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1 **Cumulate Causes for the Low Contents of Sulfide-loving**
2 **Elements in the Continental Crust**

3
4 Frances Elaine Jenner^{1,2}

5
6 *¹School of Environment, Earth and Ecosystem Sciences, The Open University, Walton Hall,*
7 *Milton Keynes, Buckinghamshire, MK7 6AA.*

8
9 *²Carnegie Institution for Science, Department of Terrestrial Magnetism, Washington DC*
10 *20015-1305, U.S.A.*

11
12 *Corresponding author: frances.jenner@open.ac.uk

13 *Phone: +44(0)1908 654334.*

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23 Despite their economic importance, surprisingly little is known about the
24 magmatic processes that cause the continental crust to become enriched in some
25 chalcophile (sulfide-loving) and siderophile (metal-loving) elements (CSE) and
26 depleted in others compared to the oceanic crust. This is in part due to limited
27 understanding of the partitioning of the CSE by both sulfide and non-sulfide
28 minerals. Using published datasets for global mid-ocean ridge basalts (MORB)
29 and subduction-related volcanic rocks, I show that mantle-derived melts
30 contributing to oceanic and continental crust formation rarely avoid sulfide-
31 saturation during cooling in the crust and, on average, subduction-zone magmas
32 fractionate sulfide at the base of the continental crust prior to ascent.
33 Differentiation of mantle-derived melts enriches lower crustal sulfide- and
34 silicate-bearing cumulates in some CSE compared to the upper crust. This
35 ‘storage’ predisposes the cumulate-hosted compatible CSE (e.g., Cu and Au) to
36 be recycled back into the mantle during subduction and delamination, resulting
37 in their low contents in the bulk continental crust and potentially contributing to
38 the scarcity of ore deposits in the upper continental crust. By contrast,
39 differentiation causes the upper oceanic and continental crust to become
40 enriched in ‘incompatible’ CSE (e.g., W) compared to the lower oceanic and
41 continental crust. Consequently, incompatible CSE are predisposed to become
42 enriched in subduction-zone magmas that contribute to continental crust
43 formation and are less susceptible to removal from the continental crust via
44 delamination compared to the compatible CSE.

45 Chalcophile and siderophile element (CSE) systematics of magmatic rocks can be
46 used to place constraints on a range of processes and parameters including the
47 evolution of the Earth’s mantle and crust, delamination, subduction, mantle redox and

48 the formation of ore deposits¹⁻¹⁰. Many of these constraints rely on knowledge of the
49 minerals partitioning the CSE and comparisons between the compositions of
50 subduction-zone magmas and MORB^{11, 12}. Ratios in average-MORB ('normal' (N)-
51 MORB) can be used to derive estimates of the composition of the MORB-source
52 depleted mantle⁹ and the primitive mantle¹, which are also important to comparative
53 geochemistry.

54 Because the contents of many CSE are hard to analyse accurately in rocks and
55 minerals¹³, compositions and ratios used for comparative geochemistry are often
56 based on scant datasets and/or relatively untested proxies^{4, 12, 14-16}. Consequently, there
57 remains a lack of consensus regarding which CSE are mobile during subduction and
58 whether the low [Cu] (where the brackets denote concentrations) of evolved
59 subduction-related magmas and the bulk continental crust can be attributed to sulfide
60 fractionation^{7, 8, 17}, accumulation and subsequent delamination² or alternatively, to
61 partitioning into exsolving fluids^{6, 18}. An added problem is that the CSE show a large
62 range in sulfide-silicate partition coefficients ($D^{sulf/sil}$) and many CSE partition into
63 non-sulfide minerals^{19, 20}, making CSE behaviour during magmatic processes difficult
64 to predict.

65 Using published datasets for natural and experimental materials^{7, 8, 19-31}, I show
66 that N-MORB values and certain ratios used for comparative geochemistry can be
67 misleading, because they do not sufficiently separate between mantle and crustal
68 processes. Both silicate and sulfide minerals host the CSE, so it is the bulk partition
69 coefficients (bulk-D) of the combined fractionating phases that determine the
70 concentration of the CSE in both the cumulates and fractionated liquids produced by
71 magmatic differentiation. The CSE hosted in the lower oceanic and continental crust
72 are recycled back into the mantle during subduction and delamination more efficiently

73 than the incompatible CSE that are enriched in the upper oceanic and continental
74 crust. Hence, differentiation of both MORB and subduction-related magmas plays a
75 role in determining the CSE composition of the mature continental crust.

76 **OCEANIC CRUST**

77 Average and log-normal mean distributions of elements in global MORB and
78 various ratios are used to derive average-MORB and N-MORB estimates^{11, 12}.
79 However, the [MgO] of average-MORB (7.6 wt.%¹¹) is lower than the bulk oceanic
80 crust (≥ 10 wt.%)³². Lower oceanic crust cumulates (14.5 wt.% MgO³²) are the
81 complementary products to the evolved basalts of the upper oceanic crust. Hence,
82 average-MORB does not reflect the integrated composition of the bulk oceanic crust
83 required for comparative geochemistry, which should correspond to the composition
84 of parental-MORB prior to differentiation.

85 The composition of parental-MORB and the upper/lower oceanic crust
86 distributions of the CSE are estimated as follows. Expanding on previous studies^{33,34},
87 the least-squares fit line between the log-mean content of a given element (M) versus
88 [MgO] in MORB glasses (see Fig. 1), together with the [MgO] of the bulk oceanic
89 crust (10.0 wt.%) and average-MORB (7.6 wt.%) are used to derive the composition
90 of average parental-MORB and evolved-MORB, respectively (Fig. 1, 2, Methods and
91 Supplementary Table 1). The relationship between the slope of the best-fit line
92 between individual CSE and [MgO] and the differences in compositions of evolved-
93 MORB and parental-MORB are used to establish the relative bulk-D of the CSE
94 during differentiation and the upper/lower oceanic crust distribution of CSE (Fig. 2a).
95 For example, lithophile (silicate-loving) elements such as Co and Sc vary consistently
96 with their bulk partition coefficients³³: Co (bulk-D=1.1) becomes slightly depleted
97 (slope <0), while Sc (bulk-D=0.89) becomes slightly enriched (slope >0) in the melt

98 during MORB differentiation (Fig. 2a). Similarly, because the slope for chalcophile
99 element Cu is positive (Fig. 1), the [Cu] of evolved-MORB (77 ppm) is significantly
100 lower than parental-MORB (115 ppm). Copper is highly chalcophile²², therefore
101 sulfide-bearing lower oceanic crust cumulates must have higher [Cu] than parental-
102 MORB and the upper oceanic crust³⁵. Thus, the upper oceanic crust is enriched in
103 incompatible CSE (slope <0), whereas the lower oceanic crust is enriched in
104 compatible elements CSE (slope >0).

105 Evolved-MORB and N-MORB (log-normal mean MORB) is enriched in
106 incompatible elements and depleted in compatible elements compared to parental-
107 MORB (Fig. 2a). This degree of elemental fractionation (e.g., elevated La/Sm) cannot
108 be achieved via simple fractional crystallization and is attributable to magma chamber
109 recharge^{33, 34}. Hence, various proxies (e.g., Supplementary Table 1) used to derive
110 representative CSE estimates for N-MORB¹², the depleted⁹ and primitive mantle¹
111 (e.g., Bi/Pb, Se/V, Rb/Tl), as redox proxies (e.g., V/Sc³), and/or as subduction tracers
112 (e.g., Cs/Tl³¹, Bi/Nd⁶), should be replaced by ratios between elements with more
113 comparable slopes (e.g., V/In instead of V/Sc). Consequently, parental-MORB is used
114 as the normalising composition in the following discussion, as this composition
115 provides a truer comparison between the fluxes from mantle-to-crust in different
116 environments than N-MORB.

