive arc magma value of ~80 ppm at 10 wt% MgO to ~10 ppm at 0.5 wt% MgO (Fig.
441 241 3d). Both FeO_{tot} and V concentration also mimics the evolution trend of Cu (Fig. 3e, f). This
442 242 suggests an apparent broad correlation between Cu, FeO_{tot} and V for both tholeiitic and calc-
444 243 alkaline series. Based on this correlation, the switch from incompatible to compatible

449
450
451 244 behavior of Cu at MgO ~3-5 wt% is ascribed to the late onset of Fe-oxides crystallization in
452 245 tholeiitic series, whereas the compatible behavior of Cu relates to the early Fe-oxides
453 246 crystallization in calc-alkaline magmas (Jenner et al., 2010; Chiaradia, 2014). In details,
454 247 however, the correlation between the three elements is weak for 17 individual
455 248 representative arc segments characterized by more than 300 whole rock analyses with
456 249 available Cu (Fig. 4a, b; Fig. C1 and D1; Table B1). For calc-alkaline and tholeiitic series, FeO_{tot}
460 250 and V are systematically positively correlated (Fig. 4b). Experiments for tholeiitic and calc-
461 251 alkaline LLDs have demonstrated that the decrease of FeO_{tot} is closely related to the onset of
462 252 crystallization of Fe-Ti-oxides (spinel hercynite, ilmenite, magnetite; Villiger et al., 2004;
463 253 Nandedkar et al., 2014; Ulmer et al., 2018) for which V have a high partition coefficient
464 254 (Kd>>1 up to 130; Luhr and Carmichael, 1980; Latourrette et al. 1991; Canil, 1999). In
465 255 contrast, the evolution of Cu is generally poorly correlated with FeO_{tot} and V (Fig.4a),
466 256 although few arcs display positive correlation (e.g., Izu-Bonin, Aleutians; Fig. C1 and D1).
467 257 Thus, Fe-oxides crystallization may not necessarily have a large effect on Cu depletion.

474 258 We use the Cu concentration at MgO~4 wt% (Cu₄) relative to the initial average Cu
475 259 concentration in primitive arc basalts of ~80 ppm to evaluate the Cu enrichment or depletion
476 260 during magmatic differentiation (Fig. 4c, d). With the exception of one arc segment (Central
477 261 America), calc-alkaline series show a systematic depletion of Cu during magma
478 262 differentiation (Fig. 4c, d), while tholeiitic series are characterized by Cu enrichment and
479 263 depletion during magmatic differentiation (Fig. 4c, d). For tholeiitic series, we observe a
480 264 systematic Cu enrichment in thin arcs (<25 km), which ultimately correlates with the highest
481 265 FeO_{tot} enrichment at MgO~4 wt% (i.e., Fe₄). For tholeiitic series formed in thicker arcs (>25
482 266 km), the Cu depletion dominates. These observations indicate that the evolution of Cu during
483 267 magma differentiation is influenced by the LLD and the pressure of magma differentiation
484 268 that are further discussed below among other parameters.

492 269

493 270 **3. Copper concentration in plutonic rocks and derivative melts**

495 271 Finally, based on the compilation of Jagoutz and Kelemen (2015) and Jagoutz and
496 272 Klein (2018), we produced a compilation of whole rock Cu analyses for lower crustal
497 273 cumulates and their derivative melts from the Kohistan arc in Pakistan, Talkeetna arc in
498 274 Alaska, Sierra Valle Fértil–Sierra Famatina complex in Argentina, Fiordland in New Zealand

505
506
507 275 (Table C1). A complementary whole rock compilation of Cu-bearing cumulates from Chin et
508
509 276 al., 2018 is also included in Table C1, which consist of deep crustal cumulates from Arizona
510
511 277 and Sierra Nevada (Western USA), Bonanza arc (British Columbia), Colombia (North
512
513 278 Volcanic Andean Zone), Kermadec islands (South Pacific Ocean), and Pontides (NE Turkey).
514
515 279 The entire dataset consists in 1606 whole rock major elements analyses, of which 985
516
517 280 include Cu analyses (Table C1).

517 281 Our compilation of lower crust plutons that are cumulates and frozen melt
518
519 282 compositions (Jagoutz, 2010; Jagoutz et al., 2011) is characterized by a range of SiO₂ from 40
520
521 283 to ~76 wt%, Mg# from 0.9 to 0.2, and Cu concentrations from <10 ppm to 250 ppm (Fig. 5,
522
523 284 Table C1). The compiled cumulates are associated with differentiated melt of calc-alkaline
524
525 285 signature (Famatina arc, e.g., Otamendi et al., 2009; Fiordland arc, e.g., Allibone et al., 2009;
526
527 286 Jijal complex in Kohistan arc, e.g., Jagoutz et al., 2011), tholeiitic signature (Chilas complex in
528
529 287 Kohistan arc, e.g., Jagoutz et al., 2011), or overlapping the tholeiitic and calc-alkaline fields
530
531 288 (Talkeetna arc, e.g., Greene et al., 2006). Most of the compiled lower crustal plutons are
532
533 289 characterized by a “Z” shape trend in the Mg# and SiO₂ space, except for the Chilas complex
534
535 290 in Kohistan (Fig. 5a). The different patterns are related to different LLD such as the “Z” shape
536
537 291 represents wet fractionation associated with calc-alkaline series, whereas the others
538
539 292 represent dry fractionation linked to tholeiitic series (Jagoutz, 2010; Jagoutz et al., 2011;
540
541 293 Müntener and Ulmer, 2018). Our global compilation of lower crustal cumulates do not show
542
543 294 any systematics difference in whole rock Cu concentrations between cumulates associated
544
545 295 with calc-alkaline or tholeiitic series (Fig. 5b).

543 297 **4. Discussion**

545 298 When melt reaches sulfide or water saturation during magmatic differentiation Cu is
546
547 299 strongly partitioned into magmatic sulfides and/or the fluid phase. Therefore, we first
548
549 300 discuss the systematic of magmatic sulfide saturation and its role for the different evolutions
550
551 301 of Cu concentration observed between tholeiitic and calc-alkaline magmas (Figs. 3 and 4).
552
553 302 Subsequently, we focus on the initial melt H₂O content and its role for the ore-forming
554
555 303 potential in arc magmas.

556 305 ***4.1 Sulfide saturation in arc magmas***

561
562
563 306 Magmatic sulfide minerals are known to be highly efficient Cu scavengers, and
564 307 therefore, it is generally assumed that sulfide saturation plays a crucial role in the ore-
565 308 forming potential of arc magmas. Indeed, magmatic sulfides are ubiquitous in mafic to felsic
566 309 volcanic and plutonic rocks (e.g., [Stavast et al., 2006](#); [Lee et al., 2012](#); [Zelenski et al., 2017](#);
567 310 [Georgatou and Chiaradia, 2019](#)). The observed volume of magmatic sulfides in igneous rocks
568 311 range from <0.1 to 0.6 vol% and directly influences the Cu budget during melt differentiation
569 312 ([Kiseeva and Wood, 2015](#); [Georgatou et al., 2018](#); [Cox et al., 2019](#)). As copper is a highly
570 313 chalcophile element ($D_{Cu}^{sulfide/melt} \sim 250-1000$; [Li and Audéat, 2012](#)), its solubility in
571 314 silicate melt strongly depends on sulfide saturation. Experiments have demonstrated a sharp
572 315 transition from sulfide (S^{2-}) to sulfate (S^{6+}), where sulfide (S^{2-}) is the dominant sulfur species
573 316 in hydrous silicate melts under more reducing conditions (fO_2), whereas sulfate (S^{6+})
574 317 dominates at higher redox conditions ([Fig. 6a](#); [Mavrogenes and O'Neill, 1999](#); [O'Neill and](#)
575 318 [Mavrogenes, 2002](#); [Jugo, 2009](#); [Jugo et al., 2010](#); [Botcharnikov et al., 2011](#); [Fortin et al., 2015](#);
576 319 [Matjuschkin et al., 2016](#)). Furthermore, higher pressure of differentiation shifts the sulfide-
577 320 sulfate transition towards higher fO_2 ([Fig. 6a](#); [Matjuschkin et al., 2016](#)). The sulfur solubility
578 321 in silicate melts strongly correlates with the sulfide-sulfate transition, such as the S solubility
579 322 increases as a function of the fraction of oxidized species in the melt ([Fig. 6a](#); [Carroll and](#)
580 323 [Rutherford, 1985](#); [Jugo, 2009](#); [Jugo et al., 2010](#); [Botcharnikov et al., 2011](#); [Matjuschkin et al.,](#)
581 324 [2016](#)). At convergent margins, the redox conditions in primitive arc basalts and sub-arc
582 325 mantle are on average higher than MORBs, but varies over several log units above the
583 326 fayalite-magnetite-quartz (FMQ) buffer assemblage from $\Delta FMQ \sim 0$ to +4 ([Fig. 6a](#); e.g.,
584 327 [Carmichael, 1991](#); [Lee et al., 2010, 2012](#); [Evans et al., 2012](#); [Kelley and Cottrell, 2012](#);
585 328 [Brounce et al., 2014](#); [Bénard et al., 2018](#); [Bucholz and Kelemen, 2019](#)). Furthermore, the
586 329 pressure of differentiation and the volatiles content (H_2O , S) of primitive melt composition
587 330 vary within and among arcs (e.g., [Grove et al., 2002](#); [Rowe et al., 2009](#); [Zimmer et al., 2010](#);
588 331 [Wallace and Edmonds, 2011](#); [Brounce et al., 2014](#); [Melekhova et al., 2019](#)). In the following,
589 332 we discuss the importance of sulfide saturation in terms of possible melt evolution paths at
590 333 different pressures of differentiation, LLD, redox conditions, and initial sulfur concentrations
591 334 ([Fig. 6a-d](#)) that could explain the Cu evolution in tholeiitic and calc-alkaline differentiation
592 335 series ([Fig. 3a, d](#)).

617
618
619 336
620
621 337
622
623 338
624 339
625
626 340
627 341
628 342
629 343
630 344
631 345
632 346
633 347
634 348
635 349
636 350
637 351
638 352
639 353
640 354
641 355
642 356
643 357
644 358
645 359
646 360
647 361
648 362
649 363
650 364
651 365
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672

The effect of variable pressure of differentiation on sulfide saturation

The contrasting Cu evolution trends between tholeiitic and calc-alkaline series could be related to different pressures of differentiation, as at low pressure sulfate stability increases towards lower fO_2 , whereas higher pressure expands the sulfide stability field (Fig. 6a; e.g., Matjuschkin et al., 2016). Here we discuss arc melts with identical initial fO_2 of $\Delta FMQ \sim 1.5$ and sulfur concentration that differentiate at 0.2 GPa and 1 GPa (Figs. 6a, b). As sulfur is highly incompatible during fractional crystallization (e.g., Ripley and Li, 2013), the sulfur concentration increases with $1/F$ (F is the remaining melt mass). At 0.2 GPa, hydrous basaltic melt will reach sulfide saturation at $S \sim 0.5$ wt% (Figs. 6a; Botcharnikov et al., 2011). At higher pressure, the sulfide-sulfate transition shift towards higher fO_2 , and so does the S solubility curve (Matjuschkin et al., 2016). Considering the lack of available experimental data for hydrous basalt at 1 GPa, we shift the experimental sulfur solubility curve obtained at 0.2 GPa and correlate the highest S solubility with the transition of sulfate-only species curve ($S^{6+}/S_{tot} = 1$) at 1 GPa (Figs. 6a). Thus, we can approximate that a hydrous basaltic melt will reach sulfide saturation at $S \sim 0.15$ wt%. Assuming the primitive melt has initially 0.12 wt% S (Fig. 6a; Wallace and Edmonds, 2011; Brounce et al., 2014), the high pressure melt will reach sulfur saturation after $\sim 20\%$ fractionation ($F=0.8$) whereas the low-pressure melt will reach sulfur saturation after 75% differentiation ($F=0.25$) (Fig. 6b, Table D1). If pressure of differentiation is the controlling parameter, then our data would indicate that tholeiitic melts on average fractionate shallower than calc-alkaline melts. This conclusion is supported by the empirical observation that the overriding plate thickness controls the Cu and FeO enrichment in thin island arc (<20 km) relative to Cu and FeO depletion in thick continental arcs (>30 km) (Chiaradia, 2014). This first-order observation would be consistent with the increase of sulfide stability with pressure (Matjuschkin et al., 2016; Cox et al., 2019). Furthermore, our results highlight that thicker crust and hence possible higher pressure of differentiation prevents Cu enrichment during magma differentiation even for tholeiitic series (Fig. 4d). This observation supports the idea that higher pressure lower crustal melt differentiation plays an important role to trigger early sulfide saturation. Yet, calc-alkaline series are characterized by early Cu depletion independently to the crustal thickness

673
674
675 366 suggesting that additional parameters control the timing of sulfide saturation during magma
676
677 367 differentiation in these series.

678
679 368
680 369 *The importance of different liquid line of descent on sulfide saturation*

681 369
682 370 For a primitive melt that differentiates at a similar initial pressure, fO_2 and S
683 371 concentrations, the contrasting Cu evolution trends could be explained by a progressive
684 371
685 372 change of FeO content and redox conditions controlled by the different LLDs (e.g., Lee et al.,
686 372
687 373 2012) due to different initial melt H₂O content (e.g., Sisson and Grove, 1993; Villiger et al.,
688 374
689 374 2004; Nandedkar et al., 2014). Since the variations of redox conditions are sensitive to the
690 375 melt Fe³⁺/ΣFe ratio, the timing of crystallization of Fe-oxides (i.e., Fe³⁺-bearing minerals) is
691 375
692 376 expected to control the redox trajectories in a closed magmatic system, lowering the melt
693 377 Fe³⁺/ΣFe ratio and hence the oxygen fugacity (e.g., Ghiorso and Carmichael, 1987; Ulmer et
694 377
695 378 al., 2018). The calc-alkaline series is characterized by an early crystallization of Fe-oxides on
696 378
697 379 the LLD compared to the tholeiitic that crystallize Fe-oxide late on the LLD (Sisson and Grove,
698 380
699 380 1993). We test the evolution of fO_2 using Rhyolite-MELTS (Gualda et al., 2012) to simulate
700 381 melt crystallization in a thick crust starting from P = 0.8 GPa to 0.15 GPa and in a thin crust
701 382 starting from P = 0.4 GPa to 0.15 GPa for temperatures ranging from ~1220-1350°C (liquidus
702 382
703 383 varies as a function of initial melt H₂O content) to ~750-800°C (Table D1). Each computation
704 383
705 384 assumes melt differentiation through progressive decompression and cooling followed by
706 385 cooling once the melt reaches 0.15 GPa (Table D1). We use a starting primitive melt
707 385
708 386 composition of continental arc calc-alkaline basalt (Schmidt and Jagoutz, 2017) having
709 386
710 387 different initial H₂O content of 4 wt%, 1wt% and 0.2 wt% H₂O to account for calc-alkaline
711 388 and tholeiitic LLDs (e.g., Sisson and Grove 1993; Tatsumi and Susuki, 2009; Zimmer et al.,
712 388
713 389 2010; Melekhova et al., 2013; Table D1).

714 390 The modelled melt evolution confirms that the onset of crystallization of ferric
715 390
716 391 bearing minerals (magnetite) triggers the melt to evolve to lower fO_2 . The onset of magnetite
717 391
718 392 fractionation is dependent on the melt H₂O content and occurs at F~0.7 for the calc-alkaline
719 392
720 393 series (4 wt% H₂O_{initial}) versus F~0.65-0.4 for the tholeiitic series (1 wt% and 0.2 wt%
721 394 H₂O_{initial}). If both calc-alkaline and tholeiitic melt are S undersaturated at the time of
722 394
723 395 magnetite crystallization, the melt evolves toward lower fO_2 as soon as the magnetite
724 396 appears on the LLD to promotes sulfide saturation, which occur at higher melt fraction for

729
730
731 397 calc-alkaline magmas compared to tholeiitic ones (Fig. 6c). For tholeiitic series with 1 wt%
732
733 398 $H_2O_{initial}$, magnetite crystallization occurs earlier on the LLD ($F \sim 0.65$) indicative of the
734
735 399 concomitant effect of pressure. Our calculations are consistent with Jenner et al. (2010) and
736 400 Chiaradia (2014) suggestion that difference in Cu depletion trends between the calc-alkaline
737
738 401 and tholeiitic differentiation series could be linked to the timing of magnetite crystallization
739
740 402 within the respective LLDs, which is ultimately controlled by the initial H_2O content and the
741
742 403 pressure of differentiation. This interpretation can explain the Cu enrichment and depletion
743
744 404 observed for tholeiitic series in thin arcs (<25 km) and thick arcs (>25 km), while calc-
745
746 405 alkaline series consistently displays Cu depletion irrespective of the crustal thickness (Fig.
747
748 407 4c, d).

408 *The importance of variable initial redox conditions on sulfide saturation*

749
750 409 The importance of the initial fO_2 of the melt is illustrated by the compatible character
751
752 410 of Cu in MORB during differentiation (Jenner and O'Neill, 2012), where the initial fO_2 is ΔFMQ
753
754 411 < 0 and sulfide saturation occurs at low S content (Jugo, 2009; Jugo et al, 2010; Botcharnikov
755
756 412 et al., 2011; Matjuschkin et al., 2016). In comparison to MORBs, arc-related tholeiitic series
757
758 413 are characterized by the early incompatible and compatible character of Cu in thin and thick
759
760 414 arcs, respectively (Figs. 3a and 4c,d). According to the experimental sulfide-sulfate transition
761
762 415 curves at different pressures (0.2-1 GPa, Fig. 6a), the incompatible character of Cu (i.e.
763
764 416 delayed sulfide saturation) in thin arcs could be explained for initial fO_2 conditions of ΔFMQ
765
766 417 > ~ 1 for the primitive arc melt. In contrast, the compatible character of Cu (i.e. early sulfide
767
768 418 saturation) in thick arcs could be explained for initial fO_2 conditions of $\Delta FMQ < \sim 2$ for the
769
770 419 primitive arc melt (Figs. 6a,c). Such range of $\Delta FMQ \sim 1-2$ is consistent with estimates for
771
772 420 tholeiitic and calc-alkaline arc basalts along the Aleutian arc ($\Delta FMQ \sim +0.4-2.1$; Zimmer et al.,
773
774 421 2010) and Mariana arc ($\Delta FMQ \sim +1-1.6$; Brounce et al., 2014), for primitive lower crustal
775
776 422 ultramafic cumulates in the Talkeetna arc ($\Delta FMQ \sim +0.4-2.3$; Bucholz and Kelemen, 2019),
777
778 423 and for sub-arc mantle xenoliths in Kamchatka arc ($\Delta FMQ \sim +1-1.5$; Bénard et al., 2018). If
779
780 424 the initial melt fO_2 controls the different behavior of Cu in arc tholeiitic and calc-alkaline
781
782 425 series in thin arcs, it would imply that the arc tholeiitic series differentiate at higher initial
783
784 426 fO_2 than calc-alkaline series at the same initial S concentrations (Fig. 6c). Although H_2O itself

785
786
787 427 is a poor oxidant, the oxidation state of arc magmas is mainly affected by the proportion of
788
789 428 subduction-related aqueous components added to the mantle wedge (e.g., Kelley and
790
791 429 Cottrell, 2009), and more specifically to the chemical components associated with the slab-
792
793 430 derived fluids or melts, i.e., Fe³⁺, S⁶⁺, C⁴⁺ (Mungall, 2002; Tomkins and Evans, 2015; Bénard
794
795 431 et al., 2018; Brounce et al., 2019). A positive correlation between H₂O and fO₂ have been
796
797 432 shown from mid-ocean ridges to back-arc tectonic settings (Kelley and Cottrell, 2009;
798
799 433 Zimmer et al., 2010; Brounce et al., 2014), while melt inclusions from primitive arc basalts
800
801 434 from fore-arc to back-arc in the Oregon Cascades do not show any significant differences in
802
803 435 fO₂ between tholeiitic and calc-alkaline melts (Rowe et al., 2009). While the role of slab-
804
805 436 derived fluids or melts for the oxidation of arc magmas remains unclear, there is no evidence
806
807 437 to assume that arc tholeiitic melts have on average higher fO₂ than calc-alkaline melts.
808
809 438 Consequently, the early sulfide saturation observed for calc-alkaline series in thin arcs
810
811 439 should reflect other processes than a systematic difference in fO₂ in primitive melts.
812
813 440

810 441 *The importance of variable initial sulfur concentrations on sulfide saturation*

811 442 It has been proposed that slab-derived fluids/melts appear to be efficient transfer
812
813 443 agent for the transport of sulfur from slab to mantle wedge (Jégo and Dasgupta, 2014), which
814
815 444 is supported by higher range of S concentrations measured in arc basalts (up to ~0.9 wt%)
816
817 445 compared to MORB (up to ~0.2 wt%; e.g., Jugo et al., 2010; Wallace and Edmonds, 2011). In
818
819 446 this case, fluid flux melting should be characterized by higher contribution of an external
820
821 447 input of S to the mantle wedge via the devolatilization of the subducting oceanic crust
822
823 448 relative to decompression melting. Accordingly, we would expect higher initial S
824
825 449 concentration in calc-alkaline series promoting early sulfide saturation compared to the
826
827 450 tholeiitic series at similar pressure of differentiation and initial fO₂ (Fig. 6d). Positive
828
829 451 correlations between melt H₂O content and S exist in arc magmas (e.g., Johnson et al., 2009;
830
831 452 Zimmer et al., 2010; Kelley and Cottrell, 2012), although it is not systematic (e.g., Wallace,
832
833 453 2005). Furthermore, any apparent positive correlation from melt inclusions studies could be
834
835 454 due to melt degassing (e.g., Wallace and Edmonds, 2011) rather than initial melt conditions.
836
837 455 The relationship between the initial H₂O and S content of primitive arc magmas remains
838
839 456 uncertain.
840