117 **AFFINITIES OF THE CSE**

118 The lithophile, chalcophile and siderophile affinities of many CSE during
119 magmatic processes remain debated^{4, 14}. The slopes (relative bulk-D) can be compared
120 with available $D^{sulf/sil}$ (Fig. 2) to place new constraints on the partitioning of the
121 CSE during magmatic processes. For example, though Ge, Mn, Ga and Se have
122 comparable bulk-Ds, $D^{sulf/sil}$ of Ge, Mn, Ga are significantly lower than Se (Fig.

123 2b), implying silicates, not sulfides, dominate the partitioning of Ge, Mn and Ga.
124 Using the CSE with the highest $D^{sulf/sil}$ at a given slope (Cu \approx Ag>Se>Bi>Pb>Tl) as
125 an approximation of the end-member ‘purely chalcophile’ trend, the partitioning of
126 the majority of CSE during MORB differentiation and probably, mantle melting¹⁹, is
127 either dominated or in part controlled by silicates and/or oxides. These elements are
128 classified here as having ‘mixed-affinity’ (Fig. 2b).

129 The question remains as to whether sulfide is molten or crystalline in the mantle,
130 which can be investigated by exploiting differences in the partitioning of CSE during
131 the petrogenesis of MORB^{24, 36}. Sulfide-melt has similar $D^{sulf/sil}$ for Cu and Ag (Fig.
132 2), whereas crystalline-sulfide (e.g., chalcopyrite, Fig. 3) and silicates favour Cu over
133 Ag^{24, 37}. The constant Cu/Ag of MORB with decreasing [MgO] (Fig. 3a) is
134 attributable to sulfide-melt fractionation^{8, 22}. The presence of crystalline-sulfide²⁴, or
135 the absence of sulfide in the mantle, should manifest as Cu/Ag variability in mantle-
136 derived melts. However, the Cu/Ag of MORB varies by only 11%. Put into context,
137 this is less variation than traditional canonical ratios Nb/U (16%) and Ce/Pb (17%)
138 and approaches that of Zr/Hf (8%) and Nb/Ta (7%). The overlapping Cu/Ag of
139 MORB, mantle xenoliths³⁸ and oceanic island basalts (Fig. 3) supports experimental
140 studies predicting mantle sulfide is molten and is residual during melting³⁶.

141 **SLAB VERSUS WEDGE COMPONENTS**

142 The key difference between the petrogenesis of MORB and subduction-zone
143 magmas is the introduction of extra components derived from the subducting slab. N-
144 MORB-normalised plots and various ratios are commonly used to distinguish between
145 slab (e.g., large ion lithophile elements, LILE) versus mantle wedge (e.g., high field
146 strength elements, HFSE) contributions to subduction-zone magmas^{30, 39}.
147 Corresponding enrichments and depletions in the parental-MORB-normalized

148 patterns of subduction-zone magmas and the bulk continental crust (Fig. 4), testify to
149 the importance of subduction-related magmatism in contributing to continental crust
150 formation²⁶.

151 Island arc magmas are often highly evolved and crystalline^{6, 30, 39}. Consequently,
152 their compositions are skewed to higher incompatible/compatible element ratios
153 compared to their parental melts and their bulk compositions often represent complex
154 mixtures between the compositions of minerals and melt. In addition, datasets for
155 island arc suites are often incomplete, missing critical CSE from the range plotted on
156 Fig. 2 and/or are not of sufficient analytical quality¹³. By contrast, comprehensive
157 datasets for primitive volcanic glasses from the Lau and Manus backarc basin (BAB)
158 contain up to 8 and 9 wt.% MgO, respectively. They also have [H₂O] and trace
159 element patterns akin to evolved Mariana-Izu island arc magmas (Fig. 4),
160 demonstrating the influence of the underlying slab^{7, 8, 25}. Hence, a combination of
161 BAB and island arc magmas are used here to constrain CSE behaviour during
162 subduction-related magmatism.

163 Primitive BAB basalts normalised to parental-MORB are enriched in W, Mo, Tl,
164 As, Pb Sb and Bi relative to the HFSE (Fig. 4), supporting previous conclusions that
165 these CSE are mobile during subduction^{6, 15, 16, 28, 30}. By contrast, Sn-In-Zn-Cd-Ga-
166 Mn-Ge-Co-Cu-Ag and Au⁷ show a relationship to neighbouring REE and HFSE that
167 is comparable to parental-MORB (Fig. 4), implying that these CSE are relatively
168 immobile during subduction and are largely derived from the mantle wedge
169 component. Evolved (4.2-5.6 wt.% MgO) Mariana-Izu arc magmas show similar trace
170 element patterns to primitive BAB (Fig. 4), but the absolute abundances of both the
171 mobile and immobile elements are more comparable to evolved BAB, which is
172 attributable to differentiation. For example, like primitive BAB (Fig. 3b), primitive

173 arc magmas (including those from the Mariana-Izu arc) have comparable or lower
174 [Cu] than parental-MORB prior to differentiation (Supplementary Figure 1). Hence,
175 the high Cu/Co of the Mariana-Izu samples (Fig. 4) can be attributed to enrichment
176 during differentiation rather than Cu mobility during subduction.

177 Normalising primitive Lau BAB basalt to evolved-MORB (N-MORB) rather than
178 parental-MORB results in a significant offset (Fig. 4). Because the evolved-
179 MORB/parental-MORB offset increases in magnitude from Sc to Rb (Fig. 4), using
180 N-MORB for normalisation results in an underestimation of (i) the fertility of the
181 mantle wedge compared to the MORB-source mantle (e.g., using La/Sm, Nb/Zr or
182 Nb/Yb³⁹), (ii) the slab-to-mantle wedge flux of incompatible elements (e.g., using
183 Pb/Yb, Th/Yb, and Cs/Tl^{4, 6, 39}) and (iii) the magnitude of the incompatible element
184 enrichments in the bulk continental crust compared to the bulk oceanic crust. The
185 opposite problem pertains to elements enriched in the lower oceanic crust, which, in
186 addition to the evolved nature of many arc magmas, has contributed to disagreements
187 regarding, for example, whether Cu is mobile^{6, 16} or not^{2, 7, 8} during subduction.

188 **CONTROLS ON THE SLAB-TO-MANTLE WEDGE FLUX**

189 The order of enrichment of As>Tl>Pb>Sb>Bi in primitive Manus BAB/parental-
190 MORB (Fig. 5a) is similar to the order of enrichment in evolved-MORB/parental-
191 MORB (Fig. 2). Hence, the upper oceanic crust appears to source the flux of
192 incompatible CSE to the mantle wedge. This implies that the majority of As-Tl-Pb-
193 Sb-Bi host-phases in the upper oceanic crust are unstable during subduction,
194 permitting their mobilization by slab-derived fluids. Obvious candidates are low-
195 temperature hydrothermal sulphides, sulfosalts and serpentinite minerals^{40, 41}. This
196 conclusion is supported Pb isotope systematics of Mariana arc magmas, which links
197 the source of the unradiogenic Pb in the fluid-component to the subducting MORB-

198 component²⁸. However, an overprinting sediment melt component is also required to
199 explain the range of Pb and Tl isotope compositions of Mariana and other arc
200 magmas^{4, 28} and probably, variations in [As]-[Tl]-[Pb]-[Sb]-[Bi] of global subduction-
201 zone magmas.

202 Tungsten and Mo have lower bulk-Ds during MORB differentiation than Pb and
203 Sb, respectively, (Fig 2), but are less mobile during subduction (Fig. 5). Hence,
204 minerals more stable than hydrothermal sulfides (e.g., rutile²⁸) probably host a
205 proportion of the W and Mo during subduction.