841
842
843 457
844

845 458 In conclusions, this section highlights the complex interplay of different parameters
846 459 that control sulfide saturation and hence the evolution of melt Cu concentration during
847 460 magmatic differentiation. Based on our compilation (Fig. 3), we propose that the liquid lines
848 461 of descent have a large effect on the timing of sulfide saturation in thin arcs (<25 km),
849 462 whereas the pressure of differentiation becomes the main controlling factor in thicker arcs
850 463 (>25 km). Finally, more chemical data specifically on the sulfur content of arc magmas and
851 464 plutons in combination with experimental studies are needed to better understanding
852 465 sulfide saturation in natural magmatic systems.
853 466

854 467 *4.2 The importance of initial melt H₂O content in arc magmas for the ore-forming potential* 855 468 *of magmas*

856 469 Most of the economic PCDs are preferentially associated with calc-alkaline
857 470 subvolcanic intrusions (Sillitoe, 2010). Yet, our global compilation shows that the average
858 471 melt Cu concentration in calc-alkaline series is systematically lower compared to tholeiitic
859 472 series at a given MgO (Fig. 3a,d). This observation questions the primary importance of melt
860 473 Cu content in the ore-forming potential. In the following, we evaluate the role of the initial
861 474 melt water content and the Cu endowment in magmatic fluids for tholeiitic and calc-alkaline
862 475 series.
863 476

864 477 *4.2.1 Modeling the liquid lines of descent (LLDs)*

865 478 Compelling lines of evidence suggest that the geochemical differences between
866 479 tholeiitic and calc-alkaline series relate to different LLDs controlled by the initial H₂O content
867 480 of the primitive arc melt showing that tholeiitic and calc-alkaline series are best reproduced
868 481 by LLD of an H₂O-poor and H₂O-rich parental melt, respectively (Sisson and Grove 1993;
869 482 Chaussidon and Sobolev, 1996; Villiger et al., 2004; Tatsumi and Susuki, 2009; Zimmer et al.,
870 483 2010; Jagoutz et al., 2011; Melekhova et al., 2013; Brounce et al., 2014; Mandler et al., 2014;
871 484 Nandedkar et al., 2014; Müntener and Ulmer, 2018). We use Rhyolite-MELTS (Gualda et al.,
872 485 2012; Ghiorso and Gualda, 2015) to model LLDs with variable initial melt H₂O content from
873 486 0.2 wt% to 4 wt% representative of the spectrum of tholeiitic to calc-alkaline series
874 487 emplaced at convergent margins (e.g., Sisson and Grove 1993; Tatsumi and Susuki, 2009;
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896

897
898
899 488 [Zimmer et al., 2010](#); [Brounce et al., 2014](#); [Melekhova et al., 2013](#); [Mandler et al., 2014](#)). We
900
901 489 used an average primitive melt composition of intra-oceanic tholeiitic basalt and continental
902
903 490 arc calc-alkaline basalt ([Table D1](#); [Schmidt and Jagoutz, 2017](#)). Our models simulate melt
904
905 491 differentiation in a thick crust starting from $P = 0.8$ GPa to 0.15 GPa and in a thin crust
906
907 492 starting from $P = 0.4$ GPa to 0.15 GPa for temperatures ranging from ~ 1220 - 1350°C (liquidus
908
909 493 varies as a function of initial melt H_2O content) to ~ 750 - 800°C at $\Delta\text{FMQ} +1$ ([Table D1](#)). Each
910
911 494 computation assumes melt differentiation through progressive decompression and cooling
912
913 495 followed by cooling once the melt reaches 0.15 GPa ([Table D1](#)). The modelled LLDs
914
915 496 reasonably reproduce the tholeiitic and calc-alkaline trends and show that the amplitude of
916
917 497 Fe enrichment decreases as the initial H_2O melt increases ([Fig. 7a](#)). Tholeiitic trends are best
918
919 498 reproduced by LLDs resulting from the differentiation of intra-oceanic tholeiitic primitive
920
921 499 basalt with initial 0.2 to 1.5 wt% H_2O , whereas calc-alkaline trends are best reproduced by
922
923 500 LLDs resulting from the differentiation of continental arc calc-alkaline primitive basalt with
924
925 501 initial 2 to 4 wt% H_2O ([Fig. 7a](#)). For a given initial melt H_2O content, the absolute Fe
926
927 502 enrichment depends on the initial melt composition, where LLDs resulting from the
928
929 503 differentiation of intra-oceanic tholeiitic primitive basalt show more Fe enrichment
930
931 504 compared to continental arc calc-alkaline primitive basalt. Our results also show that an
932
933 505 increase of the initial pressure of differentiation slightly reduces the amplitude of Fe
934
935 506 enrichment for damp LLDs ([Fig. 7a](#)), which is consistent with the broad tendency of having
936
937 507 lower Fe_4 at higher crustal thickness ([Fig. 4c](#)). Higher redox conditions ($\Delta\text{FMQ} +2$ - 3)
938
939 508 significantly limit Fe enrichment and therefore obfuscate the effect of H_2O on the LLDs.
940
941 509 Important is that our modeling allows us to quantify the melt composition in respect to the
942
943 510 remaining melt fraction (F), the melt water content and the appearance of the aqueous liquid
944
945 511 phases (i.e., fluid saturation) for the different LLDs. The latter is based on the fluid saturation
946
947 512 model of [Ghiorso and Gualda \(2015\)](#) implemented to Rhyolite-MELT, where thermodynamic
948
949 513 properties of the fluid phase are calculated from the model of [Duan and Zhang \(2006\)](#).

942 514 We also model the evolution of Cu concentration in the melt using the Rayleigh
943
944 515 fractionation equation:

$$C_l = C_0 * (F^{D-1}) \quad [1]$$

953
954
955 517 where C_1 is the concentration of Cu in the fractionated melt, C_0 is the Cu concentration
956
957 518 in the parental melt. F is the remaining melt fraction computed from Rhyolite-MELTS. While
958
959 519 Cu is incompatible in silicate minerals ($D^{silicates/Cu/melt} = <0.2$; Liu et al., 2014; Hsu et al., 2017),
960
961 520 it is highly compatible in sulfides ($D^{sulfide/Cu/melt} = \sim 250-1000$; Li and Audéat, 2012; Jenner,
962
963 521 2017). The bulk-partition coefficient (D) of Cu represents an average of partition coefficients
964
965 522 related to the volume percent of saturated magmatic sulfide and rock-forming minerals.
966
967 523 Here, we use $D^{sulfide/Cu/melt} = 800$ and $D^{silicates/Cu/melt} = 0.1$, and an average of 0.25 vol% of
968
969 524 magmatic sulfides (Kiseeva and Wood, 2015; Georgatou et al., 2018) corresponding to a
970
971 525 bulk-partition coefficient D of 2.1 at sulfide saturation and a D of 0.1 assuming no sulfide
972
973 526 saturation. For tholeiitic series in thin arc (<25 km), the evolution of the Cu is characterized
974
975 527 by an initial incompatible behavior followed by a compatible behavior related to late
976
977 528 magmatic sulfide saturation (Figs. 3a and 4c,d). In this case, we model the incompatible
978
979 529 behavior of Cu assuming no sulfide saturation with an initial Cu concentration of ~ 80 ppm
980
981 530 in the parental melt. The switch from incompatible to compatible behavior of Cu occurs at
982
983 531 MgO ~ 4 wt% (Fig. 3a). At this point, we use the melt Cu concentration at MgO ~ 4 wt% as the
984
985 532 initial Cu concentration in the parental melt (i.e., C_0 ranging from ~ 130 to 250 ppm) and we
986
987 533 assume magmatic sulfide saturation to model the decrease of Cu concentration in tholeiitic
988
989 534 series (Fig. 7b; Table D1). For tholeiitic series in thick arc (>25 km) and calc-alkaline series,
990
991 535 we assume an early magmatic sulfides saturation to reproduce the steady decrease of Cu
992
993 536 concentration (Fig. 7b; Table D1).

988 537 For melt differentiation starting at $P=4$ kbars, the computed results indicate that the
989
990 538 magmatic fluid phase saturates at $H_2O=5.7-6.3$ wt%, $F=0.35-0.63$, $P=1.7-2.3$ kbars and Cu
991
992 539 $\sim 25-50$ ppm for the wet series with an initial H_2O content of 2, 2.5, 3, 3.5 and 4 wt%. Damp
993
994 540 series with an initial H_2O content of 0.5, 1 and 1.5 wt% saturates magmatic fluid at $H_2O=5.4-$
995
996 541 5.5 wt%, $F=0.09-0.26$, $P=1.5-1.7$ kbars and Cu $\sim 15-30/\sim 5-20$ ppm (thin/thick arc model)
997
998 542 (Figs. 7c,d; Table D1). For melt differentiation starting at $P=8$ kbars, the computed results
999
1000 543 indicate that the magmatic fluid phase saturates at $H_2O=5.5-6.8$ wt%, $F=0.36-0.59$, $P=1.8-2.5$
1001
1002 544 kbars and Cu $\sim 25-45$ ppm for the wet series, and at $H_2O=5.3-5.4$ wt%, $F=0.11-0.18$, $P=1.5$
1003
1004 545 kbars and Cu $\sim 15-20/\sim 10$ ppm (thin/thick arc model) for the damp series (Figs. 7c,d; Table
1005
1006 546 D1). Independently to the initial pressure of melt differentiation, the wet calc-alkaline LLDs

1009
1010
1011 547 reach fluid saturation at higher melt fraction, melt H₂O content and melt Cu content
1012 compared to damp tholeiitic LLDs (Table D1). Damp melt with initial H₂O content of 0.2 wt%
1013 548
1014 does not reach H₂O saturation, and hence it is not further considered in the next section.
1015 549
1016 550

1017 1018 551 *4.2.2 Assessing the ore-forming potential of tholeiitic vs calc alkaline magmas*

1019 552 The Cu endowment of fluids expelled during degassing of H₂O-saturated melt
1020 primarily depends on the melt H₂O and Cu content together with the volume of melt
1021 553 present at fluid saturation (Cline and Bodnar, 1991; Chelle-Michou et al., 2017). As the mass
1022 of extractable Cu (Mt) correlates with the volume of water-saturated melt (Chelle-Michou et
1023 554 al., 2017) the remaining melt mass (F) of H₂O-saturated melt is a crucial parameter that
1024 555
1025 determine how much total Cu could be extracted from a magmatic system and hence for the
1026 556 formation of economic PCDs. Because of the different initial H₂O content in the primitive
1027 557 magma, the melt mass remaining at H₂O saturation is different for calc-alkaline vs tholeiitic
1028 558 LLD. Our models presented above have shown that the melt mass remaining at fluid
1029 559 saturation for calc-alkaline LLD is ~1.5 to 7 times that of the tholeiitic LLD.
1030 560
1031 561

1032 562 To illustrate this point, we use a simplified approach of Chelle-Michou et al. (2017) to
1033 563 quantify the mass of extractable Cu in fluids expelled during degassing of H₂O-saturated melt
1034 564 and to estimate the relative Cu endowment in expelled fluids between wet calc-alkaline and
1035 565 damp tholeiitic LLD. We estimate the volume of H₂O-saturated melt according to the
1036 566 Rhyolite-MELTS models presented above as it corresponds to the melt fraction at which an
1037 567 initial volume of primitive magma reached H₂O saturation. Here, we use an initial volume of
1038 568 primitive magma of 189 km³ km⁻¹ Myr⁻¹ based on an average arc magma production rate for
1039 569 intra-oceanic arcs (Jicha and Jagoutz, 2015). Once the magma is H₂O-saturated, we calculate
1040 570 the remaining melt fraction of H₂O-saturated melt and the volume of fluids at degassing.
1041 571 Ultimately, the mass of Cu in fluid expelled at degassing corresponds to the volume and
1042 572 density of fluids and the Cu concentration in fluids at degassing. The latter varies according
1043 573 to the melt Cu concentration and the partition coefficient of Cu between the fluid and the
1044 574 melt. The melt Cu concentration is derived from our modelling presented above, while
1045 575 partition coefficients $D_{Cu}^{fluid/melt}$ in the literature range from ~15 to ~300 and strongly
1046 576 depends on the melt salinity, the presence of CO₂, redox conditions, and H₂S content (Zajacz

1065
1066
1067 577 et al., 2008; Tattitch et al., 2015; Tattitch and Blundy, 2017). We use an intermediate value
1068
1069 578 of $D^{fluid/melt}_{Cu} = 140$ (Tattitch and Blundy, 2017). Our calculations yield a range of Cu
1070
1071 579 concentration in fluids range from ~0.03 to ~0.1 wt% (Table D1), which correspond to a
1072
1073 580 lower end estimate when compared to fluid inclusions data ranging from 0.002 to 2 wt% Cu
1074
1075 581 with an average of ~0.26 wt% in PCDs (Kouzmanov and Pokrovski, 2012). Magma degassing
1076
1077 582 occurs periodically during crystallization of H₂O-saturated melt, however the first degassing
1078
1079 583 event accounts for ~50 to 75 wt% of the total fluid expelled with fluids enriched in Cu
1080
1081 584 compared to the latest stages of degassing characterized by negligible amount of fluids (<25
1082
1083 585 wt%) depleted in Cu (Chelle-Michou et al., 2017). For this reason, we consider only a single
1084
1085 586 degassing event, hence providing minimum estimates for the mass of extractable Cu in fluid
1086
1087 587 expelled at degassing. In this simplified approach, we assume fixed parameters (percolation
1088
1089 588 threshold, fluid and melt density, partition coefficient) to assess the role of the initial melt
1089
1090 589 H₂O content and melt Cu concentration at degassing. The reader is referred to the
1091
1092 590 **Supplementary Material A1** and **Table D1** for a detailed description of the calculations.

1090 591 The results indicate a positive correlation between the relative mass of extractable
1091
1092 592 Cu in fluids expelled from H₂O-saturated magmas and the initial melt H₂O content (Fig. 8).
1093
1094 593 The mass of extractable Cu ranges from 2.6 to 9.6 Mt for wet calc-alkaline series modelled
1095
1096 594 with initial melt H₂O between 2 and 4 wt%, whereas calculations for damp tholeiitic series
1097
1098 595 modelled with initial melt H₂O between 0.5 and 1.5 wt% yield ranges from 0.3 to 2.3 Mt for
1099
1100 596 and from 0.2 to 1 Mt for thin and thick arc models, respectively. The corresponding volumes
1101
1102 597 of H₂O-saturated melt required to form PCDs >2 to ~10 Mt Cu (i.e., large to giant deposit)
1103
1104 598 range from 50 to 120 km³, which correspond to reasonable estimates compared to those
1105
1106 599 reported for ore-bearing intrusions (e.g., Cline and Bodnar, 1991; Chelle-Michou et al., 2017;
1107
1108 600 Du and Audéat, 2020). Overall, the ore-forming potential in typical calc-alkaline magmas
1109
1110 601 (initial melt H₂O content of 4 wt%) is ~4-10 times higher relative to damp tholeiitic magmas
1111
1112 602 (initial melt H₂O content of 1.5 wt%), and up to ~20-50 times relative to the dampest
1113
1114 603 tholeiitic magmas (initial melt H₂O content of 0.5 wt%) (Fig. 8). If we assume the same melt
1115
1116 604 Cu content of H₂O-saturated melt, the ore-forming potential in typical calc-alkaline magmas
1117
1118 605 is ~3 to 8 times higher relative to damp tholeiitic magmas (Table D1). Such correlation
1119
1120 606 reflects the crucial importance of the remaining H₂O-saturated melt mass, whereas the melt

1121
1122
1123 607 Cu concentration is of secondary importance. Of course, higher melt Cu content at the time
1124
1125 608 of fluid saturation increases the ore-forming potential of a given LLD, which can be envision
1126
1127 609 with high fO_2 (e.g., Richards, 2015) and/or a source enriched in Cu (e.g., Zheng et al., 2018).
1128
1129 610 Ultimately, our results are consistent with Chiaradia (2020a) suggesting that the highest ore-
1130
1131 611 forming potential coincides with an initial H₂O content of 4 wt% in the parental basaltic melt,
1132
1133 612 whereas lower ore-forming potential are modelled for initial melt H₂O content <2 wt% and
1134
1135 613 >6 wt%. Although our modelling primarily aims to evaluate the effect of initial melt H₂O
1136
1137 614 content on the ore-forming potential of arc magmas, we acknowledge that additional
1138
1139 615 parameters including favorable tectonics, long-lived thermal sustainability, magma
1140
1141 616 mingling, and metal precipitation efficiency play a complementary and important role to
1142
1143 617 modulate the size of PCDs (Tosdal and Richards, 2001; Richards, 2003, 2011a; Caricchi et al.,
1144
1145 618 2012; Wilkinson, 2013; Chiaradia and Caricchi, 2017; Chiaradia, 2020b).

1144 620 **5. Petrogenetic implications for the formation of giant PCDs**

1146 621 *5.1 Models of formation for PCDs*

1148 622 In calc-alkaline series, the compatible behavior of Cu during magmatic differentiation
1149
1150 623 (Fig. 3a,d) does not preclude the transfer of significant mass of Cu into the fluids expelled
1151
1152 624 from H₂O-saturated melts to form large economic PCDs in a single stage model (Fig. 9a),
1153
1154 625 where fluid saturation occurs at ~1.5-2.5 kbars with an important volume of fluid-saturated
1155
1156 626 melt at fairly low Cu concentrations of ~25-50 ppm. In contrast, a single stage model for the
1157
1158 627 formation of large economic PCDs associated with damp tholeiitic series is unlikely because
1159
1160 628 fluid saturation occurs late with a small volume of melt remaining and low Cu concentrations
1161
1162 629 (Fig. 9b). Our results are consistent with the fact that large economic PCDs are
1163
1164 630 predominantly associated with subvolcanic fluid-saturated calc-alkaline intrusions
1165
1166 631 emplaced at ~2 kb (Richards, 2003; Sillitoe, 2010), whereas tholeiitic series are barren in
1167
1168 632 the main arc (e.g., Kesler et al., 1977) and/or associated with shallow and smaller epithermal
1169
1170 633 Cu-Au deposits associated with bi-modal suites in rift-related setting (e.g., Sillitoe and
1171
1172 634 Hedenquist, 2003). In the case of the successive emplacement of damp tholeiitic series
1173
1174 635 followed by wet calc-alkaline series, Cu-sulfide segregated in tholeiitic crustal cumulates
1175
1176 636 could represent an additional source of Cu if remelting of lower crustal cumulates occurs
1177
1178 637 during a subsequent hydrous magmatic event (Fig. 9c). Of course, Cu-sulfide segregated in

1177
1178
1179 638 lower crustal cumulates formed from hydrous melts could equally be remobilized during a
1180
1181 639 subsequent hydrous magmatic event (Fig. 9c; Richards, 2009, 2011a, 2015; Lee et al., 2012;
1182
1183 640 Chiaradia, 2014; Hou et al., 2015). This scenario would increase the ore-forming potential
1184
1185 641 and lead to the formation of large PCDs consistent with a multi-stage model that could occur
1186
1187 642 in both subduction-related and post-subduction settings. In conclusions, we suggest that
1188
1189 643 both scenarios are likely to occur in accretionary orogens, however, Cu-sulfide segregation
1190
1191 644 and remobilization does not appear to be a prerequisite to form economic large PCDs in
1192
1193 645 subduction-related setting.
1194
1195 646

1194 647 *5.2 Source vs. crustal processes*

1195 648 The importance of the melt H₂O content has long been recognized since large
1196
1197 649 economic PCDs are predominantly associated with subvolcanic calc-alkaline intrusions
1198
1199 650 characterized by high Sr/Y and La/Yb ratios ascribed to the early crystallization of
1200
1201 651 amphibole in the deep crust (\pm garnet at high pressure) (Richards, 2011b; Chiaradia et al.,
1202
1203 652 2012; Loucks, 2014). Furthermore, these ratios positively correlate with arc crustal
1204
1205 653 thickness (Chiaradia, 2015; Profeta et al., 2015; Lieu and Stern, 2019), which ultimately
1206
1207 654 correlates with tholeiitic and calc-alkaline differentiation series at the global scale
1208
1209 655 (Miyashiro, 1974; Chiaradia, 2014). It has been proposed that the crustal thickness
1210
1211 656 primarily controls the association of large PCDs, calc-alkaline magmas and thicker arc with
1212
1213 657 a limited role for the composition of the mantle source (e.g., Chiaradia, 2014). Yet, at the arc
1214
1215 658 scale, tholeiitic and calc-alkaline arc magmas are temporally and spatially related from fore-
1216
1217 659 arc to back-arc and the different LLDs are controlled by the initial H₂O content of the
1218
1219 660 primitive arc melt independently to the pressure of differentiation (Fig. 7a; Sisson and Grove
1220
1221 661 1993; Baker et al., 1994; Villiger et al., 2004; Tatsumi and Susuki, 2009; Zimmer et al., 2010;
1222
1223 662 Melekhova et al., 2013; Brounce et al., 2014; Mandler et al., 2014; Nandedkar et al., 2014;
1224
1225 663 Ulmer et al., 2018). Here, we suggest that the importance of the initial melt H₂O content in
1226
1227 664 the ore forming potential of arc magmas reflects the primary role of flux melting in the
1228
1229 665 mantle source associated with wet calc-alkaline series, in opposition to decompression
1230
1231 666 melting associated with damp tholeiitic series (Fig. 9; Grove et al., 2002; Cervantes and
1232
1233 667 Wallace, 2003; Jagoutz et al., 2011). The first order relationship between calc-alkaline

1233
1234
1235
1236
1237
1238
1239
1240
1241
1242
1243
1244
1245
1246
1247
1248
1249
1250
1251
1252
1253
1254
1255
1256
1257
1258
1259
1260
1261
1262
1263
1264
1265
1266
1267
1268
1269
1270
1271
1272
1273
1274
1275
1276
1277
1278
1279
1280
1281
1282
1283
1284
1285
1286
1287
1288

668 magmas and crustal thicknesses (Miyashiro, 1974; Chiaradia, 2014) illustrates that the
669 crustal thickness controls the height of the mantle column and influences the relative
670 importance of decompression melting versus flux melting (Grove et al., 2002; Jagoutz et al.,
671 2011; Karlstrom et al. 2014; Turner and Langmuir, 2015). This makes intuitively sense as a
672 thicker crust reduces the mantle wedge thickness and hence is associated with a shorter
673 melting column, reducing the capability of the mantle to decompress. At the arc scale, the
674 preferential association of PCDs with the episode of crustal thickening (e.g., Cooke et al.,
675 2005) would be consistent with a shorter melting column and the dominance of flux melting
676 regimes during internal tectonic and magmatic cycles. In conclusions, the role of flux melting
677 at a given arc location remains of primary importance for the ore-forming potential in arc
678 magmas and the formation of economic PCDs.