206 Primitive BAB have [Cu]-[Ag]-[Se] (also [Re]-[Pt]-[Au]⁸) comparable to
207 parental-MORB (Fig. 4-5), implying limited mobility during subduction. Similarly,
208 global arc datasets (e.g., Supplementary Figure 1) have been used to argue that Cu is
209 immobile during subduction^{2, 17}. Hence, ‘trapping’ of Cu-Se-Ag-Au in magmatic
210 sulphides in the lower oceanic crust prior to subduction might predispose the
211 cumulate-hosted CSE to be recycled back into the mantle during subduction more
212 efficiently than the CSE that are hosted in the upper oceanic crust (Fig. 2b). The
213 MORB-like Cu/Ag of primitive BAB (Fig. 3) suggests residual sulfide-melt in the
214 mantle wedge dominates Au>Ag≈Cu>Se partitioning. Thus, the subtly higher Cu/Se
215 and Ag/Se (Fig. 5a) and the lower Nb/Zr of primitive-BAB compared to parental-
216 MORB is consistent with either higher degrees of partial melting or the more depleted
217 nature of their mantle wedge compared to the MORB-source mantle⁸.

218 Bismuth is compatible in magmatic sulfides and has a comparable bulk-D to Se
219 during MORB differentiation (Fig. 2), but unlike Cu-Se-Ag-Au, it is mobile during
220 subduction (Fig. 4-5). Despite sulfide-fractionation, volcanic glass (comprising up to
221 20 vol% of the extrusive oceanic crust⁴²) hosts a significant proportion of the
222 Bi>Se>Cu~Ag of the bulk oceanic crust prior to hydrothermal alteration and

223 precipitation of numerous types of hydrothermal sulfides. CSE-hosting minerals
224 found in sulfide ore deposits⁴³ have an extremely large range in melting temperatures.
225 Hence, the diverging behaviour of Se and Bi during subduction suggests that Se-Cu-
226 Ag-Au-hosting hydrothermal sulfides (e.g., chalcopyrite) are more stable than the
227 predominantly low-temperature Bi-Pb-Tl-Sb-As-hosting hydrothermal sulfides and
228 sulfosalts in the upper oceanic crust during subduction.

229 Despite their higher fO_2 than MORB and consequently, higher S solubility⁴⁴,
230 BAB magmas discussed here have MORB-like [S] (prior to degassing on eruption),
231 implying limited S release to the wedge during BAB magmatism⁸. However, analyses
232 of mineral-hosted melt inclusions show that some (but not all) arc magmas are
233 enriched in S compared to MORB⁴⁵. Hence, S mobility during subduction appears
234 variable.

235 Most of the ‘mixed-affinity’ CSE (Fig. 2b) appear relatively immobile during
236 subduction (Fig. 4). Analyses of [Co], [Zn], [Ga], [Ge] in accessory minerals in
237 eclogites suggest that non-sulfide minerals such as clinopyroxene, garnet, phengite,
238 apatite, rutile and allanite host the mixed-affinity CSE during subduction⁴⁶ (and by
239 inference Sn, In and Cd). Considering a broad range of silicate-hosted (Zn, Sn, In, Cd,
240 Ga, Ge, Co) and sulfide-hosted (Cu, Ag, Se, Au) CSE have comparable patterns in
241 primitive subduction-zone magmas and parental-MORB, both the mantle wedge and
242 the MORB-source mantle probably contain residual pyroxene and sulfide.

243 In summary, both oceanic crust differentiation (i.e., the upper/lower crust
244 distributions of CSE) and the mineral affinities of the CSE during differentiation and
245 alteration of the oceanic crust (Fig. 2b) predispose the CSE to be either mobile or
246 immobile during subduction.

247 **CONTINENTAL CRUST**

248 The continental crust has a bulk andesitic composition approximating evolved
249 rather than primitive subduction-related magmas²⁶ (Fig. 4). This offset is often
250 attributed to delamination of cumulates from the base of the continental crust²⁶.
251 Delamination of sulfide-bearing cumulates has also been proposed to account for the
252 Cu-deficit of the continental crust and the first Pb paradox (location of the missing
253 unradiogenic Pb)^{2, 47}. However, the role of sulfide fractionation during arc magma
254 differentiation remains debated. For example, the low [CSE] of evolved subduction-
255 zone magmas is often attributed to partitioning into exsolving volatile phase(s) rather
256 than sulfide fractionation^{6, 18}. Hence, understanding the behaviour of the CSE during
257 differentiation of subduction-related magmas might provide clues towards
258 understanding the composition of the mature continental crust.

259 Tholeiitic BAB magmas and arc magma suites developed on crust that is <20 km
260 thick (e.g., Mariana, Supplementary Figure 1), show an initial increase (sulfide under-
261 saturated) then concomitant decrease in [FeO] and [Cu] at ~4-5 wt.% MgO (Fig. 3b),
262 which has been attributed to magnetite-driven reduction of the melt triggering sulfide-
263 saturation during differentiation of high fO_2 melts^{7, 8, 17}. For example, the sample from
264 the Manus BAB with the highest [Cu] (green circle, Fig. 3b), also has higher [Se] (and
265 hence S prior to degassing on eruption; see modelling in Refs^{7, 8, 25}), [Ag] and [Au]
266 than the most primitive BAB from the region (Fig. 3c). Together with the constant
267 Cu/Se (Jenner et al.,⁸ their Figure 8), these systematics indicate that the evolving
268 melts were initially sulfide-under-saturated. As the magma evolves, magnetite-
269 triggered sulfide-fractionation causes a significant drop in [Se] (and by proxy [S]^{7, 8,}
270 ²⁵), [Ag], [Au], [Cu] (Fig. 3c). Unlike MORB, BAB suites show a drop in Cu/Ag
271 following sulfide-fractionation (Fig. 3a), implying fractionation of crystalline-sulfide
272 as opposed to sulfide-melt^{7, 8}.

273 Alternatively, Sun et al.¹⁸ used [S] versus [SiO₂] systematics to argue that the
274 Manus BAB melts contained insufficient S to achieve sulfide-saturation during
275 differentiation and consequently, attributed the drop in [CSE] to partitioning into
276 exsolving fluids. This interpretation is contrary to modelling, based on experimental
277 constraints (Figure 8b of Ref.⁷), which shows that the drop in [CSE] during
278 differentiation of the Manus suite coincides with the melts achieving the [Cu]+[S]
279 necessary for sulfide-saturation (see^{7,8,17} for detailed discussion). Furthermore, S-Se-
280 Fe-Cu-Ag-Au systematics of the Manus suite, together with the differences in [S]
281 between mineral-hosted melt inclusions and volcanic glasses indicate S degassing
282 took place after sulfide fractionation^{7,8,17}.

283 Arc magmas erupted through >30 km of crust that show calc-alkaline
284 differentiation trends (e.g., the Andes) fractionate sulfide at higher [MgO] (≥8 wt.%)
285 than arc tholeiitic suites erupted through <20 km of crust¹⁷ (Supplementary Figure
286 1b). This difference has been attributed to the higher [H₂O] and *f*O₂ of melts evolving
287 in thicker arcs and consequently, earlier magnetite fractionation¹⁷. Recent
288 experimental data demonstrating the sulfide stability field shifts towards more
289 oxidising conditions with increasing pressure⁴⁴ may offer an alternative explanation:
290 high-pressure differentiation causes magmas erupting through >30 km of crust to
291 saturate in sulfide regardless of their H₂O, *f*O₂ or consequently, the timing of
292 magnetite fractionation.

293 The bulk and lower continental crust has a CSE pattern and Cu/Ag strikingly
294 similar to the most evolved (<1 wt.% MgO) sulfide-saturated BAB rhyolites (Figs. 3
295 and 5). Consequently, crystalline-sulfide fractionation appears to dominate during
296 continental crust formation, whereas sulfide-melt fractionation dominates during
297 oceanic crust formation. The low Cu/Ag of the lower continental crust indicates

298 average arc magmas differentiate at the base of the crust long enough to permit
299 significant crystalline-sulfide fractionation prior to ascent to higher crustal levels: a
300 conclusion that is complementary to ‘deep crustal hot-zone’ models⁴⁸ and potentially
301 accounts for the lower [Cu] of even ‘primitive’ arc magmas compared to parental-
302 MORB (Supplementary Figure 1). The lower and bulk continental crust has
303 significantly higher [MgO] than BAB rhyolites, despite their comparable Cu/Ag (Fig.
304 3a). This difference suggests that continental crust formation is dominated by addition
305 of arc magmas with differentiation histories akin to calc-alkaline series magmas
306 erupting through >30 km of crust (i.e., sulfide-saturated at ≥ 8 wt.% MgO rather than
307 ~ 4 wt.% MgO). Considering H₂O solubility increases with increasing pressure⁴⁹, it is
308 unlikely that partitioning of CSE into exsolving fluids (e.g.,¹⁸) in the lowermost crust
309 (rather than magmatic sulfides) can account for the differences in CSE systematics
310 between magmas erupting through <20 km versus >30 km of crust.

311 Crystalline sulfide accumulation should cause subduction-related cumulates to
312 have higher Cu/Ag than MORB and primitive BAB. Consequently, the low Cu/Ag of
313 the bulk and lower continental crust provides strong support for delamination models.
314 Using constraints provided here, mass balance deficits attributable to delamination
315 probably exist for most CSE, which is consistent with the comparable [CSE] of the
316 bulk continental crust compared to evolved rather than primitive BAB magmas (Fig.
317 3c). Given that all CSE are less enriched in rhyolites compared to U and Th (Fig. 3c),
318 a proportion of even the incompatible CSE (e.g., Pb) is likely hosted in the lower
319 continental crust prior to delamination (e.g., Th/Pb and U/Pb show a significant
320 increase from 0.135 and 0.085 in the most primitive sample to 0.260 and 0.174 in the
321 most evolved sample, respectively). This finding supports claims that delamination
322 may contribute to the first Pb paradox^{2,47}.

323 ORE DEPOSITS

324 It is perhaps unsurprising that porphyry ore-deposits in the upper continental
325 crust are rare considering: (i) Cu-Ag-Au are immobile during subduction; (ii) mantle-
326 melts rarely avoid sulfide-saturation during differentiation; (iii) Cu-Au-Ag are hosted
327 by minerals in the lower continental crust, which can be delaminated. Given the
328 effects of pressure on the sulfide stability field⁴⁴, magmas intruded into the lower
329 continental crust are unlikely to destabilise/assimilate pre-existing sulfides. However,
330 because the sulfide stability field shifts to lower fO_2 with decreasing pressure, rapid
331 ascent of magmas could permit subduction-zone magmas to safely reach the upper
332 continental crust without sustaining significant sulfide fractionation and/or would
333 cause dissolution of entrained sulfides. In the upper continental crust numerous
334 processes can be invoked to either decrease the chances of sulfide-saturation during
335 differentiation (e.g., S degassing^{8,44}) or reverse the effects of sulfide-saturation (e.g.,
336 sulfide dissolution by subsequent exsolving volatiles⁵), which may account for why
337 porphyries are typically located at crustal depths of <10 km⁵. Such processes would
338 generate co-enrichment in elements that are highly incompatible (e.g., Mo, W) and
339 highly chalcophile (e.g., Cu, Au), which are characteristics of porphyries that are
340 distinct from the typical upper/lower crust distribution of CSE (Fig. 3).

341 Mixed-affinity CSE, such as In and Zn, are not typically enriched in porphyries,
342 implying their partitioning into silicates and/or oxides rather than less stable sulfides
343 limits their potential to partition into late-stage exsolving fluids. However, these
344 mixed-affinity CSE are likely released during crustal anatexis, which, in addition to
345 differences in the fractionating mineral assemblages between mantle versus
346 predominantly crustal melts, might explain why In-Zn-Sn mineralisation is associated
347 with granitic intrusions⁵⁰, rather than subduction-related porphyries.

348 **References**

- 349 1. Palme, H. & O'Neill, H. St C. in Treatise on Geochemistry: The Mantle and
350 Core (ed. Carlson, R.W.) 1-39 (Elsevier-Pergamon, Oxford, 2014).
- 351 2. Lee, C.-T.A. et al. Copper Systematics in Arc Magmas and Implications for
352 Crust-Mantle Differentiation. *Science* **336**, 64-68 (2012).
- 353 3. Lee, C.-T.A., Leeman, W.P., Canil, D. & Li, Z.-X.A. Similar V/Sc Systematics in
354 MORB and Arc Basalts: Implications for the Oxygen Fugacities of their
355 Mantle Source Regions. *Journal of Petrology* **46**, 2313-2336 (2005).
- 356 4. Nielsen, S.G. et al. Tracking along-arc sediment inputs to the Aleutian arc
357 using thallium isotopes. *Geochimica et Cosmochimica Acta* **181**, 217-237
358 (2016).
- 359 5. Wilkinson, J.J. Triggers for the formation of porphyry ore deposits in
360 magmatic arcs. *Nature Geoscience* **6**, 917-925 (2013).
- 361 6. Timm, C., de Ronde, C.E.J., Leybourne, M.I., Layton-Matthews, D. &
362 Graham, I.J. Sources of Chalcophile and Siderophile Elements in Kermadec
363 Arc Lavas. *Economic Geology* **107**, 1527-1538 (2012).
- 364 7. Jenner, F.E., O'Neill, H. St C., Arculus, R.J. & Mavrogenes, J.A. The Magnetite
365 Crisis in the Evolution of Arc-related Magmas and the Initial
366 Concentration of Au, Ag, and Cu. *Journal of Petrology* **51**, 2445-2464
367 (2010).
- 368 8. Jenner, F.E. et al. The competing effects of sulfide saturation versus
369 degassing on the behavior of the chalcophile elements during the
370 differentiation of hydrous melts. *Geochemistry, Geophysics, Geosystems* **16**,
371 1490-1507 (2015).

- 372 9. Salters, V.J.M. & Stracke, A. Composition of the depleted mantle.
373 *Geochemistry geophysics geosystems* **5**, Q05004 (2004).
- 374 10. Richards, J.P. The oxidation state, and sulfur and Cu contents of arc
375 magmas: implications for metallogeny. *Lithos* **233**, 27-45 (2015).
- 376 11. Gale, A., Dalton, C.A., Langmuir, C.H., Su, Y. & Schilling, J.-G. The mean
377 composition of ocean ridge basalts. *Geochemistry, Geophysics, Geosystems*,
378 489-518 (2013).
- 379 12. Arevalo, R. & McDonough, W.F. Chemical variations and regional diversity
380 observed in MORB. *Chemical Geology* **271**, 70-85 (2010).
- 381 13. Jenner, F.E. & Arevalo, R.D. Major and Trace Element Analysis of Natural
382 and Experimental Igneous Systems using LA-ICP-MS. *Elements* **12**, 311-
383 316 (2016).
- 384 14. Yi, W. et al. Cadmium, indium, tin, tellurium, and sulfur in oceanic basalts:
385 Implications for chalcophile element fractionation in the Earth. *J. Geophys.*
386 *Res.* **105**, 18927-18948 (2000).
- 387 15. Jochum, K.P. & Hofmann, A.W. Constraints on earth evolution from
388 antimony in mantle-derived rocks. *Chemical Geology* **139**, 39-49 (1997).
- 389 16. Noll, J.P.D., Newsom, H.E., Leeman, W.P. & Ryan, J.G. The role of
390 hydrothermal fluids in the production of subduction zone magmas:
391 Evidence from siderophile and chalcophile trace elements and boron.
392 *Geochimica et Cosmochimica Acta* **60**, 587-611 (1996).
- 393 17. Chiaradia, M. Copper enrichment in arc magmas controlled by overriding
394 plate thickness. *Nature Geoscience* **7**, 43-46 (2014).
- 395 18. Sun, W. et al. Porphyry deposits and oxidized magmas. *Ore Geology*
396 *Reviews* **65**, Part 1, 97-131 (2015).