6. Conclusions

681 In this study, we reviewed the Cu concentrations in primitive arc melts, plutonic rocks
682 and derivative melts, and volcanic rocks to discuss the role of mantle source and crustal
683 magmatic processes to generate fertile magmatism associated with large economic PCDs.
684 The compilation of primitive arc melt does not indicate any particular Cu endowment for a
685 specific type of primitive arc melt and/or geodynamic setting. Our results are consistent with
686 previous studies (Lee et al., 2012) showing an average Cu concentration in different types of
687 primitive arc basalts similar to MORBs (~80 ppm) indicative of the predominant
688 contribution of Cu from the mantle wedge and limited slab-related fluid/melts input. This
689 suggests that the initial Cu endowment in the primitive arc melt is unlikely to represent a
690 crucial prerequisite to form large economic PCDs. Our global compilation of plutonic rocks
691 illustrates that Cu-rich arc (> 100 ppm) cumulates are associated with both calc-alkaline and
692 tholeiitic series. In contrast, our global compilation of volcanic rocks documents
693 systematically different Cu evolution during magma differentiation in calc-alkaline and
694 tholeiitic series for each arc. The contrasting evolution of Cu in tholeiitic and calc-alkaline
695 systematically correlates with FeO_{tot} and V, which is consistent with previous studies
696 suggesting that the different timing of magmatic sulfide saturation relates to the onset of Fe-
697 oxides crystallization on the respective LLDs (Jenner et al., 2010; Chiaradia, 2014).
698 Additional parameters (pressure of magma differentiation, LLDs, fO_2 , and/or sulfur

1289
1290
1291
1292
1293
1294
1295
1296
1297
1298
1299
1300
1301
1302
1303
1304
1305
1306
1307
1308
1309
1310
1311
1312
1313
1314
1315
1316
1317
1318
1319
1320
1321
1322
1323
1324
1325
1326
1327
1328
1329
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1340
1341
1342
1343
1344

699 concentration) may locally play a role and account for the large range of Cu concentration
700 observed in the compiled data. Although the average Cu concentrations during melt
701 differentiation is systematically higher for tholeiitic series compared to calc-alkaline series,
702 we propose that the melt Cu concentrations have minor implications for the ore-forming
703 potential of arc magmas. Instead, we demonstrate that the initial melt H₂O content in
704 primitive arc melts controls the LLD and the volume of remaining melt mass at fluid
705 saturation. We showed that the melt mass remaining is a key parameter for calculating the
706 total mass of Cu transferred into exsolving hydrothermal fluids. We propose that the single
707 stage model for the formation of large economic PCDs is most applicable for melts from the
708 calc-alkaline series. The importance of the initial melt H₂O content ultimately reflects the key
709 role of flux melting associated with wet calc-alkaline series and high ore-forming potential,
710 in opposition to decompression melting associated with damp tholeiitic series.

Acknowledgments

713 H. R. acknowledges the support by the Swiss National Foundation through the early post-doc
714 mobility research grant P2GEP2_178008. The work of O. J and H. R. was supported by
715 National Science Foundation under grant number EAR-1552202. The authors are grateful
716 for the active discussions during group meetings at MIT that contribute to shape our ideas.
717 The authors thank the reviewers for their insightful comments that helped to clarify and
718 improve the manuscript.

Disclosure Statement

721 No potential conflict of interest was reported by the authors.

FIGURE CAPTION

724 **Fig. 1:** World map showing the distribution of arc magmatism and porphyry copper deposits.
725 The location of calc-alkaline and tholeiitic magmatism compiled in this study is from the
726 Georoc database (<http://georoc.mpch-mainz.gwdg.de/georoc/>). The location of porphyry
727 copper deposits and the deposit size are from [Singer et al. \(2005\)](#). Phanerozoic felsic
728 magmatism is after [Jagoutz and Klein \(2018\)](#). The location of active margins is from [Hayes
729 et al. \(2018\)](#).

1345
1346
1347
1348
1349
1350
1351
1352
1353
1354
1355
1356
1357
1358
1359
1360
1361
1362
1363
1364
1365
1366
1367
1368
1369
1370
1371
1372
1373
1374
1375
1376
1377
1378
1379
1380
1381
1382
1383
1384
1385
1386
1387
1388
1389
1390
1391
1392
1393
1394
1395
1396
1397
1398
1399
1400

730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758

Fig. 2: Compilation of Cu concentrations in primitive arc melts and mid-oceanic ridge basalts (MORBs). (a) Whisker plot showing the Cu concentrations in primitive arc melt based on variable tectonic settings using the classification scheme of Schmidt and Jagoutz (2017). The ranges of Cu values for primitive MORBs are compiled from Gale et al. (2013). (b) Average Cu concentration and associated uncertainties (1 SD) for primitive arc basalts (blue), primitive arc high-Mg andesites (orange), and primitive MORBs (grey). (c) Histogram showing the distribution of Cu concentrations for primitive arc basalts, primitive arc high-Mg andesites (HMA), and primitive MORBs. Abbreviations in (a): C for continental arc, IO for Intra-oceanic arc, and BAB for back-arc basin.

Fig. 3: Plots of Cu, FeO_{tot} and V versus MgO for volcanic rocks of 28 arcs. (a-c) Tholeiitic rocks (n=6,114) (d-f) Calc-alkaline rocks (n=9,275). Median values for each compiled arc are also plotted at every MgO = 0.5 wt% for tholeiitic series (dark red circle) and calc-alkaline series (light blue circle) (see details in Fig. C1). Median values of Cu, FeO_{tot} and V for every MgO = 0.5 wt% are shown for the global compilation of tholeiitic and calc-alkaline series (yellow diamond). The average Cu concentration and associated uncertainties (1 SD) for primitive arc basalts (black bar) is shown in (a) and (d).

Fig. 4: Geochemical relationships between Cu, FeO_{tot}, V and crustal thicknesses for 17 volcanic arcs with representative whole rock geochemical data set (n>300). (a) Cu versus FeO_{tot}. (b) V versus FeO_{tot}. (c) Cu₄ versus Fe₄, where Cu₄ and Fe₄ correspond to the average of median values and associated uncertainties (1 SD) of Cu and Fe between MgO = 3 and MgO = 5 wt% (see Table B1). Circles and squares represent thin (<25 km) and thick arc (>25 km). (d) Cu₄ versus crustal thickness. References for crustal thicknesses and associated uncertainties (1 SD) are available in Table B1. The average Cu concentration and associated uncertainties (1 SD) for primitive arc basalts (black bar) is shown in (c) and (d).

1401
1402
1403
1404
1405
1406
1407
1408
1409
1410
1411
1412
1413
1414
1415
1416
1417
1418
1419
1420
1421
1422
1423
1424
1425
1426
1427
1428
1429
1430
1431
1432
1433
1434
1435
1436
1437
1438
1439
1440
1441
1442
1443
1444
1445
1446
1447
1448
1449
1450
1451
1452
1453
1454
1455
1456

Fig. 5: (a) Plots of Mg# (molar Mg/(Mg+Fe)) versus SiO₂ for compiled whole-rock compositions of plutonic rocks for four crustal sections (Famatina, Fjordland, Kohistan and Talkeetna; [Jagoutz and Kelemen, 2015](#); [Jagoutz and Klein, 2018](#) and references therein) together with other cumulates xenoliths from the Bonanza arc, Sierra Nevada, Arizona, Eastern Pontides and Kermadec ([Chin et al., 2018](#) and references therein). Red dots are used for the Chilas complex in Kohistan arc as it represents a damp tholeiitic fractionation, whereas dots with different shades of blue represent plutonic rocks and cumulates xenoliths associated with wet calc-alkaline fractionation ([Jagoutz et al., 2011](#); [Jagoutz and Klein, 2018](#)). (b) Histogram showing the density of Cu concentrations for the four crustal sections and other cumulates xenoliths. See discussion for details and the full data set and references in **Table C1**.

Fig. 6: Sulfur speciation in melt and sulfur solubility as a function of oxygen fugacity, expressed log units relative to the fayalite-magnetite-quartz buffer (ΔFMQ). (a) The different black curves illustrates the changes in S₆₊/S_{tot} in hydrous silicate melts with pressure from [Jugo et al., \(2010\)](#), [Botcharnikov et al., \(2011\)](#) and [Matjuschkin et al. \(2016\)](#). The brown line represents the sulfur solubility curve at sulfide and sulfate saturation at 0.2 GPa after [Botcharnikov et al. \(2011\)](#), whereas the brown dotted line represents an hypothetical similar sulfur solubility curve at higher pressure of 1 GPa. The upper inset indicates the redox ranges for mid-ocean ridge basalt (MORB), sub-arc mantle and arc basalts from [Ballhaus \(1993\)](#), [Carmichael \(1991\)](#), [Parkinson and Arculus \(1999\)](#), [Arai and Ishimaru \(2008\)](#), [Wallace and Edmons \(2011\)](#), [Evans et al., \(2012\)](#) and [Bénard et al., \(2018\)](#). We report a range of sulfur concentrations (orange whisker plot with a median values of 0.12 wt%) measured in olivine-hosted melt inclusions for arc-related basalts and basalt-andesites compiled from the Georoc database (n=456). (b-e) Sulfur solubility curves simplified from Figure 6a to illustrate the effect of different parameters on sulfide saturation, including (b) variable pressure of differentiation, (c) different liquid line of descent, (d) variable initial redox conditions, and (e) variable initial sulfur content [S]_i. In (b) and (c), the values of F and the timing of

magnetite is quantified in [Table D1](#). The different scenarios are also discussed in details in the section 4.1 of the manuscript.

Fig. 7: Computed melt composition, melt Cu concentration, melt H₂O content, melt fraction (F), during magmatic differentiation for wet (2 to 4 wt% H₂O - blue) and damp (0.2 to 1.5 wt% H₂O - red) at $\Delta\text{FMQ} = 1$ for variable starting pressure of differentiation (i.e., 8-1.5 kbars (dotted lines) and 4-1.5 kbars (plain lines)) using Rhyolite-MELTS ([Gualda et al., 2012](#)). (a) Computed melt evolution of FeO_{tot} versus MgO. For damp LLDs, the highest and lowest Fe enrichment at MgO ~4-5 wt% corresponds to initial H₂O of 0.2 and 1.5 wt%, respectively. The black line corresponds to modelled LLD with initial H₂O of 1 wt% at $\Delta\text{FMQ} = 1$ from [Zimmer et al. \(2010\)](#), showing the effect of the initial primitive melt composition for the Fe enrichment. Shaded dots are single data and median data per arc from our global compilation of tholeiitic and calc-alkaline volcanic rocks in [Figure 3b,e](#). (b) Evolution of the Cu concentration versus MgO in wet, damp and dry melt modelled using Rayleigh fractionation assuming 0.25 vol.% sulfide ($D_{\text{Cu}}^{\text{sulfide/melt}} = 800$) and 99.75 vol.% silicate ($D_{\text{Cu}}^{\text{silicate/melt}} = 0.1$). Shaded dots are single data and median data per arc from our global compilation of tholeiitic and calc-alkaline volcanic rocks in [Figure 3a,d](#). The steady depletion assumes early sulfide saturation to simulate the trends observed in all calc-alkaline series and some tholeiitic series in thick arcs (>25 km). In contrast, the early enrichment in Cu followed by a sharp depletion simulates late sulfide saturation at MgO ~4 wt% to reproduce the evolution of Cu concentration displayed by tholeiitic series in thin arcs (<25 km). (c, d) Rhyolite-MELTS computed melt H₂O content versus the remaining melt mass (F) and pressure (P). See text for detailed discussion and [Table D1](#) for full data sets.

Fig. 8: Relationship between the initial melt H₂O content and the ore-forming potential for the different liquid lines of descents modelled in Figure 7. The ore-forming potential is expressed as the relative Cu endowment in fluid expelled at degassing of a H₂O-saturated magma normalized to damp tholeiitic melts modelled with an initial H₂O content of 0.5 wt% (circles) and 1.5 wt% (squares) according to the variable pressure of differentiation from 4 to 1.5 kbars (4 kb – filled symbol) from 8 to 1.5 kbars (8 kb – empty symbol). The different

1513
1514
1515
1516
1517
1518
1519
1520
1521
1522
1523
1524
1525
1526
1527
1528
1529
1530
1531
1532
1533
1534
1535
1536
1537
1538
1539
1540
1541
1542
1543
1544
1545
1546
1547
1548
1549
1550
1551
1552
1553
1554
1555
1556
1557
1558
1559
1560
1561
1562
1563
1564
1565
1566
1567
1568

818 colors reflect melt Cu content at H₂O saturation in tholeiitic series assuming late sulfide
819 saturation in thin arc (grey) and early sulfide saturation in thick arc (yellow). Details of the
820 calculation is provided in [Table D1](#) and [Supplementary Material A1](#). See text for discussion.

821
822 **Fig. 9:** Conceptual cartoon of the single-stage and multi-stage models for the formation of
823 porphyry Cu deposits (PCDs). (a) The single stage model assumes the formation of large
824 economic PCDs associated with the generation of wet calc-alkaline melts, where flux melting
825 is predominant in the main arc. (b) The single stage model assumes the formation of barren
826 upper crustal intrusions associated with the generation of damp tholeiitic melts, where
827 decompression melting is predominant in the main arc. (c) The multi-stage model assumes
828 the remobilization of Cu-sulfide sequestered in crustal cumulates during a later hydrous and
829 oxidized magmatic event in the main arc, which may result in the formation of large PCDs.

830
831 **Fig. A1:** Plots of Cu versus MgO for primitive arc basalts and primitive high-Mg Andesites
832 using the classification scheme of [Schmidt and Jagoutz \(2017\)](#).

833
834 **Fig. B1:** Classification of tholeiitic and calc-alkaline volcanic rocks (n=15,389) based on the
835 FeO/MgO versus SiO₂ after [Miyashiro \(1974\)](#).

836
837 **Fig. C1:** Plots of Cu, FeO_{tot} and V versus MgO for calc-alkaline and tholeiitic volcanic rocks for
838 each compiled arc. Median Cu, FeO_{tot} and V values for each arc are plotted at every MgO = 0.5
839 wt%.

840
841 **Fig. D1:** Plots of Cu and V versus FeO_{tot} for calc-alkaline and tholeiitic volcanic rocks for each
842 compiled arc.

843 .

844 **REFERENCES**

845 Allibone, A. H., Jongens, R., Scott, J. M., Tulloch, A. J., Turnbull, I. M., Cooper, A. F., Powell, N. G., Ladley, E. B., King,
846 R. P., Rattenbury, M. S., 2009. Plutonic rocks of the Median Batholith in eastern and central Fiordland, New
847 Zealand. Field relations, geochemistry, correlation, and nomenclature: *New Zeal. J. of Geol. Geop.* 52, 101–
848 148.

1569
1570
1571 849 Arai, S., Ishimaru, S., 2008. Insights into petrological characteristics of the lithosphere of mantle wedge beneath
1572 850 arcs through peridotite xenoliths: a review. *J. Petrol.* 49, 665-695.
1574 851 Parkinson, I. J., Arculus, R. J., 1999. The redox state of subduction zones: insights from arc-peridotites. *Chem.*
1575 852 *Geol.* 160, 409-423.
1576 853 Audéat, A., Simon, A. C., 2012. Magmatic Controls on Porphyry Copper Genesis. In *Geology and Genesis of Major*
1578 854 *Copper Deposits and Districts of the World: A Tribute to Richard H. Sillitoe*, eds. Jeffrey W. Hedenquist,
1579 855 Michael Harris, Francisco Camus. Society of Economic Geologists, Special Publication 16, 553-572.
1580 856 Baker, M. B., Grove, T. L., Price, R., 1994. Primitive basalts and andesites from the Mt. Shasta region, N. California:
1582 857 products of varying melt fraction and water content. *Contrib Mineral Petrol.* 118, 111-129.
1583 858 Ballhaus, C., 1993. Redox states of lithospheric and asthenospheric upper mantle. *Contrib Mineral Petrol.* 114,
1584 859 331-348.
1586 860 Bénard, A., Klimm, K., Woodland, A. B., Arculus, R. J., Wilke, M., Botcharnikov, R. E., Shimizu, N., Nebel, O., Rivard,
1587 861 C., Ionov, D. A., 2018. Oxidising agents in sub-arc mantle melts link slab devolatilisation and arc magmas.
1588 862 *Nat. Commun.* 9, 3500.
1590 863 Botcharnikov, R. E., Linnen, R. L., Wilke, M., Holtz, F., Jugo, P. J., and Berndt, J., 2011. High gold concentrations in
1591 864 sulphide-bearing magma under oxidizing conditions. *Nat. Geo.* 4, 112-115.
1593 865 Brounce, M. N., Kelley, K. A., and Cottrell, E., 2014. Variations in $Fe^{3+}/\Sigma Fe$ of Mariana Arc basalts and mantle
1594 866 wedge fO_2 . *J. Petrol.* 55, 2513-2536.
1595 867 Brounce, M., Cottrell, E., and Kelley, K. A., 2019. The redox budget of the Mariana subduction zone. *Earth Planet.*
1597 868 *Sci. Lett.* 528, 115859.
1598 869 Bucholz, C. E., Kelemen, P. B., 2019. Oxygen fugacity at the base of the Talkeetna arc, Alaska. *Contrib Mineral*
1599 870 *Petrol.* 174, 79.
1601 871 Canil, D., 1999. Vanadium partitioning between orthopyroxene, spinel and silicate melt and the redox states of
1602 872 mantle source regions for primary magmas *Geochim. Cosmochim. Acta* 63, 557-572.
1603 873 Carmichael, I. S., 1991. The redox states of basic and silicic magmas: a reflection of their source regions?. *Contrib*
1605 874 *Mineral Petrol.* 106, 129-141.
1606 875 Caricchi, L., Simpson, G., Schaltegger, U., 2014. Zircons reveal magma fluxes in the Earth's crust. *Nature* 511,
1607 876 457-461.
1609 877 Cervantes, P., and Wallace, P. J., 2003. Role of H₂O in subduction-zone magmatism: new insights from melt
1610 878 inclusions in high-Mg basalts from central Mexico. *Geology* 31, 235-238.
1612 879 Chelle-Michou, C., Rottier, B., Caricchi, L., Simpson, G., 2017. Tempo of magma degassing and the genesis of
1613 880 porphyry copper deposits. *Sci. Rep.* 7, 40566.
1614 881 Chiaradia, M., 2014. Copper enrichment in arc magmas controlled by overriding plate *Nat. Geo.* 7, 43-46.
1616 882 Chiaradia, M., 2015. Crustal thickness control on Sr/Y signatures of recent arc magmas: an Earth scale
1617 883 perspective. *Sci. Rep.* 5, 8115.
1618 884 Chiaradia, M., 2020a. How much water in basaltic melts parental to porphyry copper deposits?. *Frontiers in*
1620 885 *Earth Sciences*, 8, 313.

1625
1626
1627 886 Chiaradia, M., 2020b. Gold endowments of porphyry deposits controlled by precipitation efficiency. *Nat.*
1628 887 *Commun.* 11, 1-10.
1629
1630 888 Chiaradia, M., Caricchi, L., 2017. Stochastic modelling of deep magmatic controls on porphyry copper deposit
1631 889 endowment. *Sci. Rep.* 7, 44523.
1632
1633 890 Chiaradia, M., Ulianov, A., Kouzmanov, K., Beate, B., 2012. Why large porphyry Cu deposits like high Sr/Y
1634 891 magmas? *Sci. Rep.* 2, 685.
1635 892 Chin, E.J., Shimizu, K., Bybee, G.M., Erdman, M.E., 2018. On the development of the calc-alkaline and tholeiitic
1636 893 magma series: a deep crustal cumulate perspective. *Earth Planet. Sci. Lett.* 482, 277–287.
1637 894 Ciazela, J., Dick, H. J., Koepke, J., Pieterek, B., Muszynski, A., Botcharnikov, R., Kuhn, T., 2017. Thin crust and
1638 895 exposed mantle control sulfide differentiation in slow-spreading ridge magmas. *Geology* 45, 935-938.
1639
1640 896 Cline, J. S., Bodnar, R. J., 1991. Can economic porphyry copper mineralization be generated by a typical
1641 897 calc-alkaline melt?. *J. Geophys. Res. Solid Earth* 96(B5), 8113-8126.
1642
1643 898 Cooke, D. R., Hollings, P., Walshe, J. L., 2005. Giant porphyry deposits: characteristics, distribution, and tectonic
1644 899 controls. *Econ. Geol.* 100, 801-818.
1645
1646 900 Cox, D., Watt, S. F., Jenner, F. E., Hastie, A. R., Hammond, S. J., 2019. Chalcophile element processing beneath a
1647 901 continental arc stratovolcano. *Earth Planet. Sci. Lett.* 522, 1-11.
1648
1649 902 Du, J., Audétat, A., 2020. Early sulfide saturation is not detrimental to porphyry Cu-Au formation. *Geology*, 48,
1650 903 519-524
1651 904 Duan, Z., Zhang, Z., 2006. Equation of state of the H₂O, CO₂, and H₂O–CO₂ systems up to 10 GPa and 2573.15 K:
1652 905 molecular dynamics simulations with ab initio potential surface. *Geochim Cosmochim Acta* 70:2311–2324
1653 906 Evans, K. A., Elburg, M. A., Kamenetsky, V. S., 2012. Oxidation state of subarc mantle. *Geology* 40, 783-786.
1654 907 Fliedner, M. M., Klemperer, S. L., 1999. Structure of an island-arc: Wide-angle seismic studies in the eastern
1655 908 Aleutian Islands, Alaska. *Journal of Geophysical Research: Solid Earth*, 104(B5), 10667-10694.
1656 909 Fortin, M. A., Riddle, J., Desjardins-Langlais, Y., Baker, D. R., 2015. The effect of water on the sulfur concentration
1657 910 at sulfide saturation (SCSS) in natural melts. *Geochim Cosmochim Acta* 160, 100-116.
1658 911 Gale, A., Dalton, C. A., Langmuir, C. H., Su, Y., Schilling, J. G., 2013. The mean composition of ocean ridge basalts.
1659 912 *Geochem Geophys Geosyst.* 14, 489-518.
1660 913 Georgatou, A., Chiaradia, M., 2019. Magmatic sulphides in high-K calc-alkaline to shoshonitic and alkaline rocks.
1661 914 *Solid Earth.* <https://doi.org/10.5194/se-2019-106>
1662 915 Georgatou, A., Chiaradia, M., Rezeau, H., Wälle, M., 2018. Magmatic sulphides in Quaternary Ecuadorian arc
1663 916 magmas. *Lithos* 296, 580-599.
1664 917 Ghiorso, M. S., Carmichael, I. S., 1987. Modeling magmatic systems; petrologic applications. *Rev Mineral*
1665 918 *Geochem*, 17, 467-499.
1666 919 Ghiorso, M. S., Gualda, G. A., 2015. An H₂O–CO₂ mixed fluid saturation model compatible with rhyolite-MELTS.
1667 920 *Contrib Mineral Petrol.*, 169, 1-30.
1668 921 Duan Z, Zhang Z (2006) Equation of state of the H₂O, CO₂, and H₂O–CO₂ systems up to 10 GPa and 2573.15 K:
1669 922 molecular dynamics simulations with ab initio potential surface. *Geochim Cosmochim Acta* 70:2311–2324
1670
1671
1672
1673
1674
1675
1676
1677
1678
1679
1680

1681
1682
1683 923 Giacometti, F., Evans, K. A., Rebay, G., Cliff, J., Tomkins, A. G., Rossetti, P., Vaggelli, G., Adams, D. T. (2014). Sulfur
1684 924 isotope evolution in sulfide ores from Western Alps: Assessing the influence of subduction-related
1685 925 metamorphism. *Geochem Geophys Geosyst* 15, 3808-3829.
1687 926 Greene, A. R., DeBari, S. M., Kelemen, P. B., Blusztajn, J., Clift, P. D., 2006. A detailed geochemical study of island
1688 927 arc crust: the Talkeetna arc section, south-central Alaska. *J Petrol*, 47, 1051-1093.
1690 928 Grove, T., Parman, S., Bowring, S., Price, R., Baker, M., 2002. The role of an H₂O-rich fluid component in the
1691 929 generation of primitive basaltic andesites and andesites from the Mt. Shasta region, N California. *Contrib*
1692 930 *Mineral Petrol.* 142, 375-396.
1694 931 Grove, T. L., Till, C. B., Krawczynski, M. J., 2012. The role of H₂O in subduction zone magmatism. *Annu. Rev. Earth*
1695 932 *Planet. Sci*, 40, 413-439.
1697 933 Gualda, A.R., Ghiorso, M.S., Lemons, R. V., Tamara L., Carley, T. L., 2012. Rhyolite-MELTS: a Modified Calibration
1698 934 of MELTS Optimized for Silica-rich, Fluid-bearing Magmatic Systems, *J Petrol.* 53, 875-890.
1699 935 Hayes, G. P., Moore, G. L., Portner, D. E., Hearne, M., Flamme, H., Furtney, M., Smoczyk, G. M., 2018. Slab2, a
1701 936 comprehensive subduction zone geometry model. *Science* 362, 58-61.
1702 937 Hedenquist, J.W., Lowenstern, J.B., 1994. The role of magmas in the formation of hydrothermal ore deposits.
1703 938 *Nature* 370, 519.
1705 939 Hou, Z., Yang, Z., Lu, Y., Kemp, A., Zheng, Y., Li, Q., Tang, J., Yang, Z. and Duan, L., 2015. A genetic linkage between
1706 940 subduction-and collision-related porphyry Cu deposits in continental collision zones. *Geology* 43, 247-
1707 941 250.
1709 942 Hsu, Y. J., Zajacz, Z., Ulmer, P., Heinrich, C. A., 2017. Copper partitioning between silicate melts and amphibole:
1710 943 Experimental insight into magma evolution leading to porphyry copper ore formation. *Chem. Geol.* 448,
1711 944 151-163.
1713 945 Jagoutz, O. E., 2010. Construction of the granitoid crust of an island arc. Part II: a quantitative petrogenetic
1714 946 model. *Contrib Mineral Petrol.* 160, 359-381.
1716 947 Jagoutz, O., Klein, B., 2018. On the importance of crystallization-differentiation for the generation of SiO₂-rich
1717 948 melts and the compositional build-up of arc (and continental) crust. *Am. J. Sci*, 318, 29-63.
1718 949 Jagoutz, O., Kelemen, P. B., 2015. Role of arc processes in the formation of continental crust. *Annu. Rev. Earth*
1720 950 *Planet. Sci*, 43, 363-404.
1721 951 Jagoutz, O., Müntener, O., Schmidt, M. W., Burg, J. P., 2011. The roles of flux-and decompression melting and
1722 952 their respective fractionation lines for continental crust formation: Evidence from the Kohistan arc. *Earth*
1723 953 *Planet Sc Lett.* 303, 25-36.
1725 954 Jégo, S., Dasgupta, R., 2014. The fate of sulfur during fluid-present melting of subducting basaltic crust at
1726 955 variable oxygen fugacity. *J. Petrol.* 55, 1019-1050.
1728 956 Jenner, F. E., 2017. Cumulate causes for the low contents of sulfide-loving elements in the continental crust. *Nat.*
1729 957 *Geo.* 10, 524-529.
1730 958 Jenner, F. E., O'Neill, H. S. C., 2012. Analysis of 60 elements in 616 ocean floor basaltic glasses. *Geochem,*
1732 959 *Geophys, Geosyst.* 13.
1733
1734
1735
1736

1737
1738
1739 960 Jenner, F.E., O'Neill, H.S.C., Arculus, R.J., Mavrogenes, J.A., 2010. The magnetite crisis in the evolution of arc-
1740 related magmas and the initial concentration of Au, Ag and Cu. *J. Petrol.* 51, 2445–2464.
1741 961
1742 962 Jicha, B. R., Jagoutz, O., 2015. Magma production rates for intraoceanic arcs. *Elements* 11, 105-111.
1743 963 Johnson, E. R., Wallace, P. J., Delgado Granados, H., Manea, V. C., Kent, A. J., Bindeman, I. N., and Donegan, C. S.,
1744 964 2009. Subduction-related volatile recycling and magma generation beneath Central Mexico: insights from
1746 965 melt inclusions, oxygen isotopes and geodynamic models. *J. Petrol.* 50, 1729-1764.
1747 966 Jugo, P. J., 2009. Sulfur content at sulfide saturation in oxidized magmas. *Geology* 37, 415-418.
1748 967 Jugo, P.J., Wilke, M., Botcharnikov, R.E., 2010. Sulfur K-edge XANES analysis of natural and synthetic basaltic
1750 968 glasses: implications for S speciation and S content as function of oxygen fugacity. *Geochim. Cosmochim.*
1751 969 *Acta* 74, 5926–5938
1752 970 Karlstrom, L., Lee, C.T., Manga, M., 2014. The role of magmatically driven lithospheric thickening on arc front
1754 971 migration. *Geochem. Geophys. Geosyst.* 15, 2655–2675.
1755 972 Kelemen, P. B., Shimizu, N., Salters, V. J. M., 1995. Formation of harzburgite by pervasive melt/rock reaction
1756 973 in the upper mantle, *Nature* 358, 635–641.
1758 974 Kelemen, P., Hanghøj, B., K., Greene, A. R., 2014. One view of the geochemistry of subduction-related magmatic
1759 975 arcs, with an emphasis on primitive andesite and lower crust. In *The Crust, Treatise on Geochemistry*,
1761 976 edited by H. D. Holland and K. K. Turekian, pp. 669–701, Elsevier-Pergamon, Oxford, U. K.
1762 977 Kelley, K.A., Cottrell, E., 2009. Water and the oxidation state of subduction zone magmas. *Science* 325, 605–607
1763 978 Kelley, K. A., Cottrell, E., 2012. The influence of magmatic differentiation on the oxidation state of Fe in a basaltic
1765 979 arc magma. *Earth Planet. Sci.* 329, 109-121.
1766 980 Kesler, S.E., Jones, L.M., Walker, R.L., 1975, Intrusive rocks associates with porphyry copper mineralization in
1767 981 island arc areas. *Econ. Geol.* 70, 515-526.
1769 982 Kesler, S. E., Sutter, J. F., Issigonis, M. J., Jones, L. M., Walker, R. L., 1977. Evolution of porphyry copper
1770 983 mineralization in an oceanic island arc; Panama. *Econ. Geol.* 72, 1142-1153.
1771 984 Kiseeva, E. S., Wood, B. J., 2015. The effects of composition and temperature on chalcophile and lithophile
1773 985 element partitioning into magmatic sulphides. *Earth Planet. Sci.* 424, 280-294.
1774 986 Kouzmanov, K., Pokrovski, G. S., 2012. Hydrothermal controls on metal distribution in porphyry Cu(–Au–Mo)
1776 987 systems. In *Geology and Genesis of Major Copper Deposits and Districts of the World: A Tribute to Richard*
1777 988 *H. Sillitoe*, eds. Jeffrey W. Hedenquist, Michael Harris, Francisco Camus. Society of Economic Geologists,
1778 989 *Special Publication* 16, 573–618.
1780 990 La Tourrette, T. Z., Burnett, D. S., and Bacon, C. R., 1991. Uranium and minor-element partitioning in Fe-Ti oxides
1781 991 and zircon from partially melted granodiorite, Crater Lake, Oregon. *Geochim. Cosmochim. Acta* 55, 457-
1782 992 469.
1783 993 Lee, C. T. A., Tang, M., 2020. How to make porphyry copper deposits. *Earth Planet. Sci.* 529, 115868.
1784 994 Lee, C. T. A., Luffi, P., Le Roux, V., Dasgupta, R., Albaréde, F., Leeman, W. P., 2010. The redox state of arc mantle
1786 995 using Zn/Fe systematics. *Nature* 468, 681-685.
1787
1788
1789
1790
1791
1792

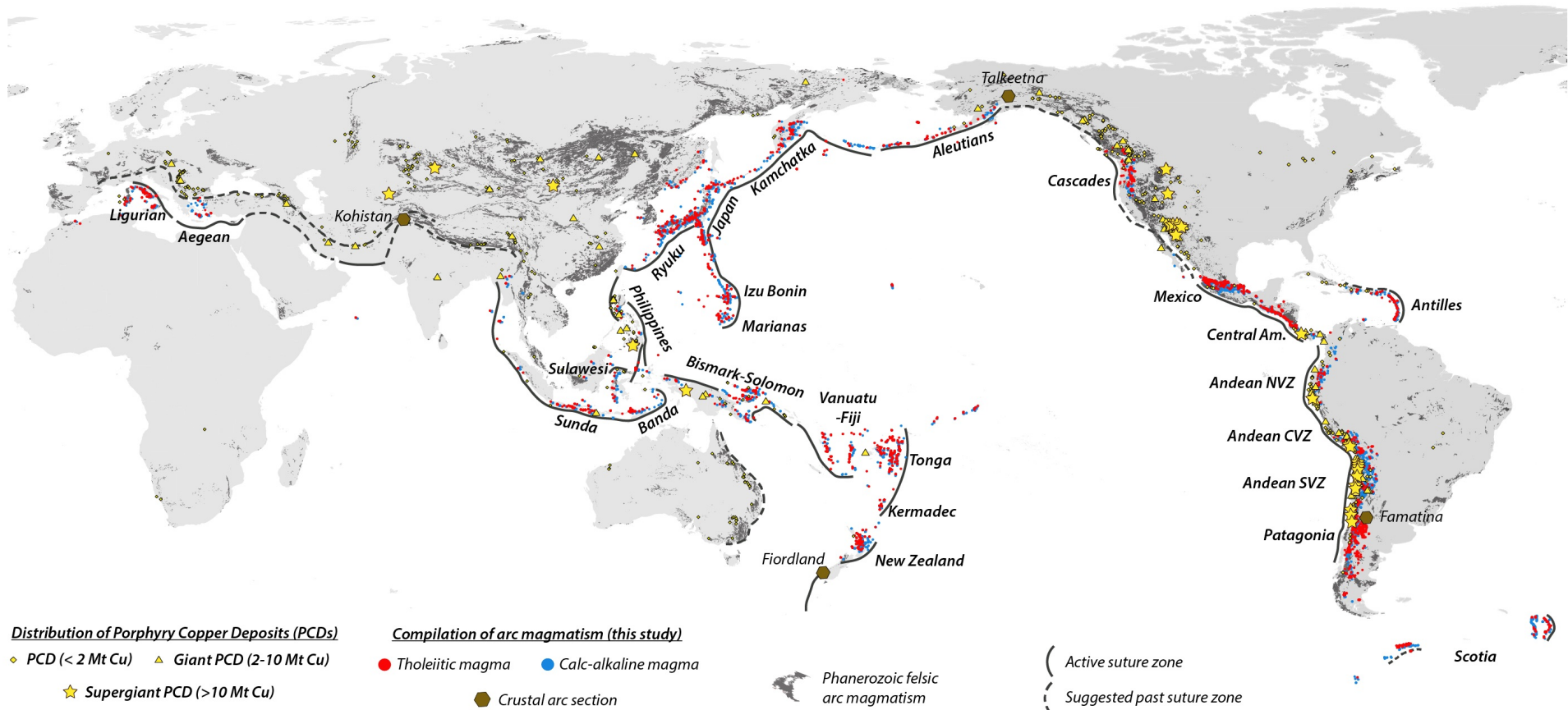
1793
1794
1795 996 Lee, C.-T.A., Luffi, P., Chin, E.J., Bouchet, R., Dasgupta, R., Morton, D.M., Le Roux, V., Yin, Q.-z., Jin, D., 2012. Copper
1796 997 systematics in arc magmas and implications for crust–mantle differentiation. *Science* 336, 64–68.
1798 998 Li, Y., Audétat, A., 2012. Partitioning of V, Mn, Co, Ni, Cu, Zn, As, Mo, Ag, Sn, Sb, W, Au, Pb, and Bi between sulfide
1799 999 phases and hydrous basanite melt at upper mantle conditions. *Earth Planet. Sci. Lett.* 355–356, 327–340.
1800 1000 Lieu, W. K., Stern, R. J., 2019. The robustness of Sr/Y and La/Yb as proxies for crust thickness in modern arcs.
1801 1001 *Geosphere* 15, 621-641.
1803 1002 Liu, X., Xiong, X., Audétat, A., Li, Y., Song, M., Li, L., Sun, W., Ding, X., 2014. Partitioning of copper between olivine,
1804 1003 orthopyroxene, clinopyroxene, spinel, garnet and silicate melts at upper mantle conditions. *Geochim.*
1805 1004 *Cosmochim. Acta* 125, 1–22.
1806 1005 Loucks, R., 2014. Distinctive composition of copper–ore-forming arc magmas. *Aust. J. Earth Sci.* 61, 5–16.
1807 1006 Luhr, J. F., Carmichael, I. S., 1980. The colima volcanic complex, Mexico. *Contrib Mineral Petrol.* 71, 343-372.
1808 1007 Mandler, B. E., Donnelly-Nolan, J. M., Grove, T. L., 2014. Straddling the tholeiitic/calc-alkaline transition: the
1810 1008 effects of modest amounts of water on magmatic differentiation at Newberry Volcano, Oregon. *Contrib*
1811 1009 *Mineral Petrol.* 168, 1066.
1814 1010 Matjuschkin, V., Blundy, J.D., Brooker, R.A., 2016. The effect of pressure on sulphur speciation in mid-to deep-
1815 1011 crustal arc magmas and implications for the formation of porphyry copper deposits. *Contrib. Mineral.*
1816 1012 *Petrol.* 171, 66.
1818 1013 Mavrogenes, J. A., O'Neill, H. S. C., 1999. The relative effects of pressure, temperature and oxygen fugacity on
1819 1014 the solubility of sulfide in mafic magmas. *Geochim Cosmochim Acta* 63, 1173-1180.
1821 1015 McInnes, B. I., McBride, J. S., Evans, N. J., Lambert, D. D., Andrew, A. S., 1999. Osmium isotope constraints on ore
1822 1016 metal recycling in subduction zones. *Science* 286, 512-516.
1823 1017 Melekhova, E., Annen, C., Blundy, J., 2013. Compositional gaps in igneous rock suites controlled by magma
1824 1018 system heat and water content. *Nat. Geo.* 6, 385.
1825 1019 Melekhova, E., Schlaphorst, D., Blundy, J., Kendall, J. M., Connolly, C., McCarthy, A., Arculus, R., 2019. Lateral
1826 1020 variation in crustal structure along the Lesser Antilles arc from petrology of crustal xenoliths and seismic
1827 1021 receiver functions. *Earth Planet. Sci.* 516, 12-24.
1828 1022 Miyashiro, A., 1974. Volcanic rock series in island arcs and active continental margins. *Am. J. Sci.* 274, 321–355.
1829 1023 Mungall, J. E., 2002. Roasting the mantle: Slab melting and the genesis of major Au and Au-rich Cu deposits.
1830 1024 *Geology* 30, 915-918.
1831 1025 Müntener, O., Ulmer, P., 2018. Arc crust formation and differentiation constrained by experimental petrology.
1832 1026 *Am. J. Sci.* 318, 64-89.
1833 1027 Nandedkar, R. H., Ulmer, P., and Müntener, O., 2014. Fractional crystallization of primitive, hydrous arc
1834 1028 magmas: an experimental study at 0.7 GPa. *Contrib Mineral Petrol.* 167, 1015.
1835 1029 O'Neill, H. S. C., Mavrogenes, J. A., 2002. The sulfide capacity and the sulfur content at sulfide saturation of
1836 1030 silicate melts at 1400 C and 1 bar. *J. Petrol.* 43, 1049-1087.
1837
1838
1839
1840
1841
1842
1843
1844
1845
1846
1847
1848

1849
1850
1851 1031 Otamendi, J. E., Vujovich, G. I., de la Rosa, J. D., Tibaldi, A. M., Castro, A., Martino, R. D., and Pinotti, L. P., 2009.
1852
1853 1032 Geology and petrology of a deep crustal zone from the Famatinian paleo-arc, Sierras de Valle Fértil and La
1854 1033 Huerta, San Juan, Argentina. *J. S. Am. Earth Sci.* 27, 258-279.
1855 1034 Park, J. W., Campbell, I. H., Malaviarachchi, S. P., Cocker, H., Hao, H., & Kay, S. M., 2019. Chalcophile element
1856
1857 1035 fertility and the formation of porphyry Cu±Au deposits. *Min. Dep.* 54, 657-670.
1858 1036 Portnyagin, M., Hoernle, K., Plechov, P., Mironov, N., and Khubunaya, S., 2007. Constraints on mantle melting
1859
1860 1037 and composition and nature of slab components in volcanic arcs from volatiles (H₂O, S, Cl, F) and trace
1861 1038 elements in melt inclusions from the Kamchatka Arc. *Earth Planet. Sci.* 255, 53-69.
1862 1039 Profeta, L., Ducea, M. N., Chapman, J. B., Paterson, S. R., Gonzales, S. M. H., Kirsch, M., Petrescu, L., and DeCelles,
1863
1864 1040 P. G., 2015. Quantifying crustal thickness over time in magmatic arcs. *Sci. Rep.* 5, 17786.
1865 1041 Rezeau, H., Moritz, R., Wotzlaw, J. F., Tayan, R., Melkonyan, R., Ulianov, A., Selby, D., d'Abzac, F. X., Stern, R. A.,
1866 1042 2016. Temporal and genetic link between incremental pluton assembly and pulsed porphyry Cu-Mo
1867
1868 1043 formation in accretionary orogens. *Geology* 44, 627-630.
1869 1044 Richards, J. P., 2003. Tectono-magmatic precursors for porphyry Cu-(Mo-Au) deposit formation. *Econ. Geol.* 98,
1870
1871 1045 1515-1533.
1872 1046 Richards, J.P., 2009. Postsubduction porphyry Cu–Au and epithermal Au deposits: products of remelting of
1873 1047 subduction-modified lithosphere. *Geology* 37, 247–250.
1874 1048 Richards, J. P., 2011a. Magmatic to hydrothermal metal fluxes in convergent and collided margins. *Ore Geol.*
1875
1876 1049 *Rev.* 40, 1-26.
1877 1050 Richards, J. P., 2011b. High Sr/Y arc magmas and porphyry Cu±Mo±Au deposits: just add water. *Econ. Geol.* 106,
1878
1879 1051 1075-1081.
1880 1052 Richards, J. P., 2015. The oxidation state, and sulfur and Cu contents of arc magmas: implications for
1881 1053 metallogeny. *Lithos* 233, 27-45.
1882 1054 Richards, J. P., 2018. A shake-up in the porphyry world?. *Econ. Geol.* 113, 1225-1233.
1883
1884 1055 Ripley, E. M., Li, C., 2013. Sulfide saturation in mafic magmas: Is external sulfur required for magmatic Ni-Cu-
1885 1056 (PGE) ore genesis?. *Econ. Geol.*, 108, 45-58.
1886
1887 1057 Rowe, M. C., Kent, A. J., Nielsen, R. L., 2009. Subduction influence on oxygen fugacity and trace and volatile
1888 1058 elements in basalts across the Cascade Volcanic Arc. *J. Petrol.* 50, 61-91.
1889 1059 Schmidt, M. W., Jagoutz, O. 2017. The global systematics of primitive arc melts. *Geochem Geophys Geosyst*, 18,
1890
1891 1060 2817-2854.
1892 1061 Seedorff, E., J. H. Dilles, J. M. Proffett, M. T. Einaudi, L. Zurcher, W. J. A. Stavast, D. A. Johnson, and M. D. Barton,
1893
1894 1062 2005, Porphyry deposits: characteristics and origin of hypogene features. *Economic Geology* 100th
1895 1063 Anniversary Volume, eds. Jeffrey W. Hedenquist, John F. H. Thompson, Richard J. Goldfarb, Jeremy P.
1896 1064 Richards
1897 1065 Sillitoe, R.H., 2010. Porphyry copper systems. *Econ. Geol.* 105, 3–41.
1898
1899 1066 Sillitoe, R. H., 1997. Characteristics and controls of the largest porphyry copper-gold and epithermal gold
1900 1067 deposits in the circum-Pacific region, *Aust. J. Earth Sci.* 44, 373-388.
1901
1902
1903
1904