- 397 19. Witt-Eickschen, G., Palme, H., O'Neill, H. St C. & Allen, C.M. The
398 geochemistry of the volatile trace elements As, Cd, Ga, In and Sn in the
399 Earth's mantle: New evidence from in situ analyses of mantle xenoliths.
400 *Geochimica et Cosmochimica Acta* **73**, 1755-1778 (2009).
- 401 20. Tanner, D., Mavrogenes, J.A., Arculus, R.J. & Jenner, F.E. Trace Element
402 Stratigraphy of the Bellevue Core, Northern Bushveld: Multiple Magma
403 Injections Obscured by Diffusive Processes. *Journal of Petrology* **55**, 859-
404 882 (2014).
- 405 21. Jenner, F.E. & O'Neill, H. St C. Analysis of 60 Elements in 616 Ocean Floor
406 Basaltic Glasses. *Geochemistry geophysics geosystems* **13**, Q02005 (2012).
- 407 22. Patten, C., Barnes, S.-J., Mathez, E.A. & Jenner, F.E. Partition coefficients of
408 chalcophile elements between sulfide and silicate melts and the early
409 crystallization history of sulfide liquid: LA-ICP-MS analysis of MORB
410 sulfide droplets. *Chemical Geology* **358**, 170-188 (2013).
- 411 23. Kiseeva, E.S. & Wood, B.J. The effects of composition and temperature on
412 chalcophile and lithophile element partitioning into magmatic sulphides.
413 *Earth and Planetary Science Letters* **424**, 280-294 (2015).
- 414 24. Li, Y. & Audétat, A. Partitioning of V, Mn, Co, Ni, Cu, Zn, As, Mo, Ag, Sn, Sb,
415 W, Au, Pb, and Bi between sulfide phases and hydrous basanite melt at
416 upper mantle conditions. *Earth and Planetary Science Letters* **355-356**,
417 327-340 (2012).
- 418 25. Jenner, F.E. et al. Chalcophile element Systematics in Volcanic Glasses
419 from the Northwestern Lau Basin. *Geochemistry geophysics geosystems* **13**,
420 Q06014 (2012).

- 421 26. Rudnick, R.L. & Gao, S. in *Treatise on Geochemistry: The Crust* (ed.
422 Rudnick, R.L.) 1-64 (Elsevier, Oxford, 2003).
- 423 27. Dare, S.S., Barnes, S.-J. & Prichard, H. The distribution of platinum group
424 elements (PGE) and other chalcophile elements among sulfides from the
425 Creighton Ni–Cu–PGE sulfide deposit, Sudbury, Canada, and the origin of
426 palladium in pentlandite. *Mineralium Deposita* **45**, 765-793 (2010).
- 427 28. Freymuth, H., Vils, F., Willbold, M., Taylor, R.N. & Elliott, T. Molybdenum
428 mobility and isotopic fractionation during subduction at the Mariana arc.
429 *Earth and Planetary Science Letters* **432**, 176-186 (2015).
- 430 29. Freymuth, H., Ivko, B., Gill, J.B., Tamura, Y. & Elliott, T. Thorium isotope
431 evidence for melting of the mafic oceanic crust beneath the Izu arc.
432 *Geochimica et Cosmochimica Acta* **186**, 49-70 (2016).
- 433 30. Elliott, T., Plank, T., Zindler, A., White, W. & Bourdon, B. Element transport
434 from slab to volcanic front at the Mariana arc. *Journal of Geophysical*
435 *Research: Solid Earth* **102**, 14991-15019 (1997).
- 436 31. Prytulak, J., Nielsen, S.G., Plank, T., Barker, M. & Elliott, T. Assessing the
437 utility of thallium and thallium isotopes for tracing subduction zone
438 inputs to the Mariana arc. *Chemical Geology* **345**, 139-149 (2013).
- 439 32. White, W.M. & Klein, E.M. in *Treatise on Geochemistry (Second Edition):*
440 *The Crust* (ed. Turekian, H.D.H.K.) 457-496 (Elsevier, Oxford, 2014).
- 441 33. O'Neill, H. St C. & Jenner, F.E. The global pattern of trace-element
442 distributions in ocean floor basalts. *Nature* **491**, 698-704 (2012).
- 443 34. O'Neill, H. St C. & Jenner, F.E. Causes of the Compositional Variability
444 among Ocean Floor Basalts. *Journal of Petrology* **57**, 2163-2194 (2017).

- 445 35. Li, Y. Chalcophile element partitioning between sulfide phases and
446 hydrous mantle melt: Applications to mantle melting and the formation of
447 ore deposits. *Journal of Asian Earth Sciences* **94**, 77-93 (2014).
- 448 36. Zhang, Z. & Hirschmann, M.M. Experimental constraints on mantle sulfide
449 melting up to 8 GPa. *American Mineralogist* **101**, 181-192 (2016).
- 450 37. Adam, J. & Green, T. Trace element partitioning between mica- and
451 amphibole-bearing garnet lherzolite and hydrous basanitic melt: 1.
452 Experimental results and the investigation of controls on partitioning
453 behaviour. *Contributions to Mineralogy and Petrology* **152**, 1-17 (2006).
- 454 38. Wang, Z. & Becker, H. Abundances of Ag and Cu in mantle peridotites and
455 the implications for the behavior of chalcophile elements in the mantle.
456 *Geochimica et Cosmochimica Acta* **160**, 209-226 (2015).
- 457 39. Pearce, J.A., Stern, R.C., Bloomer, S.H. & Fryer, P. Geochemical mapping of
458 the Mariana arc-basin system: Implications for the nature and
459 distribution of subduction components. *Geochemistry geophysics*
460 *geosystems* **6**, Q07006 (2005).
- 461 40. Guillot, S. & Hattori, K. Serpentinites: Essential Roles in Geodynamics, Arc
462 Volcanism, Sustainable Development, and the Origin of Life. *Elements* **9**,
463 95-98 (2013).
- 464 41. Peucker-Ehrenbrink, B., Hofmann, A.W. & Hart, S.R. Hydrothermal lead
465 transfer from mantle to continental crust: the role of metalliferous
466 sediments. *Earth and Planetary Science Letters* **125**, 129-142 (1994).
- 467 42. Staudigel, H. in *Treatise on Geochemistry (Second Edition): The Crust*
468 (eds. Holland, H.D. & Turekian, K.K.) 583-606 (Elsevier, Oxford, 2014).

- 469 43. Tomkins, A.G., Pattison, D.R.M. & Frost, B.R. On the Initiation of
470 Metamorphic Sulfide Anatexis. *Journal of Petrology* **48**, 511-535 (2007).
- 471 44. Matjuschkin, V., Blundy, J.D. & Brooker, R.A. The effect of pressure on
472 sulphur speciation in mid- to deep-crustal arc magmas and implications
473 for the formation of porphyry copper deposits. *Contributions to*
474 *Mineralogy and Petrology* **171**, 1-25 (2016).
- 475 45. Wallace, P.J. Volatiles in subduction zone magmas: concentrations and
476 fluxes based on melt inclusion and volcanic gas data. *Journal of*
477 *Volcanology and Geothermal Research* **140**, 217-240 (2005).
- 478 46. Hermann, J. Allanite: thorium and light rare element carrier in subducted
479 crust. *Chemical Geology* **192**, 287-306 (2002).
- 480 47. Blichert-Toft, J. et al. Large-scale tectonic cycles in Europe revealed by
481 distinct Pb isotope provinces. *Geochemistry, Geophysics, Geosystems*, 3854-
482 3864 (2016).
- 483 48. Annen, C., Blundy, J.D. & Sparks, R.S.J. The Genesis of Intermediate and
484 Silicic Magmas in Deep Crustal Hot Zones. *Journal of Petrology* **47**, 505-
485 539 (2006).
- 486 49. Plank, T., Kelley, K.A., Zimmer, M.M., Hauri, E.H. & Wallace, P.J. Why do
487 mafic arc magmas contain ~4 wt% water on average? *Earth and Planetary*
488 *Science Letters* **364**, 168-179 (2013).
- 489 50. Simons, B., Andersen, J.C.Ø., Shail, R.K. & Jenner, F.E. Fractionation of Li,
490 Be, Ga, Nb, Ta, In, Sn, Sb, W and Bi in the peraluminous Early Permian
491 Variscan granites of the Cornubian Batholith: Precursor processes to
492 magmatic-hydrothermal mineralisation. *Lithos* **278-281**, 491-512
493 (2017).