1905
1906
1907 1068 Sillitoe, R.H., Hedenquist, J.W., 2003. Linkages between volcanotectonic settings, ore-fluid compositions, and
1908 1069 epithermal precious metal deposits. SEG Special Publication 10, 315–343.
1910 1070 Singer, D. A., Berger, V. I., Menzie, W. D., Berger, B. R., 2005. Porphyry copper deposit density. *Econ. Geol.* 100,
1911 1071 491-514.
1912 1072 Sisson, T. W., Grove, T. L., 1993. Experimental investigations of the role of H₂O in calc-alkaline differentiation
1913 1073 and subduction zone magmatism. *Contrib Mineral Petrol.* 113, 143-166.
1915 1074 Sobolev, A. V., and Chaussidon, M., 1996. H₂O concentrations in primary melts from supra-subduction zones
1916 1075 and mid-ocean ridges: implications for H₂O storage and recycling in the mantle. *Earth Planet. Sci. Lett.*
1918 1076 137, 45-55.
1919 1077 Solomon, M., 1990. Subduction, arc reversal, and the origin of porphyry copper-gold deposits in island arcs.
1920 1078 *Geology* 18, 630-633.
1922 1079 Stavast, W. J., Keith, J. D., Christiansen, E. H., Dorais, M. J., Tingey, D., Larocque, A., Evans, N., 2006. The fate of
1923 1080 magmatic sulfides during intrusion or eruption, Bingham and Tintic districts, Utah. *Econ. Geol.* 101, 329-
1924 1081 345.
1926 1082 Sun, W., Wang, J. T., Zhang, L. P., Zhang, C. C., Li, H., Ling, M. X., Ding, X., Li, C-y., Liang, H. Y., 2017. The formation
1927 1083 of porphyry copper deposits. *Acta Geochim*, 36, 9-15.
1929 1084 Sun, W., Huang, R. F., Li, H., Hu, Y. B., Zhang, C. C., Sun, S. J., Zhang, L-p., Ding, X., Li, C.Y., Zartman, R.E., Ling, M. X.,
1930 1085 2015. Porphyry deposits and oxidized magmas. *Ore Geol. Rev.* 65, 97-131.
1931 1086 Tatsumi, Y., and Suzuki, T., 2009. Tholeiitic vs calc-alkalic differentiation and evolution of arc crust: constraints
1932 1087 from melting experiments on a basalt from the Izu-Bonin-Mariana Arc. *J. Petrol.* 50, 1575-1603.
1934 1088 Tattitch, B. C., and Blundy, J. D., 2017. Cu-Mo partitioning between felsic melts and saline-aqueous fluids as a
1935 1089 function of X NaC_l, f O₂, and f S₂. *Am. Mineral* 102, 1987-2006.
1937 1090 Tattitch, B. C., Candela, P. A., Piccoli, P. M., Bodnar, R. J., 2015. Copper partitioning between felsic melt and H₂O-
1938 1091 CO₂ bearing saline fluids. *Geochim Cosmochim Acta* 148, 81-99.
1940 1092 Titley, S.R., 1975, Geological characteristics and environment of some porphyry copper occurrences in the
1941 1093 southwestern Pacific. *Econ. Geol.* 70, 499-514.
1942 1094 Tomkins, A. G., 2010. Windows of metamorphic sulfur liberation in the crust: Implications for gold deposit
1943 1095 genesis. *Geochim Cosmochim Acta* 74, 3246-3259.
1945 1096 Tomkins, A. G., and Evans, K. A., 2015. Separate zones of sulfate and sulfide release from subducted mafic
1946 1097 oceanic crust. *Earth Planet. Sci.* 428, 73-83.
1948 1098 Tosdal, R.M., Richards, J.P., 2001. Magmatic and structural controls on the development of porphyry Cu ± Mo ±
1949 1099 Au deposits: *Rev. Econ. Geol.* 14, p. 157–181.
1950 1100 Turner, S. J., and Langmuir, C. H., 2015. What processes control the chemical compositions of arc front
1951 1101 stratovolcanoes?. *Geochem Geophys Geosyst*, 16, 1865-1893.
1953 1102 Ulmer, P., Kaegi, R., and Müntener, O., 2018. Experimentally derived intermediate to silica-rich arc magmas by
1954 1103 fractional and equilibrium crystallization at 1.0 GPa: An evaluation of phase relationships, compositions,
1955 1104 liquid lines of descent and oxygen fugacity. *J. Petrol.* 59, 11-58.
1957
1958
1959
1960

1961
1962
1963 1105 Vasseur, J., and Wadsworth, F. B., 2017. Sphere models for pore geometry and fluid permeability in
1964 1106 heterogeneous magmas. *Bull. Volcanol.* 79, 77.
1966 1107 Villiger, S., Ulmer, P., Müntener, O., and Thompson, A. B., 2004. The liquid line of descent of anhydrous, mantle-
1967 1108 derived, tholeiitic liquids by fractional and equilibrium crystallization—an experimental study at 1.0 GPa.
1968 1109 *J. Petrol.* 45, 2369-2388.
1970 1110 Wallace, P. J., 2005. Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion
1971 1111 and volcanic gas data. *J Volcanol Geoth Res* 140, 217-240.
1972 1112 Wallace, P. J., and Edmonds, M., 2011. The sulfur budget in magmas: evidence from melt inclusions, submarine
1973 1113 glasses, and volcanic gas emissions. *Rev Mineral Geochem*, 73, 215-246.
1974 1114 Walsh, S. D., and Saar, M. O. 2008. Magma yield stress and permeability: Insights from multiphase percolation
1975 1115 theory. *Volcanol. Geotherm. Res.* 177, 1011-1019.
1978 1116 Wang, R., Weinberg, R. F., Collins, W. J., Richards, J. P., and Zhu, D. C., 2018. Origin of postcollisional magmas and
1979 1117 formation of porphyry Cu deposits in southern Tibet. *Earth Sci. Rev.* 181, 122-143.
1981 1118 Wilkinson, J.J., 2013. Triggers for the formation of porphyry ore deposits in magmatic arcs. *Nat. Geosci.* 6, 917.
1982 1119 Zajacz, Z., Halter, W. E., Pettke, T., and Guillong, M., 2008. Determination of fluid/melt partition coefficients by
1983 1120 LA-ICPMS analysis of co-existing fluid and silicate melt inclusions: controls on element partitioning.
1984 1121 *Geochim Cosmochim Acta* 72, 2169-2197.
1986 1122 Zelenski, M., Kamenetsky, V. S., Mavrogenes, J. A., Danyushevsky, L. V., Matveev, D., Gurenko, A. A. 2017.
1987 1123 Platinum-group elements and gold in sulfide melts from modern arc basalt (Tolbachik volcano,
1988 1124 Kamchatka). *Lithos* 290, 172-188.
1990 1125 Zellmer, G. F., 2008. Some first-order observations on magma transfer from mantle wedge to upper crust at
1991 1126 volcanic arcs. *Geological Society, London, Special Publications*, 304, 15-31.
1993 1127 Zimmer, M. M., Plank, T., Hauri, E. H., Yogodzinski, G. M., Stelling, P., Larsen, J., Singer, B., Jicha, B., Mandeville, C.,
1994 1128 and Nye, C. J., 2010. The role of water in generating the calc-alkaline trend: new volatile data for Aleutian
1995 1129 magmas and a new tholeiitic index. *J. Petrol.* 51, 2411-2444.
1997 1130 Zheng, Y. C., Liu, S. A., Wu, C. D., Griffin, W. L., Li, Z. Q., Xu, B., Yang, Z. M., Hou, Z-Q., O'Reilly, S. Y., 2018. Cu isotopes
1998 1131 reveal initial Cu enrichment in sources of giant porphyry deposits in a collisional setting. *Geology* 47, 135-
1999 1132 138.
2000 1133
2001 1134
2002 1135
2003 1136
2004 1137
2005 1138
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36



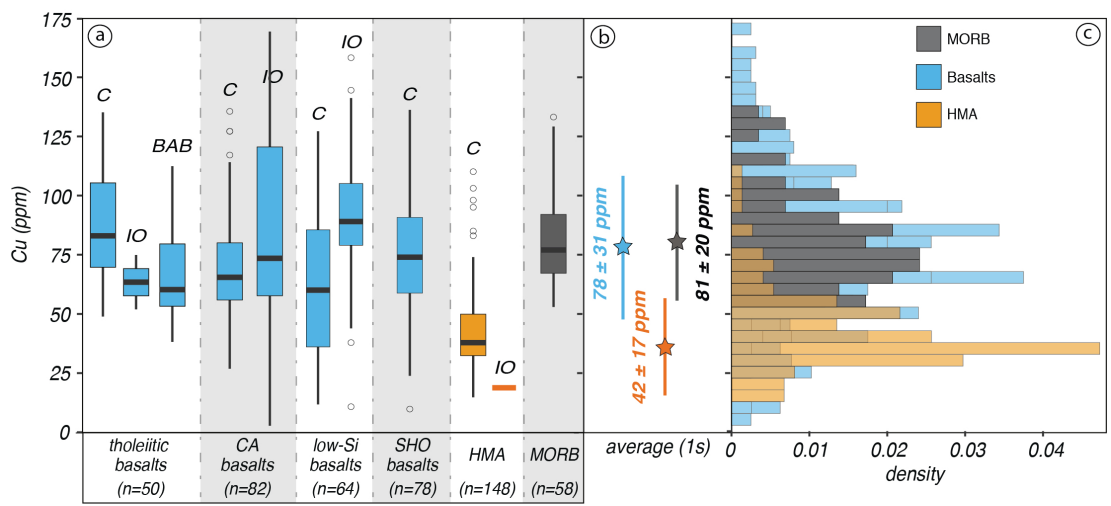


Figure 2

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55

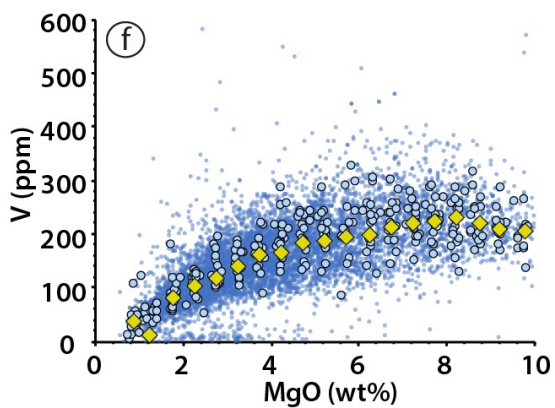
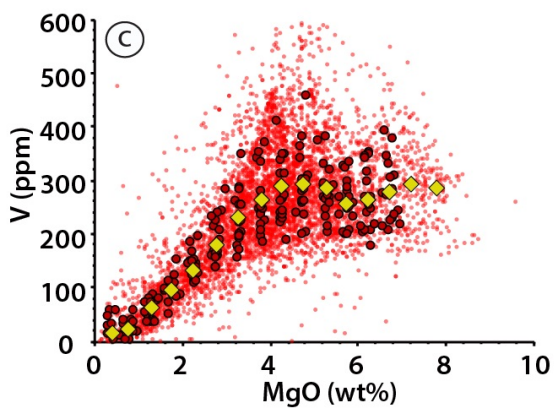
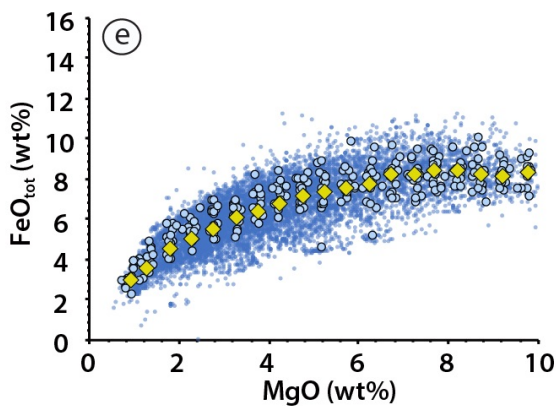
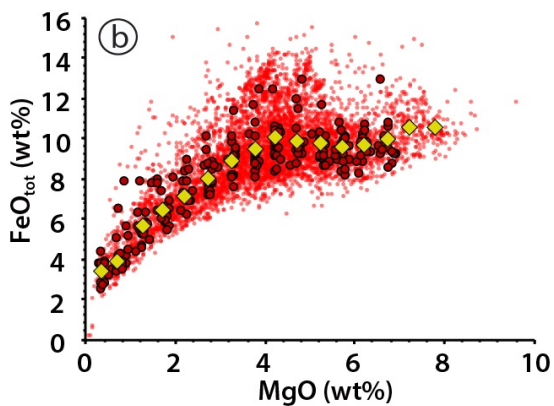
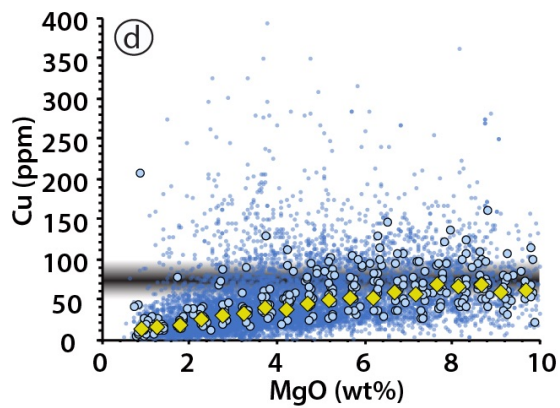
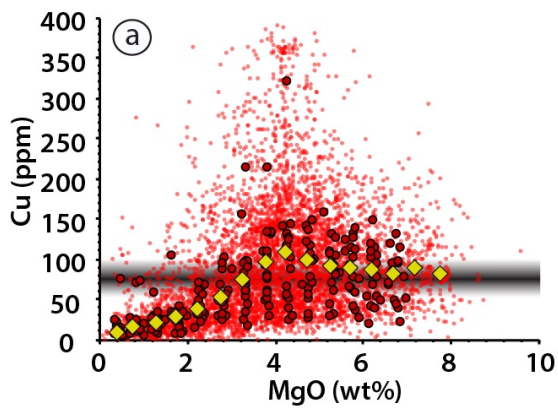


Figure 3

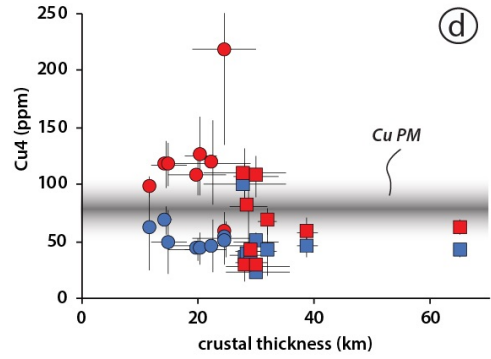
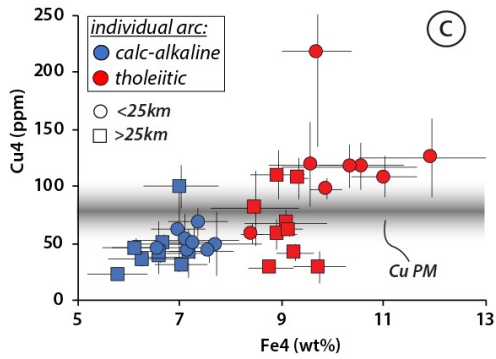
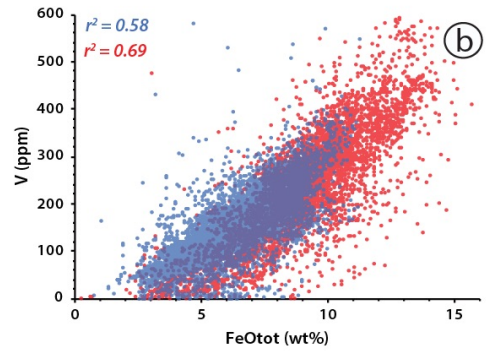
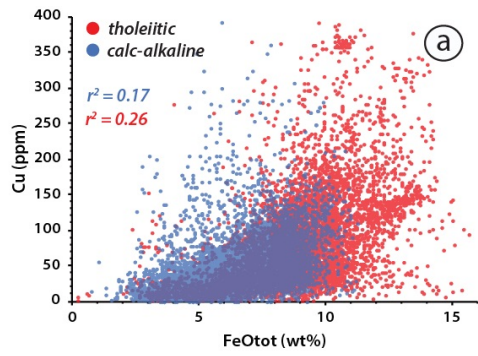


Figure 4

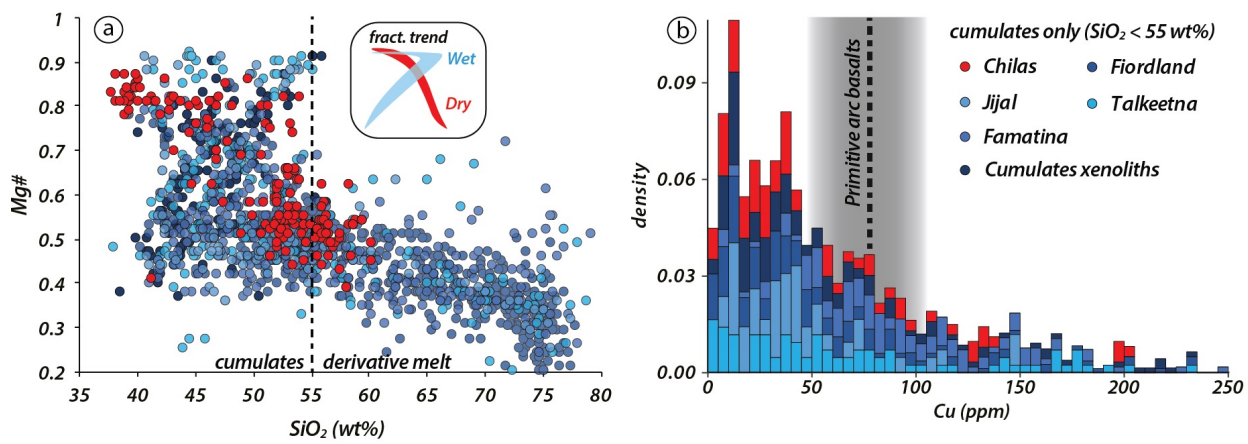
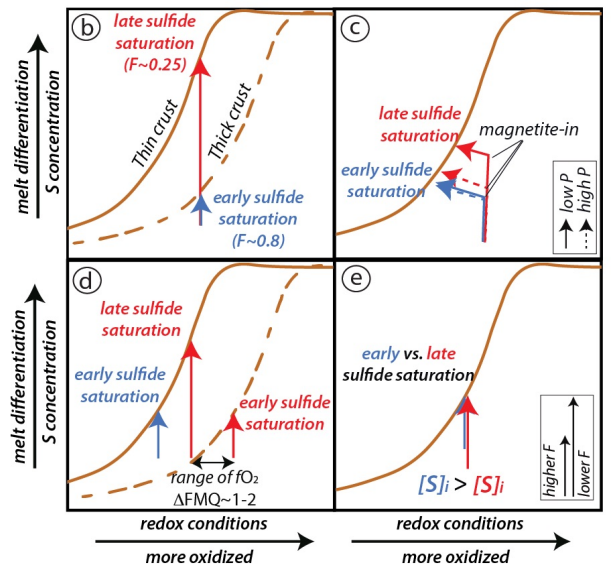
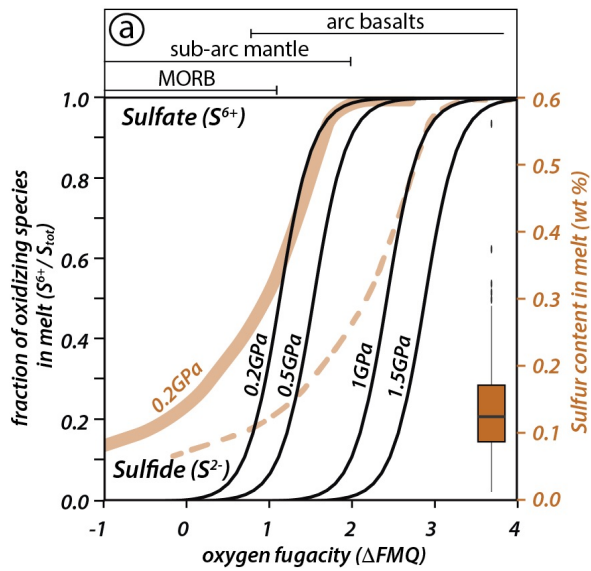