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503

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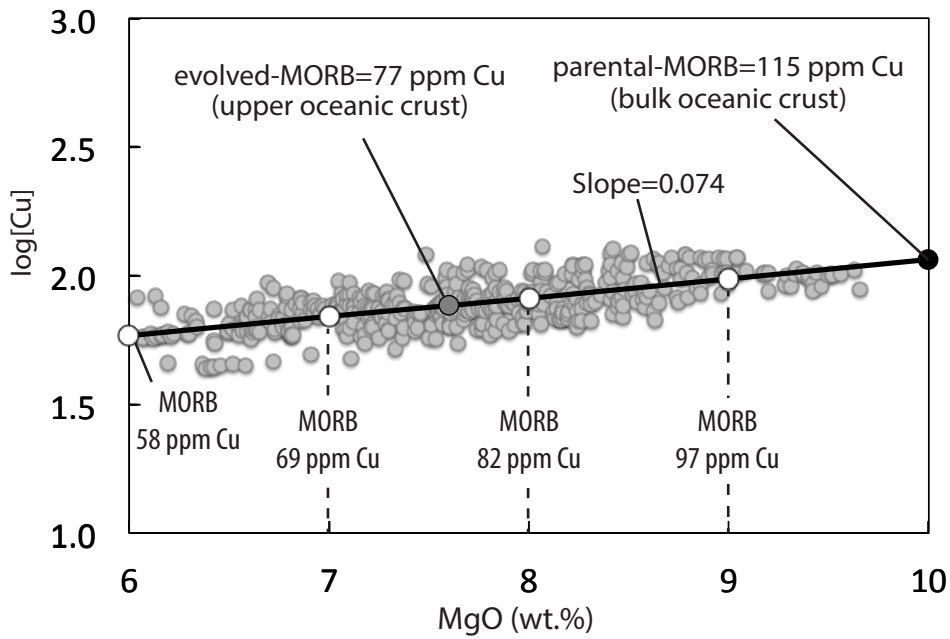
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506 **Supplementary Materials** are linked to the online version of the paper at
507 www.nature.com/nature.

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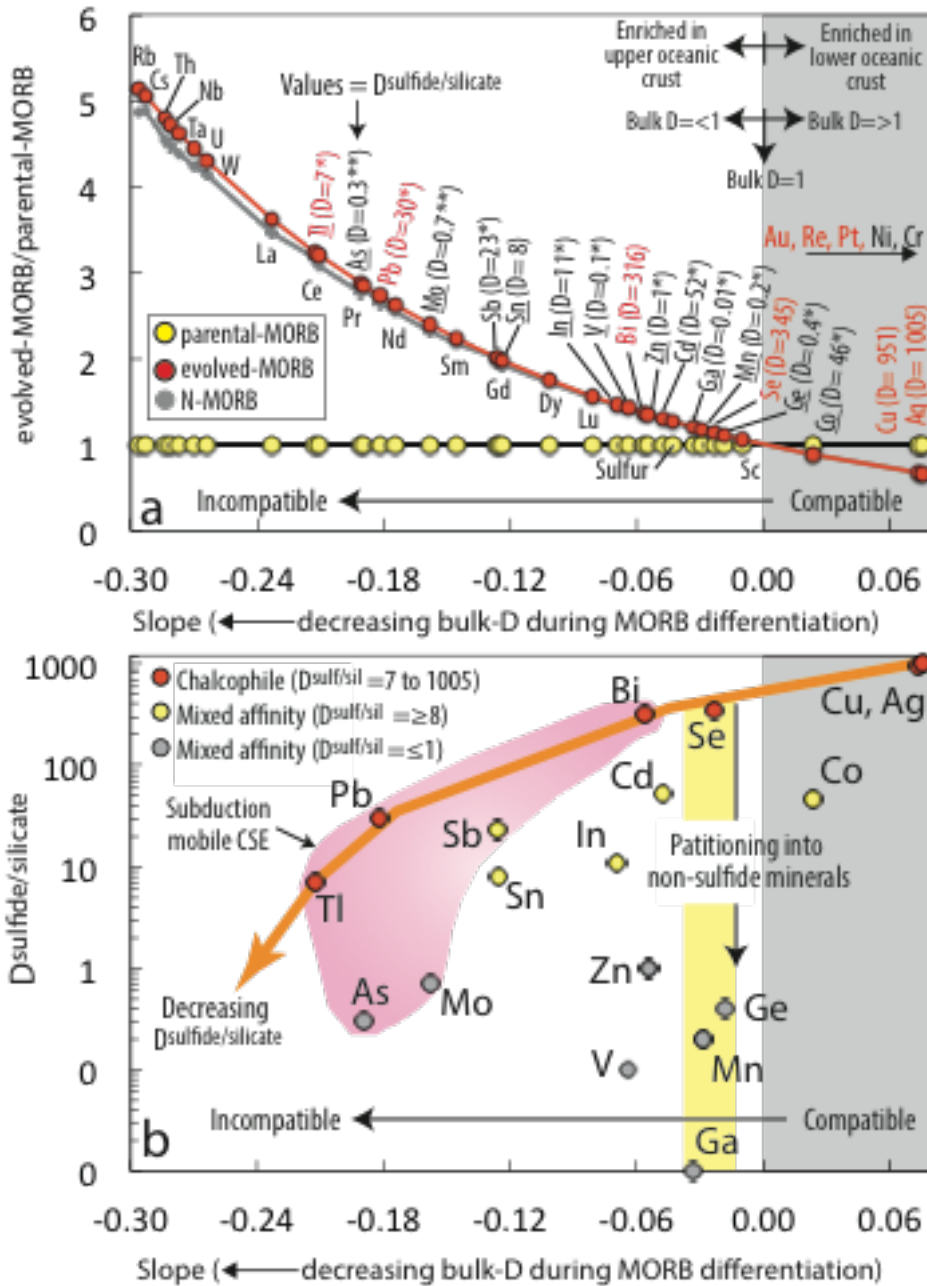
510 **FIGURE CAPTIONS**
511



512
513

514 **Figure 1: Global MORB log[Cu] versus [MgO].** The slope (0.074) of the best-fit
515 line through the global MORB array (490 samples, data filtering methods described in
516 Methods), together with the [Cu] at various [MgO] along the trend, is used to estimate
517 the composition of parental-MORB (10 wt.% MgO: a proxy for the bulk oceanic crust
518 composition) and evolved-MORB (7.6 wt.% MgO: a proxy for the composition of the
519 upper oceanic crust). [Cu] versus [MgO] shows a positive correlation because Cu is a
520 compatible element (bulk- $D \gg 1$).

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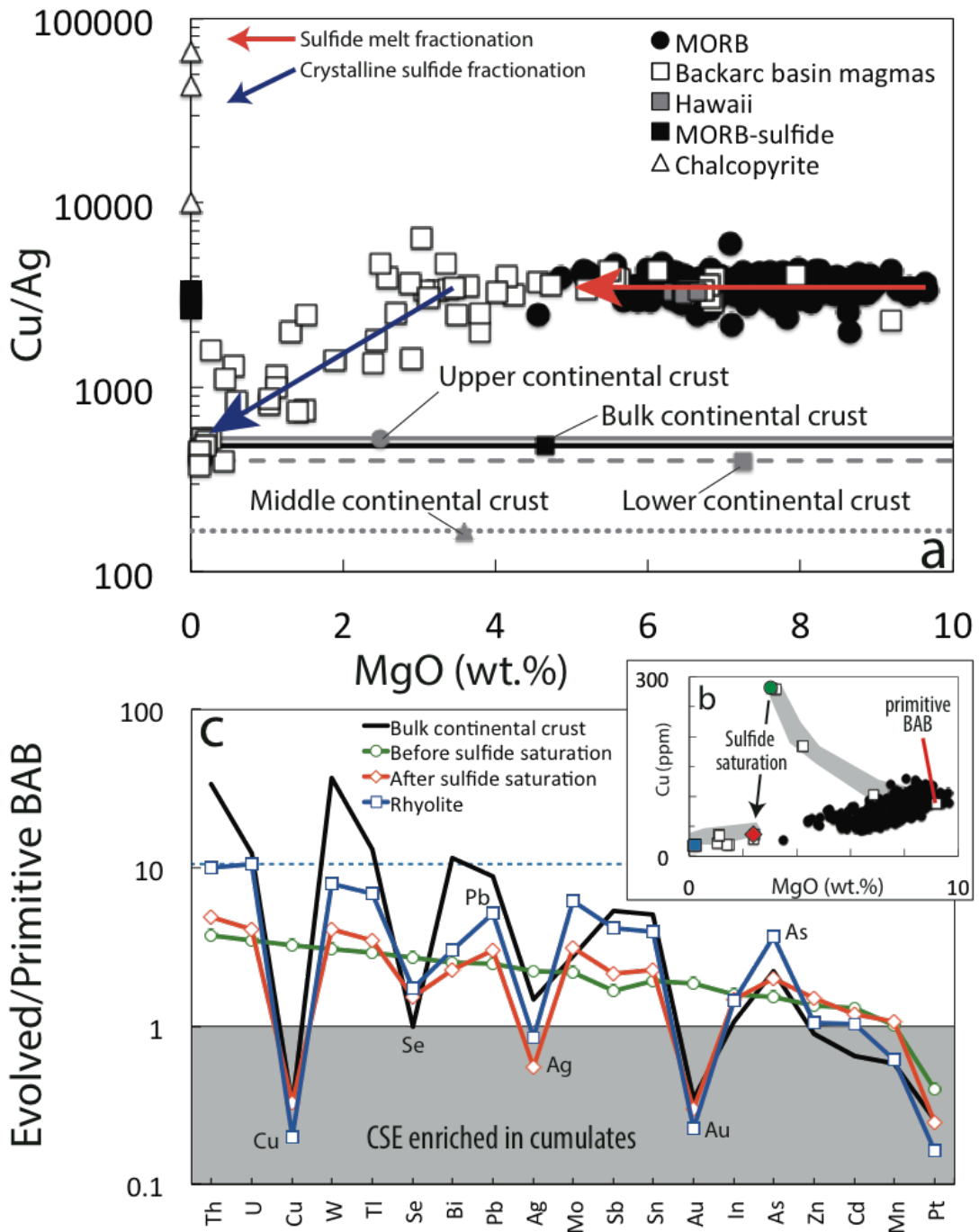


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523 **Figure 2: CSE partitioning during MORB differentiation;** a) Elements with
 524 negative slopes are enriched whereas those with positive slopes are depleted during
 525 MORB differentiation. $D^{\text{sulph/sil}}$ for MORB-hosted sulphides²² except ‘*’ derived
 526 using the $D^{\text{sulph/sil}}$ calculator²³, (for a melt with 9 wt.% FeO_{TOT} and [Ni] and [Cu]
 527 from MORB-hosted sulphide RC28-02-07re-G1²²) and ‘**’ from experiment LY-
 528 29²⁴, which has $D^{\text{sulph/sil}}$ Cu/Ag comparable to MORB sulphides. b) scatter between

529 $D^{sulph/sil}$ versus slopes can be attributed to the mixed-affinities of CSE for sulfides
 530 and non-sulfide minerals, except potentially those with the highest $D^{sulph/sil}$ at a
 531 given slope (orange arrow).

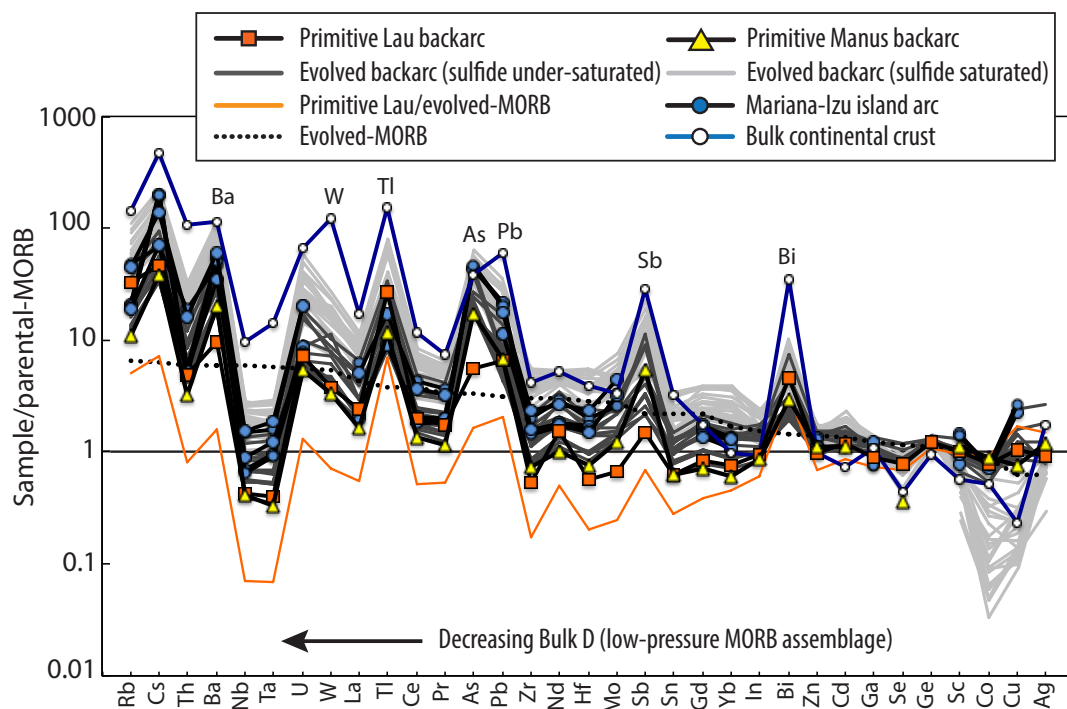
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534

535 **Figure 3: CSE partitioning during crustal differentiation.** a) Cu/Ag versus [MgO]
 536 of MORB²¹, MORB-hosted sulfide²², Hawaiian basalts²⁵, BAB magmas^{7, 8},
 537 continental crust estimates²⁶ and chalcopyrite²⁷ (see text for discussion). b) Unlike
 538 MORB, Manus BAB are initially sulphide under-saturated ([Cu] increases with
 539 decreasing [MgO]), until sulphide-saturation at <4 wt.% MgO. c) Samples from along
 540 the [Cu] versus [MgO] Manus trend (see b) and the bulk continental crust estimate are
 541 normalised to the most primitive Manus sample to constrain the partitioning of the
 542 CSE during differentiation of subduction-related melts (e.g., [Cu] is higher before
 543 sulfide-saturation and lower after sulfide-saturation). Note, [Pt] is depleted by
 544 partitioning into Pt-rich alloy^{7, 8} prior to sulfide saturation.
 545