Figure 5



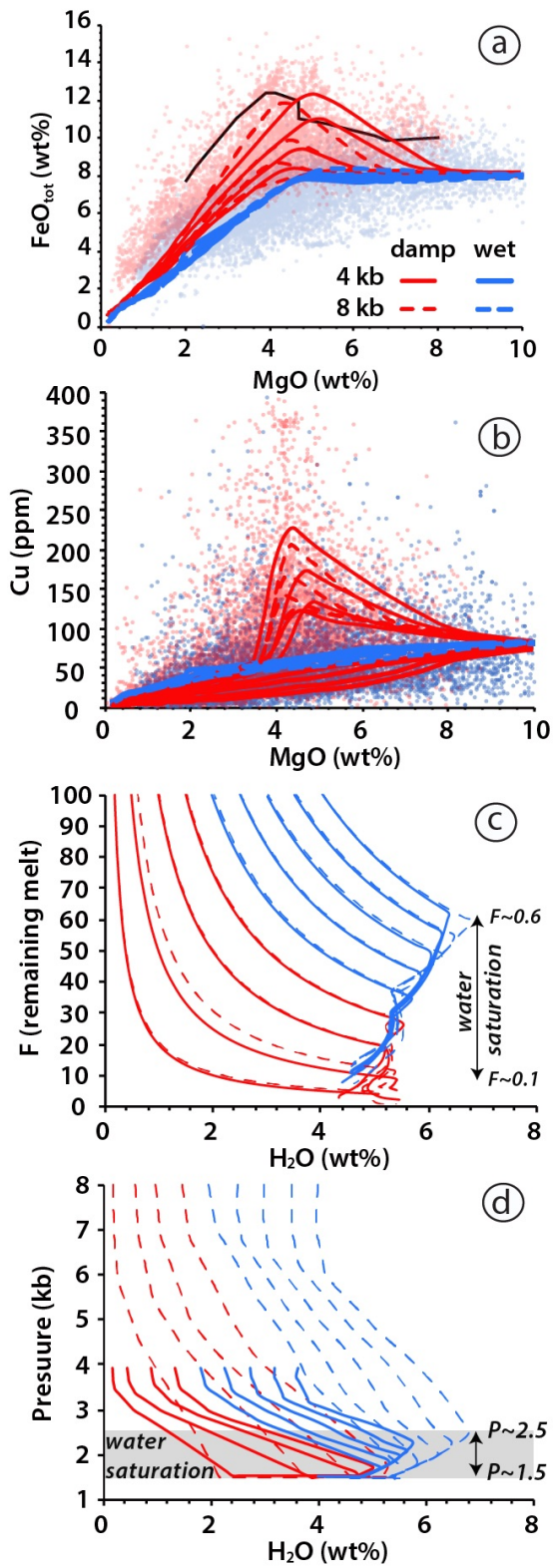


Figure 7

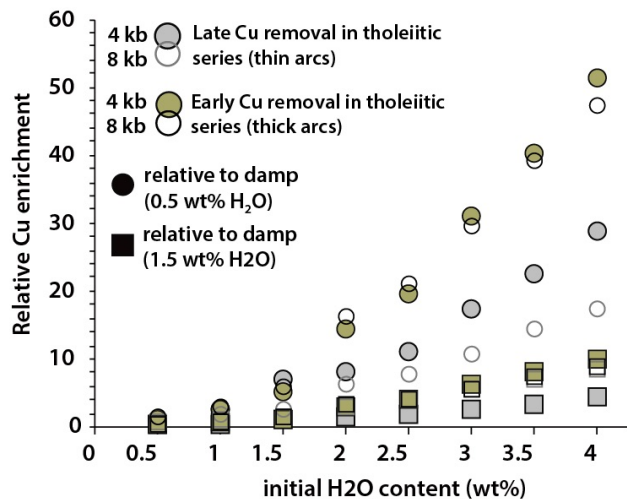


Figure 8

single stage models

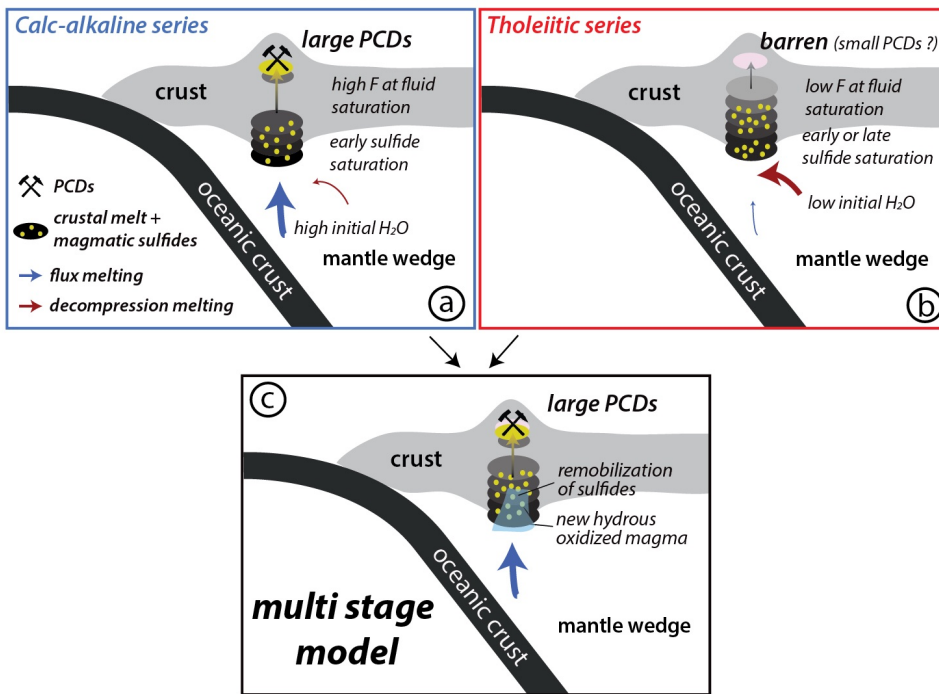


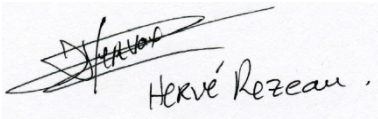
Figure 9

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

I declare that we have no competing interests.



Hervé Rozeau .

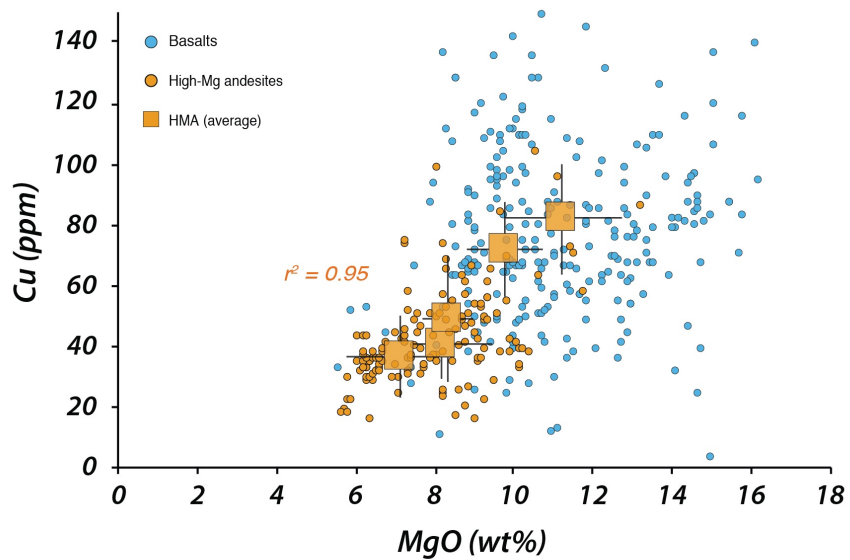


Figure A1

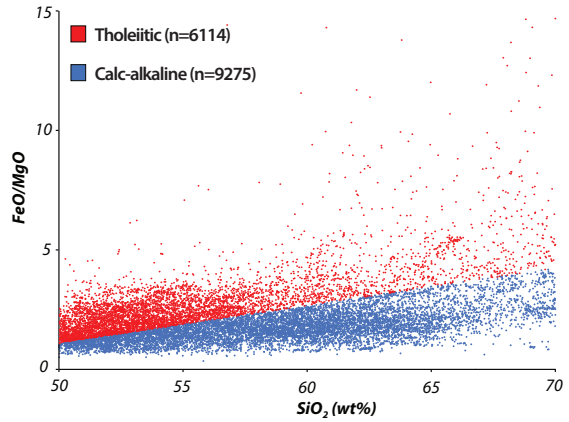
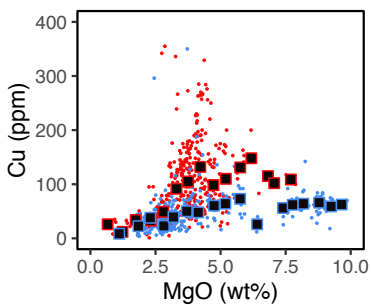
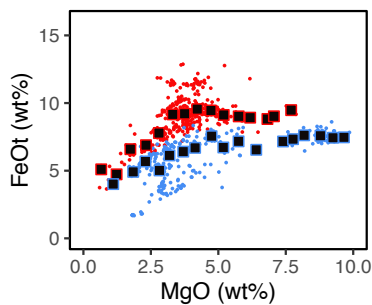


Figure A1

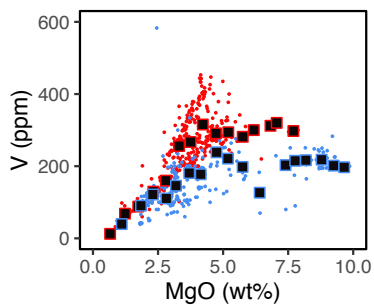
ALEUTIAN



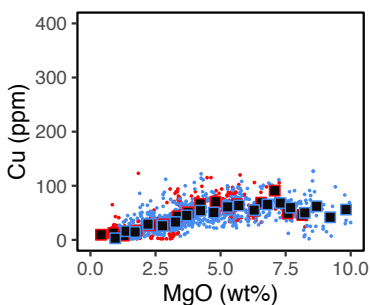
ALEUTIAN



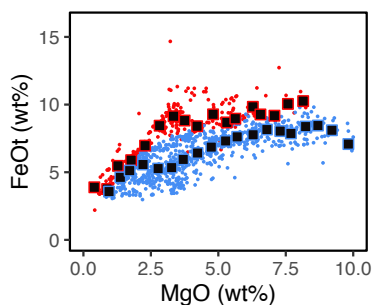
ALEUTIAN



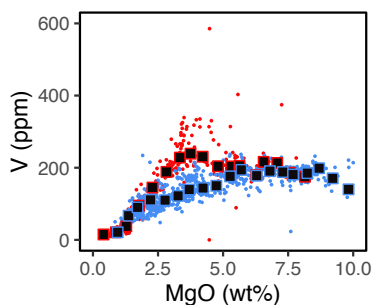
CASCADES



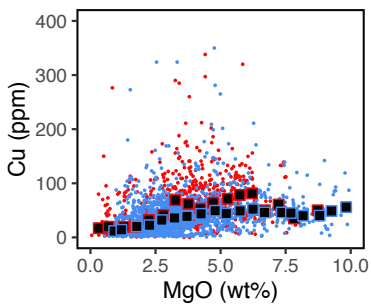
CASCADES



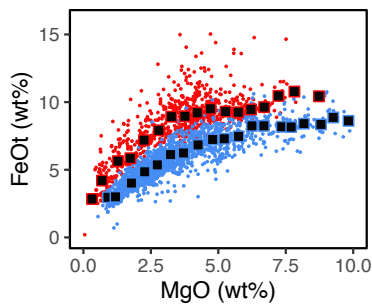
CASCADES



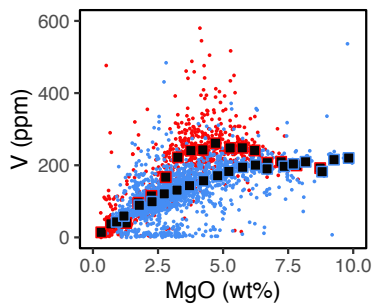
ANDEAN



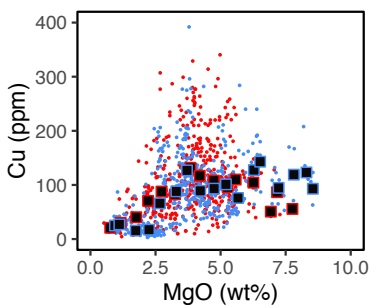
ANDEAN



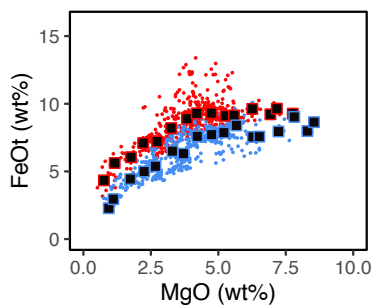
ANDEAN



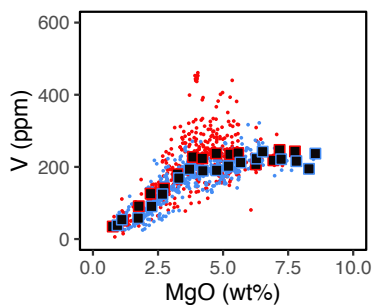
CENTRAL AMERICA

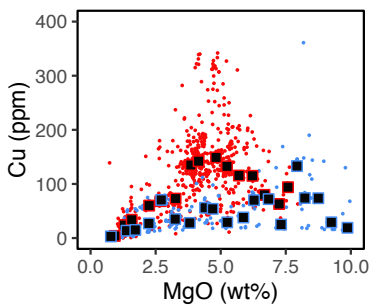
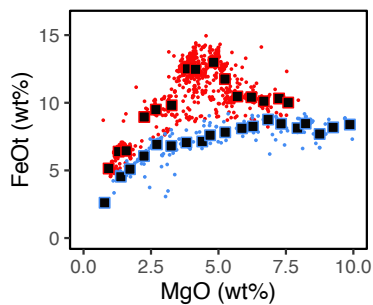
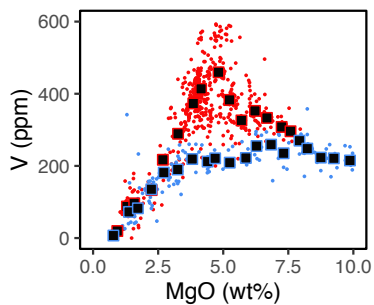
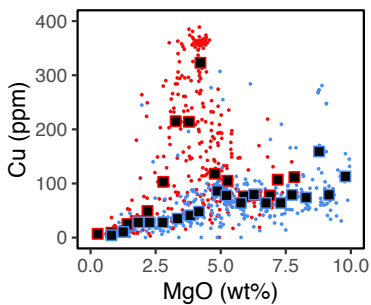
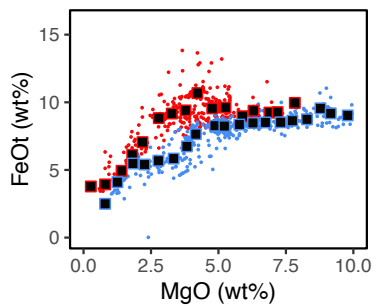
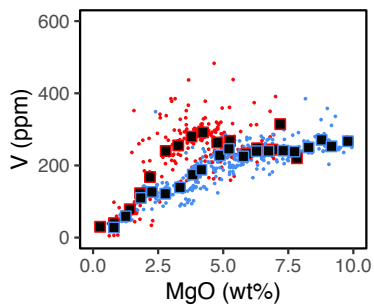
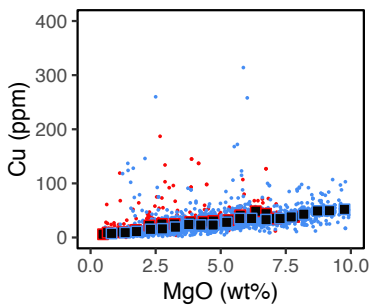
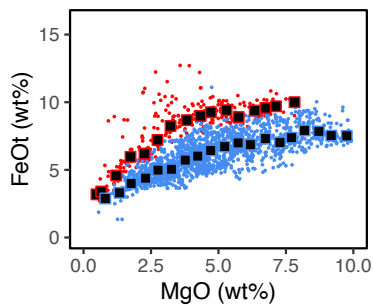
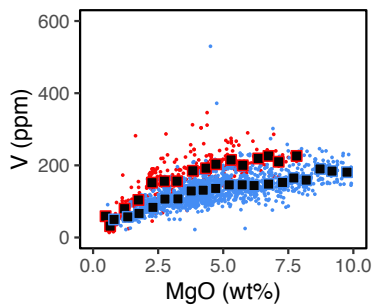
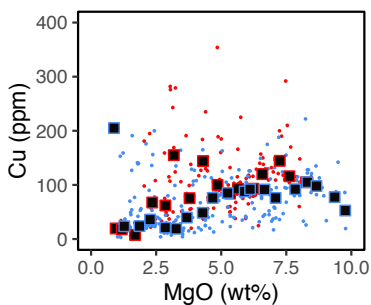
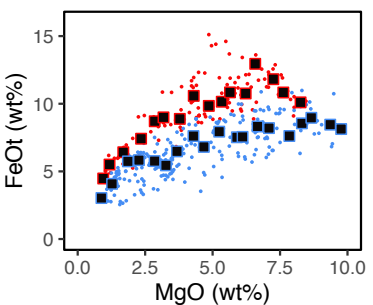
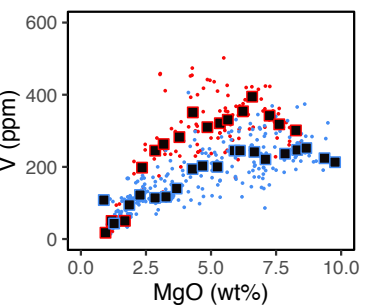


CENTRAL AMERICA

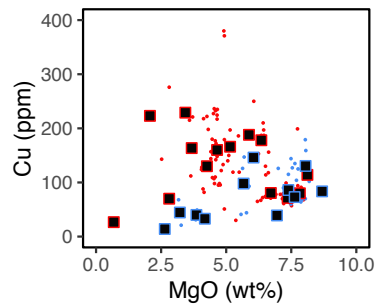


CENTRAL AMERICA

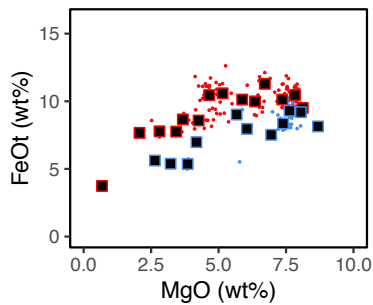


IZU BONIN**IZU BONIN****IZU BONIN****KAMCHATKA****KAMCHATKA****KAMCHATKA****MEXICO****MEXICO****MEXICO****BISMARCK****BISMARCK****BISMARCK**

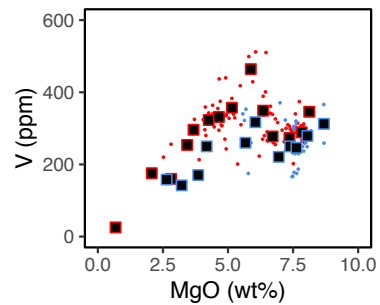
NEW HEBRIDES



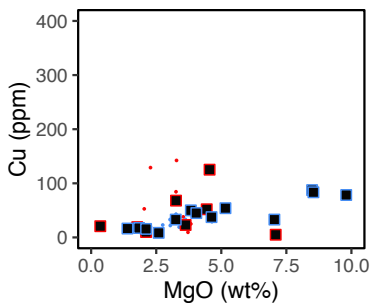
NEW HEBRIDES



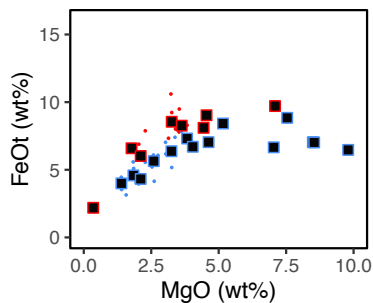
NEW HEBRIDES



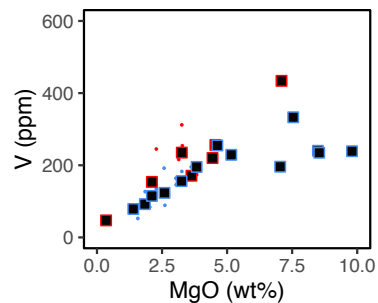
BANDA



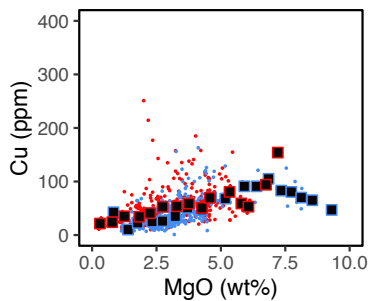
BANDA



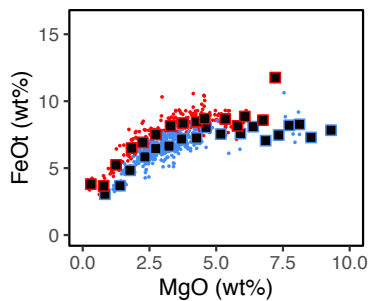
BANDA



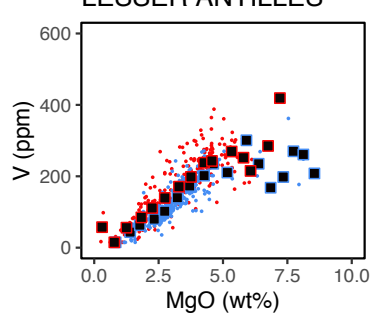
LESSER ANTILLES



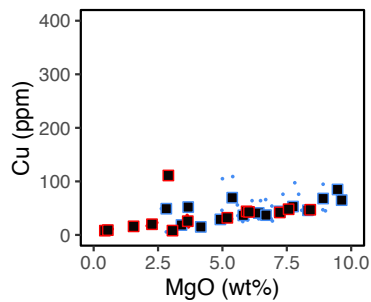
LESSER ANTILLES



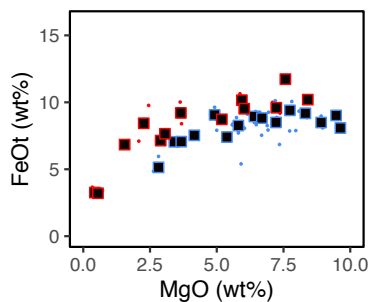
LESSER ANTILLES



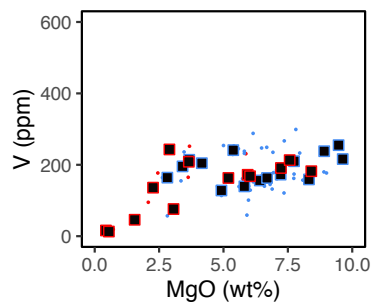
LIGURIA



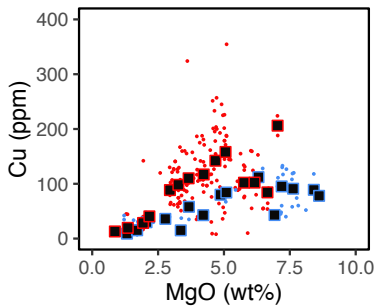
LIGURIA



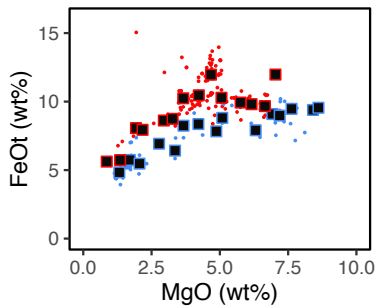
LIGURIA



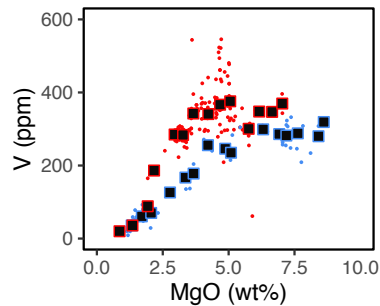
KERMADEC



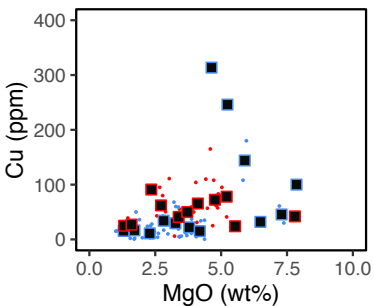
KERMADEC



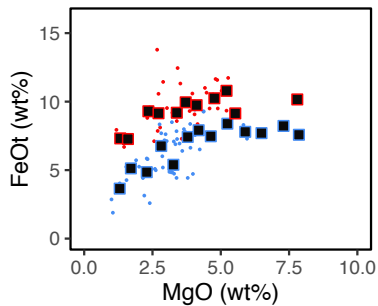
KERMADEC



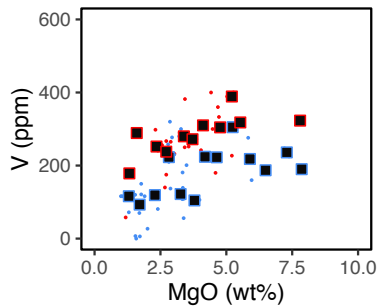
KURILE



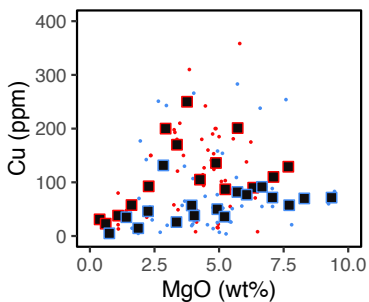
KURILE



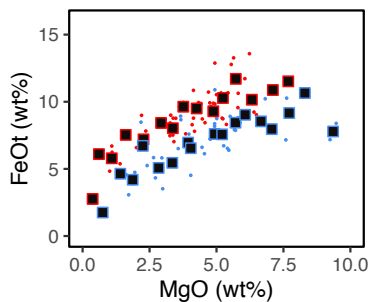
KURILE



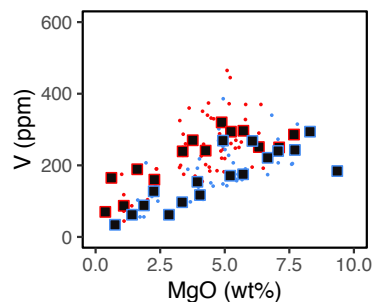
GREATER ANTILLES



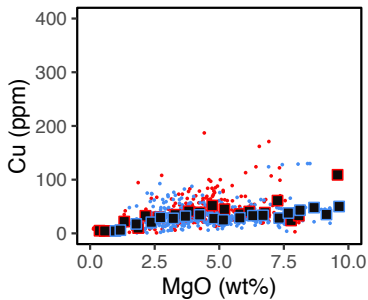
GREATER ANTILLES



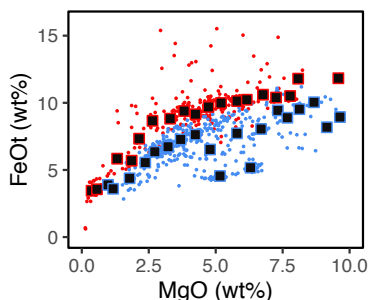
GREATER ANTILLES



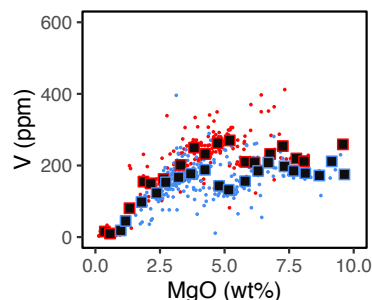
HONSHU

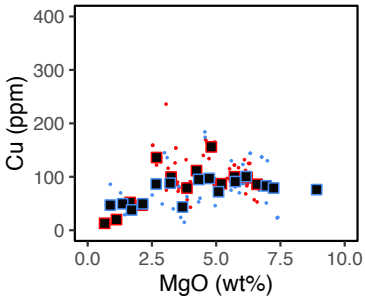
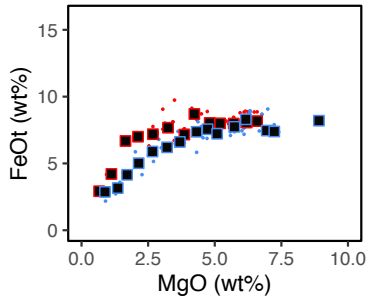
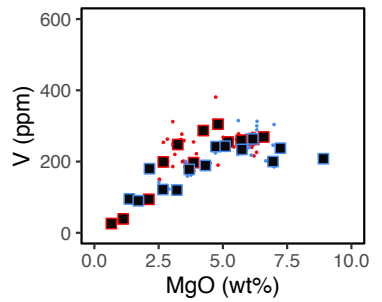
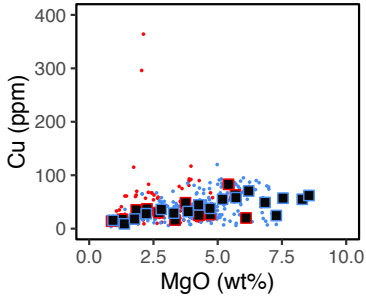
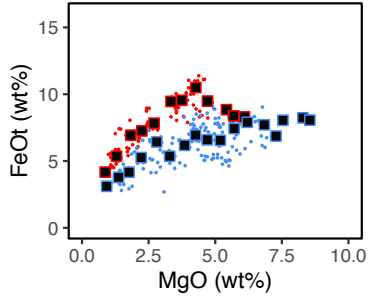
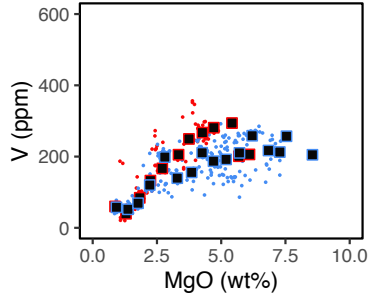
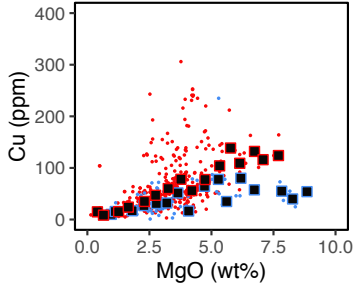
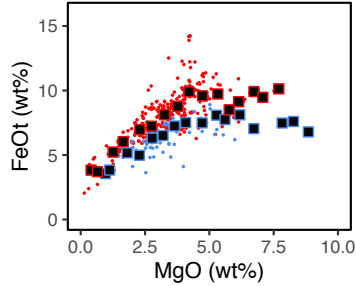
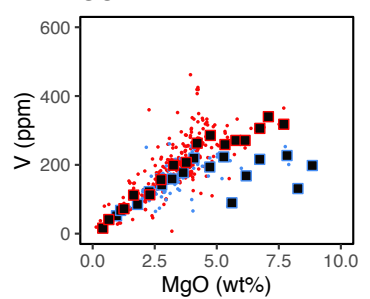
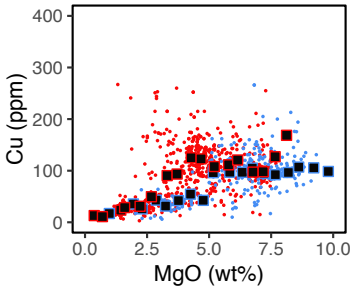
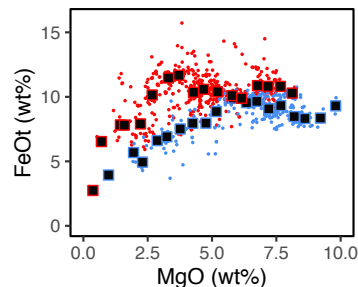
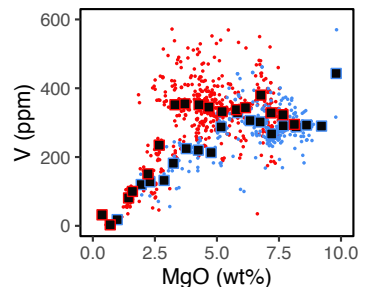


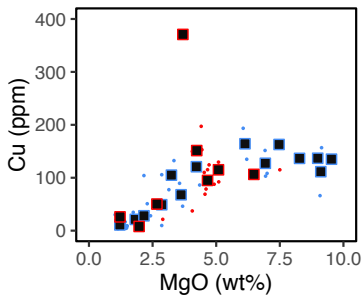
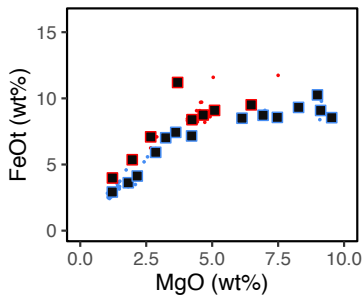
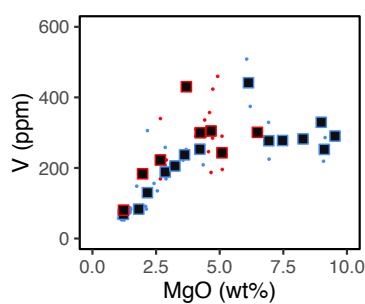
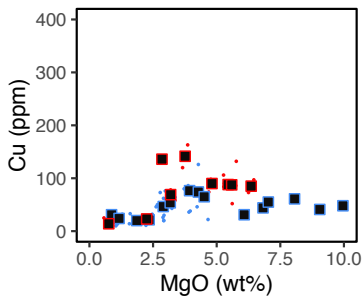
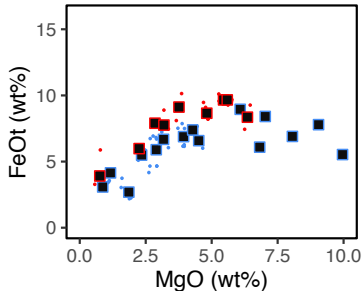
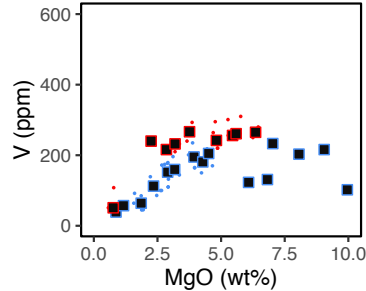
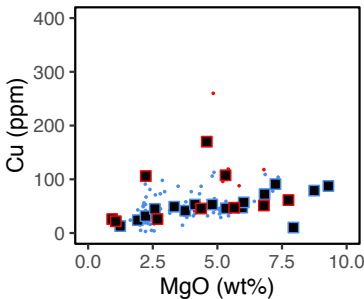
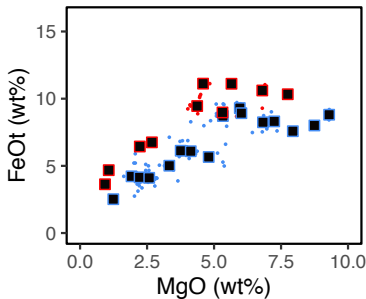
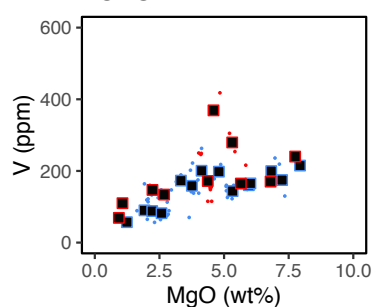
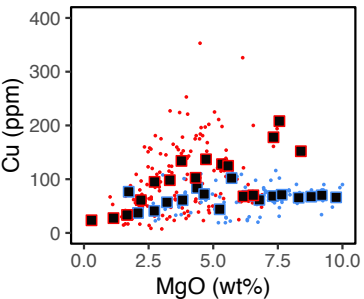
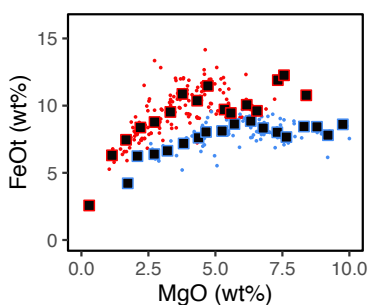
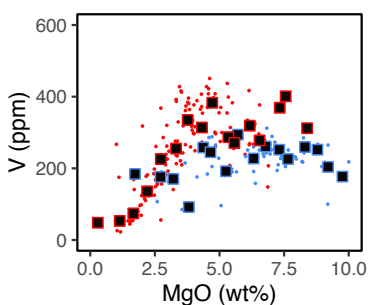
HONSHU



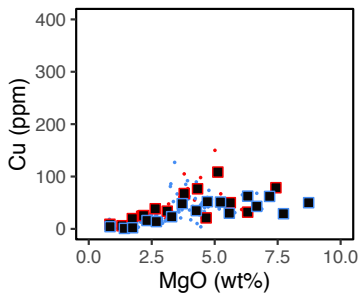
HONSHU



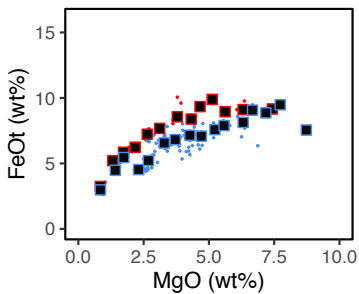
AEOLIAN**AEOLIAN****AEOLIAN****AEGEAN****AEGEAN****AEGEAN****SUNDA****SUNDA****SUNDA****TONGA****TONGA****TONGA**

SOLOMON**SOLOMON****SOLOMON****SULAWESI****SULAWESI****SULAWESI****LUZON****LUZON****LUZON****MARIANA****MARIANA****MARIANA**

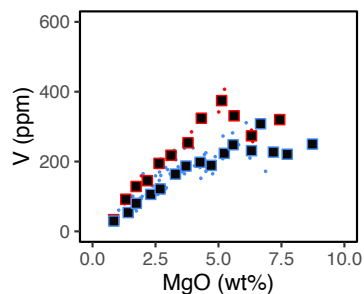
RYUKU



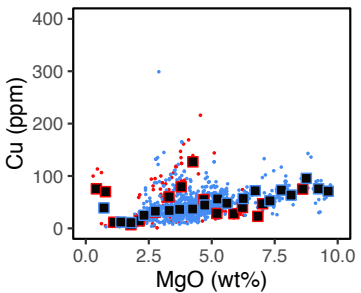
RYUKU



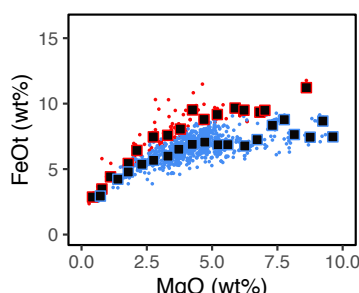
RYUKU



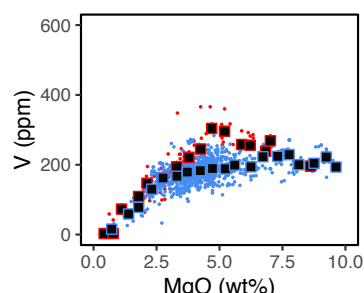
NEW ZEALAND



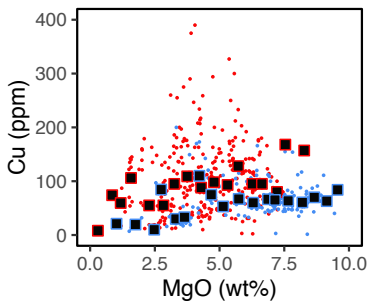
NEW ZEALAND



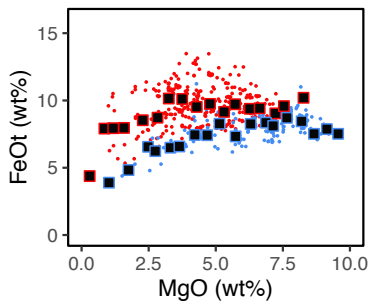
NEW ZEALAND



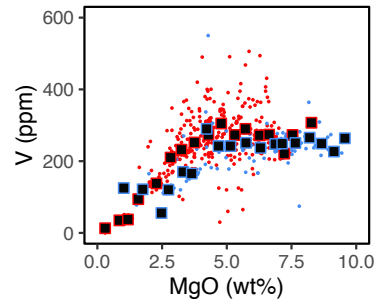
SCOTIA



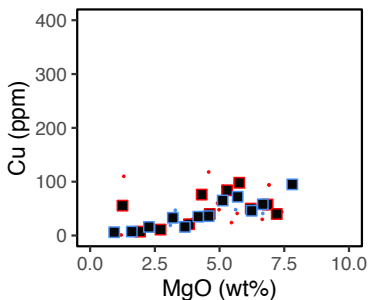
SCOTIA



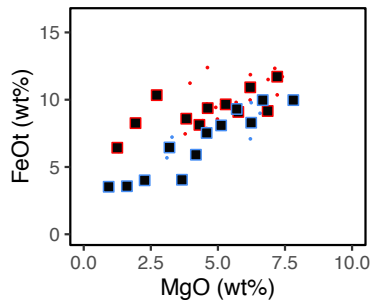
SCOTIA



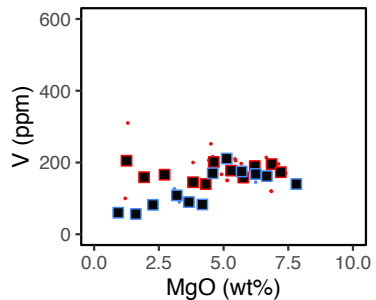
SIKHOTE

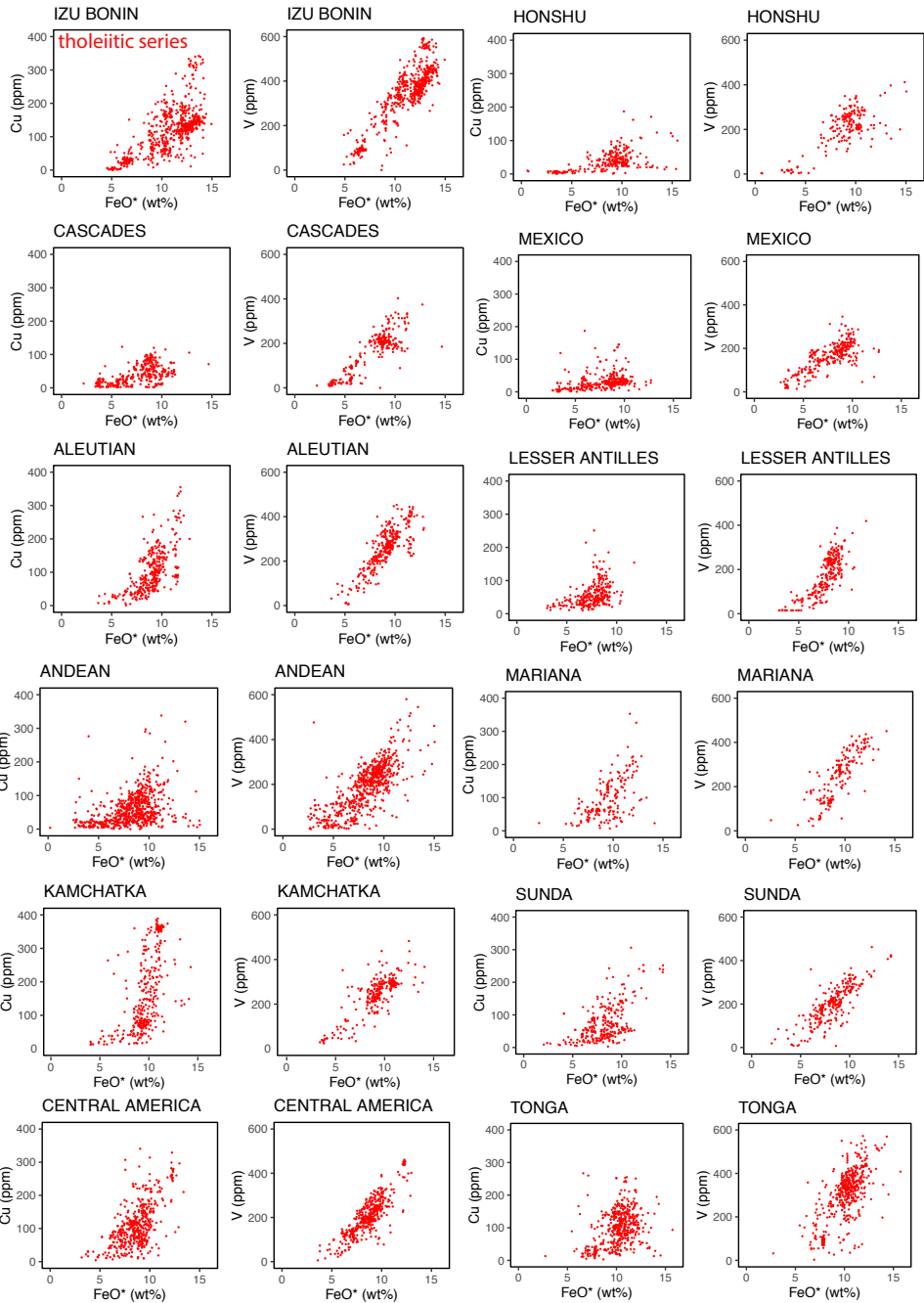


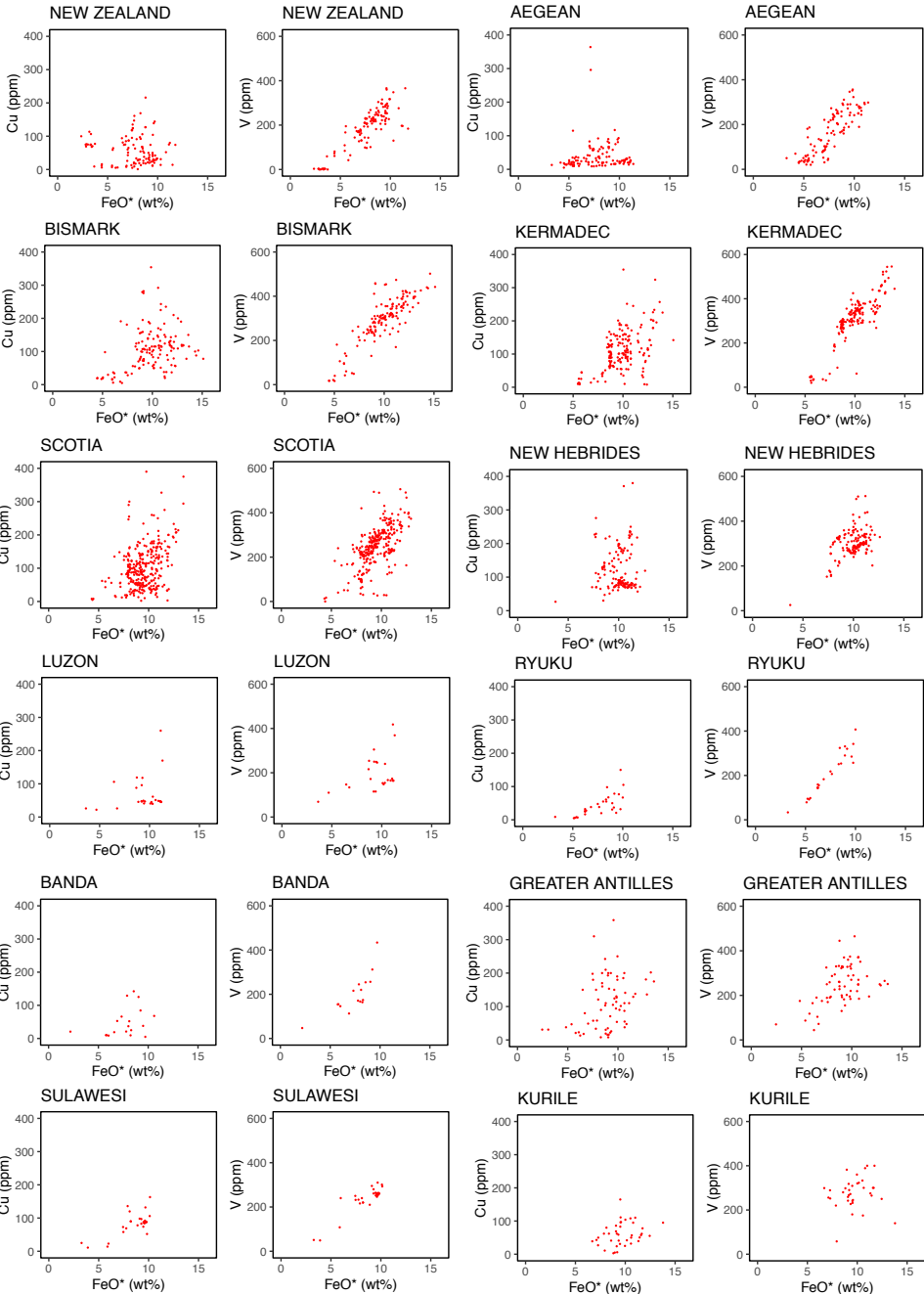
SIKHOTE



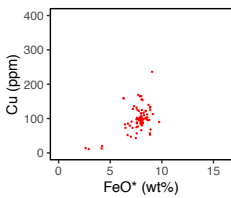
SIKHOTE



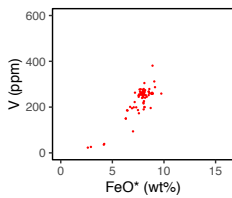




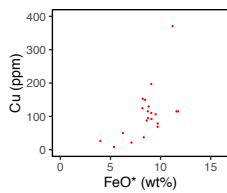
AEOLIAN



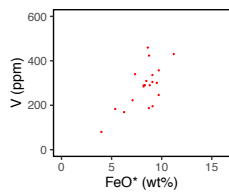
AEOLIAN



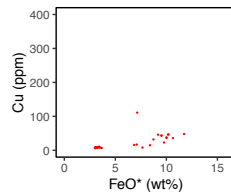
SOLOMON



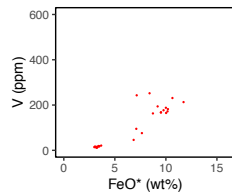
SOLOMON

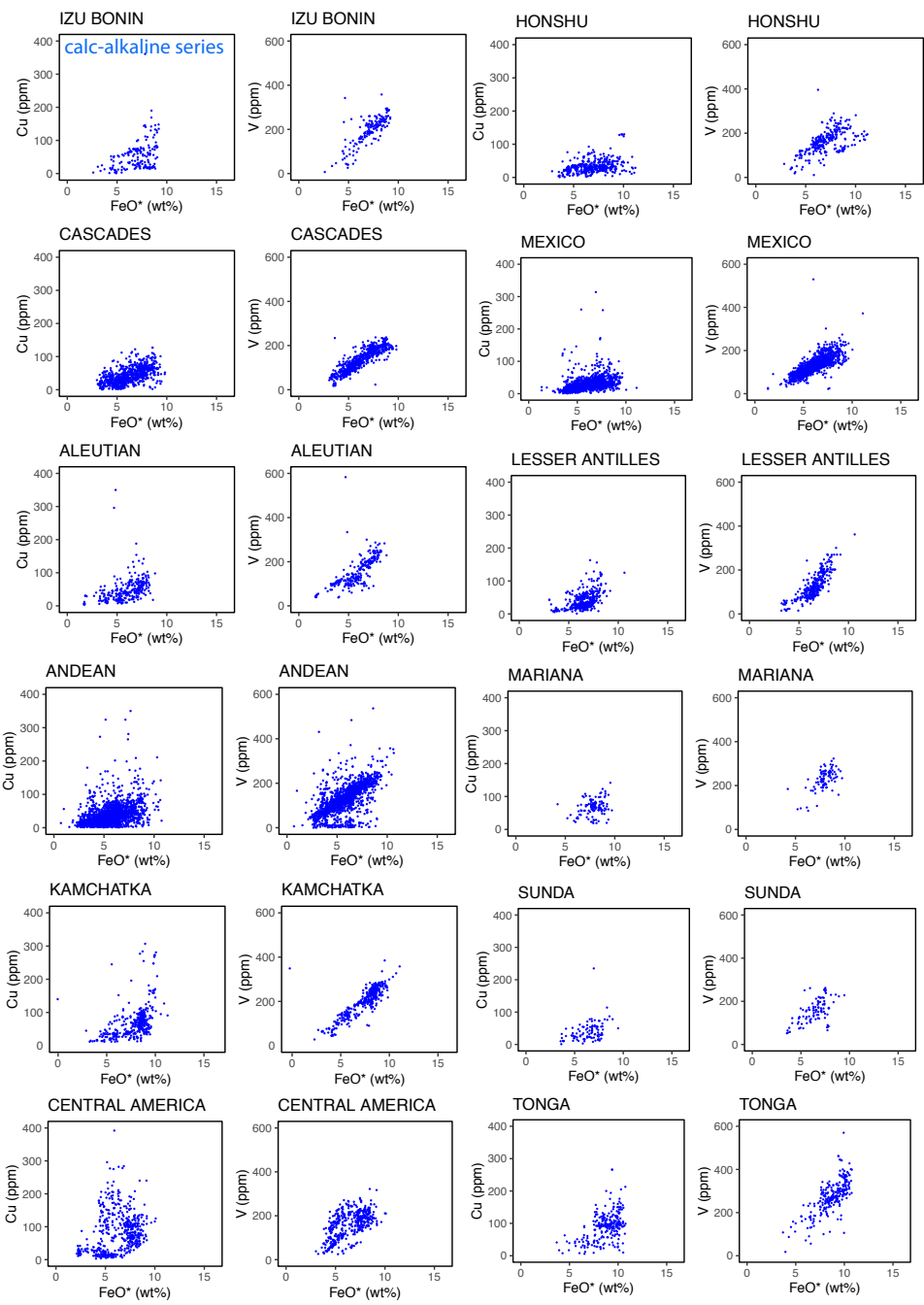


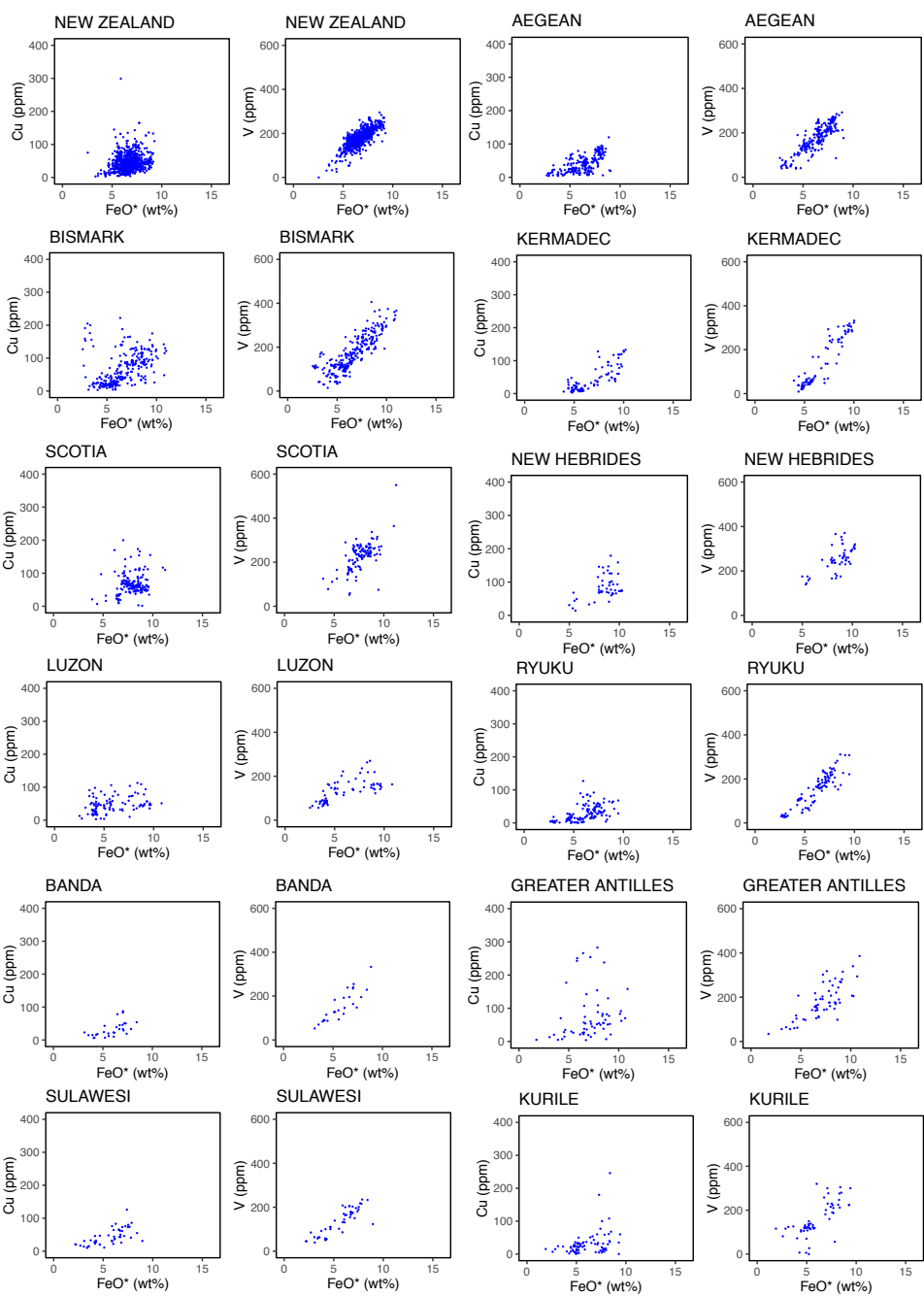
LIGURIA



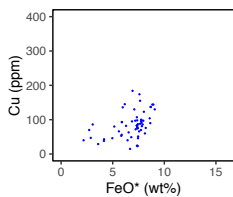
LIGURIA



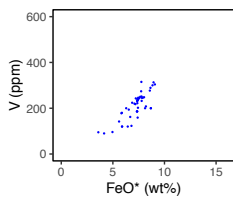




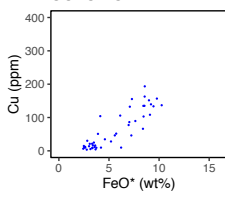
AEOLIAN



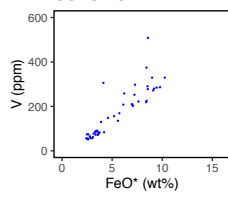
AEOLIAN



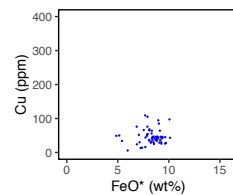
SOLOMON



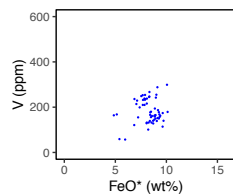
SOLOMON

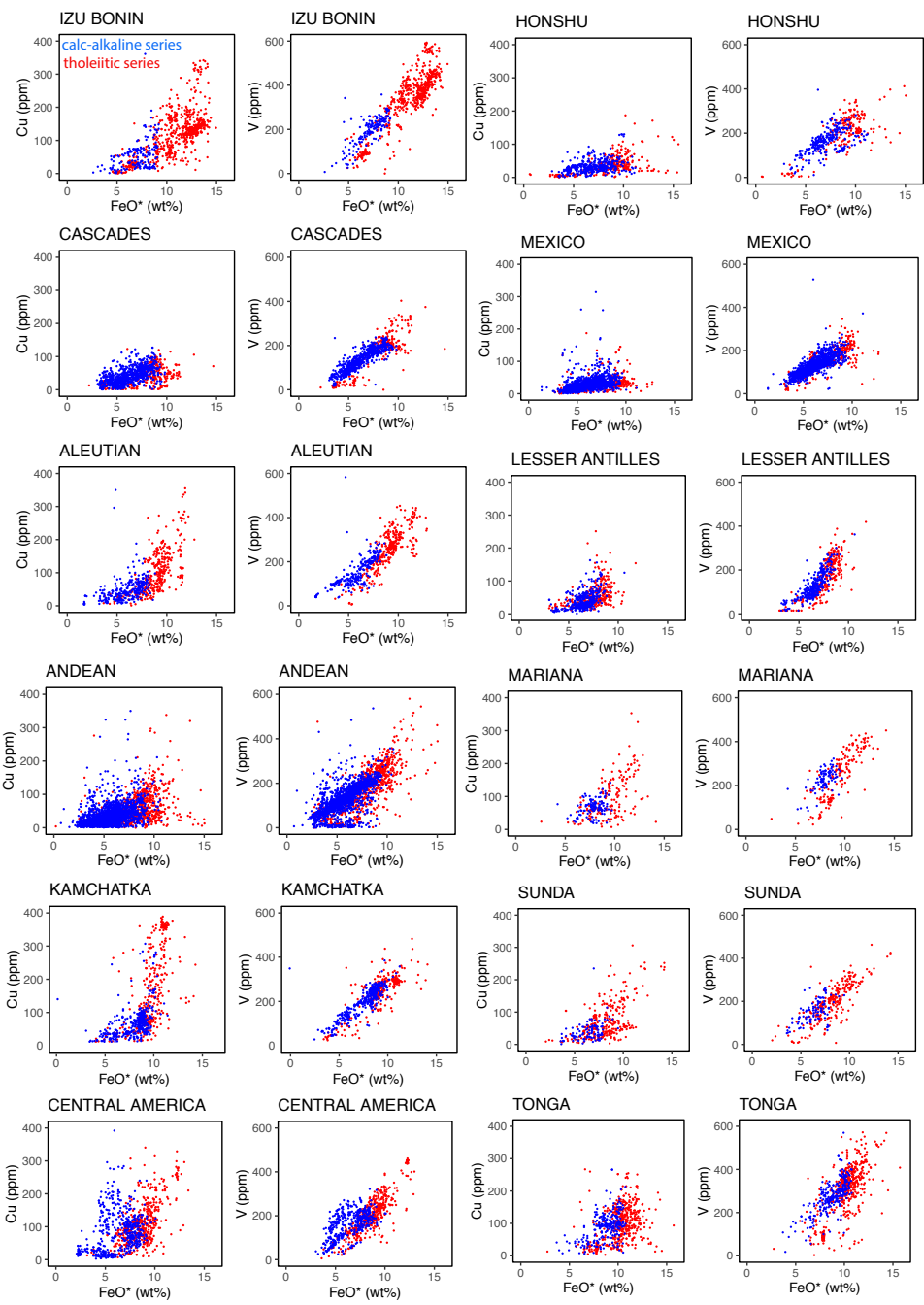


LIGURIA

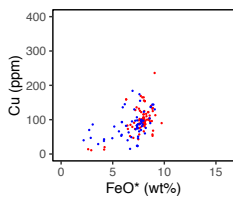


LIGURIA

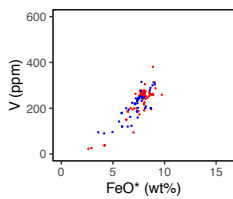




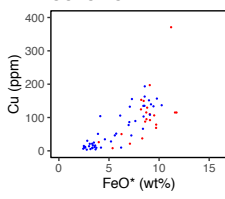
AEOLIAN



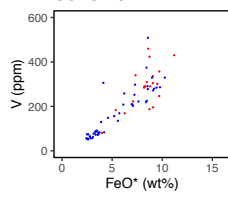
AEOLIAN



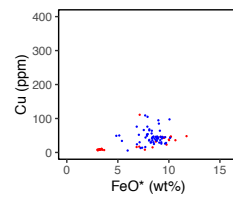
SOLOMON



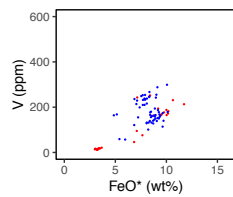
SOLOMON



LIGURIA



LIGURIA



Calculation of Cu endowment in fluid

The volume of the H₂O-saturated melt (V_{ini}) corresponds to the melt fraction at which an initial volume of magma (V_0) reached H₂O saturation (F_{ini})

$$V_{ini}^{melt} = V_0^{melt} * F_{ini}$$

Where V_0 is the initial volume of magma based on an average arc magma production rate of 189 km³ km⁻¹ Myr⁻¹ in intra-oceanic arcs (Jicha and Jagoutz, 2015) and F_{ini} is determined from the Rhyolite-MELT modeling (Table. D1). The remaining melt fraction of H₂O-saturated melt at degassing depends on the H₂O dissolved in the melt (W), the percolation threshold (ϕ_c), and the density of melt (d_{melt}) and fluid (d_{fluid}):

$$F_{degas} = \frac{W}{d_{fluid}} / \left(\frac{\phi_c}{d_{melt} (1 - \phi_c)} + \frac{W}{d_{fluid}} \right)$$

Where, the percolation threshold (Φ_c) correspond to the critical porosity at which the transition from an impermeable to permeable magma allowing degassing occurs and fixed at 0.3 based on percolation theory for overlapping spheres that predict $\Phi_c \sim 0.28-0.35$ (Walsh and Saar, 2008; Vasseur and Wadsworth, 2017), W and density (Mt/km³) of melt and fluid are obtained from the Rhyolite-MELT modeling (Table. D1).

The volume (km³) of H₂O-saturated melt and fluid at degassing corresponds to

$$V_{degas}^{melt} = V_{ini}^{melt} * F_{degas}$$

$$V_{degas}^{fluid} = V_{ini}^{melt} * W * (F_{n-1} - F_{degas}) \frac{d_{melt}}{d_{fluid}}$$

where $F_{n-1}=1$.

The concentration of Cu (wt%) in the melt and fluid at degassing corresponds to

$$C_{Cu}^{melt} = \frac{C_{Cuini}^{melt}}{D_{Cu} + F_{degas} (1 - D_{Cu})}$$

$$D_{Cu} = D_{Cu}^{crystals/melt}(1 - W) + D_{fluid/melt}^{Cu} W$$

$$C_{Cu}^{fluid} = C_{Cu}^{melt} * D_{Cu}^{fluid/melt}$$

Where C_{Cu}^{melt} is the melt copper content at fluid saturation obtained from the Rhyolite-MELT modeling (Table D1), $D_{Cu}^{crystals/melt}$ and $D_{Cu}^{fluid/melt}$ are the partition coefficient of Cu between fractionated phases (silicates, oxides, phosphates, sulfide) or fluid with respect to the melt. $D_{Cu}^{crystals/melt} = 2.1$ corresponds to the one used in the Rayleigh fractionation model (Table D1), whereas $D_{Cu}^{fluid/melt} = 140$ (Tattitch and Blundy, 2017).

The mass (Mt) of Cu transferred in expelled fluids corresponds to

$$m_{Cu}^{fluid} = V_{degas}^{fluid} * d_{fluid} * C_{Cu}^{fluid}$$

References

- Chelle-Michou, C., Rottier, B., Caricchi, L., Simpson, G., 2017. Tempo of magma degassing and the genesis of porphyry copper deposits. *Sci. Rep.* 7, 40566.
- Jicha, B. R., Jagoutz, O., 2015. Magma production rates for intraoceanic arcs. *Elements* 11, 105-111.
- Kouzmanov, K., Pokrovski, G. S., 2012. Hydrothermal controls on metal distribution in porphyry Cu(-Au-Mo) systems. *Society of Economic Geologists*, Special Publication 16, 573-618.
- Tattitch, B. C., Blundy, J. D., 2017. Cu-Mo partitioning between felsic melts and saline-aqueous fluids as a function of X_{NaCl} , f_{O_2} , and f_{S_2} . *Am. Miner.* 102, 1987-2006.
- Vasseur, J., Wadsworth, F. B., 2017. Sphere models for pore geometry and fluid permeability in heterogeneous magmas. *Bull. Volcanol.* 79, 77.
- Walsh, S. D., and Saar, M. O. 2008. Magma yield stress and permeability: Insights from multiphase percolation theory. *Volcanol. Geotherm. Res.* 177, 1011-1019.