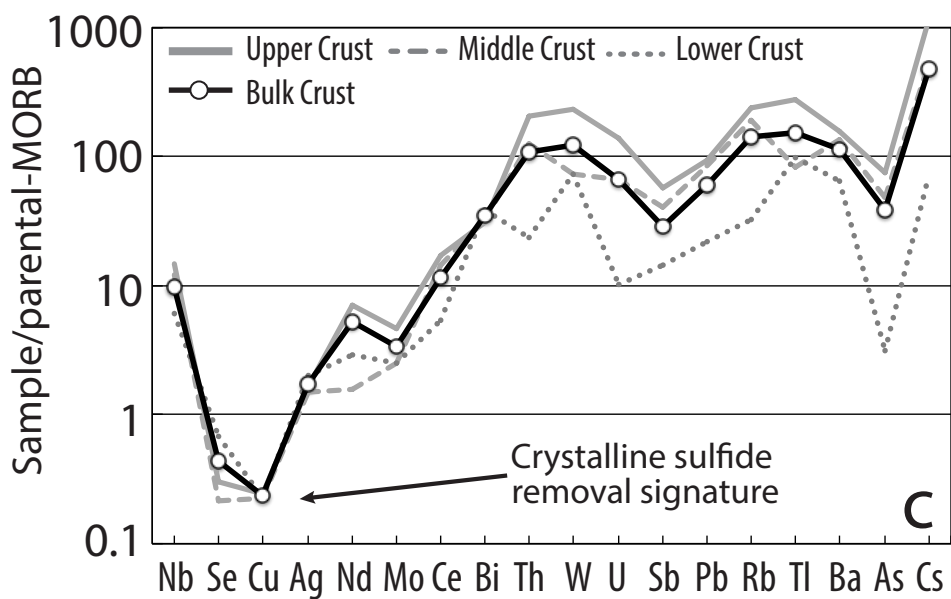
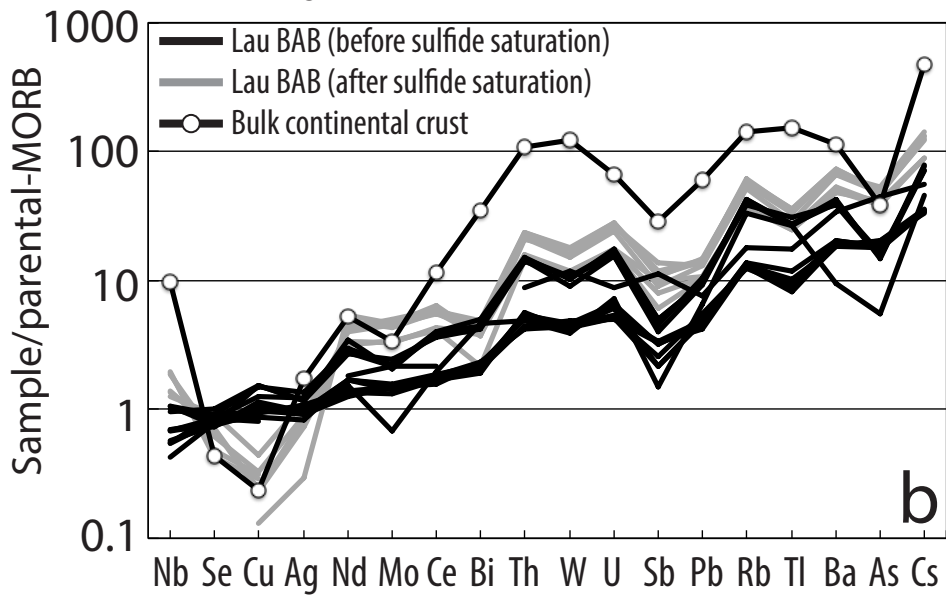
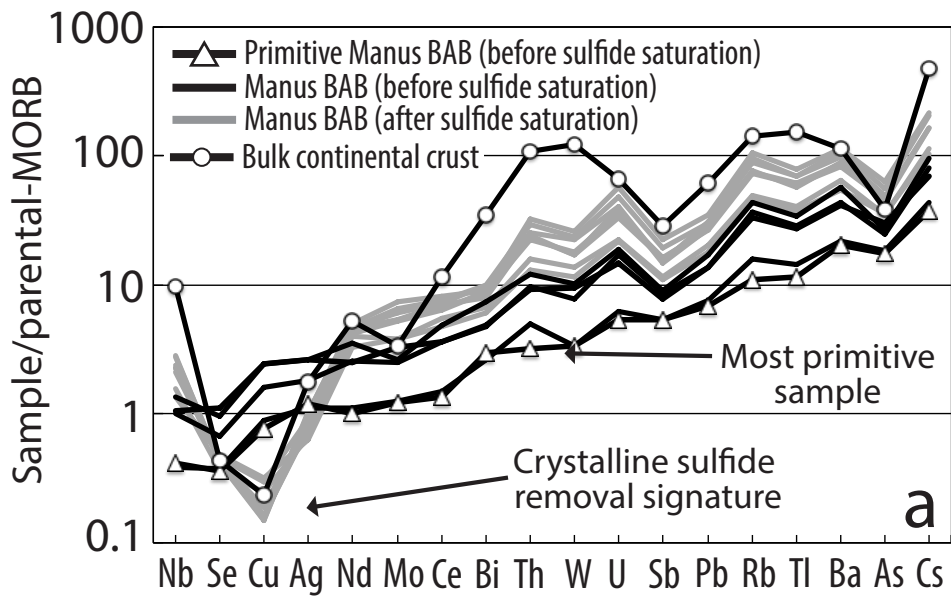


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547

548 **Figure 4: Parental-MORB-normalized trace element patterns.** Primitive and
 549 evolved BAB basalts^{7, 8, 25}, Mariana-Izu island arc magmas²⁸⁻³¹ and the bulk
 550 continental crust²⁶ have comparable trace element patterns. The orange line shows the

551 composition of the primitive Lau BAB normalized to evolved-MORB rather than
552 parental-MORB, demonstrating average-MORB (N-MORB) and evolved-MORB are
553 inappropriate for comparative geochemistry. Element ordering is determined by bulk
554 partitioning (slopes) during MORB differentiation, because partitioning information
555 required to accurately define the ordering in the mantle peridotite assemblage are
556 unavailable. Of the CSE, only W, Tl, As, Pb, Mo, Sb and Bi are mobile during
557 subduction.
558



560

561 **Figure 5: Parental-MORB normalized trace element patterns.** The bulk
562 continental crust estimate²⁶ is compared to a-b) sulphide under-saturated (black lines)
563 and sulfide-saturated BAB samples (grey lines) from a) the Manus BAB^{7, 25} b) the
564 Lau BAB⁸. Element ordering is defined by the enrichments in the primitive Manus
565 sample compared to parental-MORB. c) All layers of the continental crust show
566 patterns similar to sulphide-saturated BAB magmas, indicating the majority of
567 convergent margin magmas reach sulphide saturation prior to ascent to higher crustal
568 levels.

569

570 **METHODS**

571 *Data filtering*

572 Source data for Figures 1-5 and Supplementary Figure 1 are provided with the paper.
573 The MORB dataset of Jenner and O'Neill²¹ was used to constrain the relative bulk-D
574 of the CSE during the petrogenesis of MORB, excluding plume-proximal samples
575 (see^{21, 25}) and highly evolved samples with <6 wt.% MgO (see^{33, 34}). As discussed in
576 Jenner and O'Neill²¹ (their Figures 2 and 3) and Jenner et al.²⁵ (their Figure 9), plume-
577 proximal samples have elevated [Cu] at a given [MgO] compared to the majority of
578 the MORB array. Hence, plume-proximal samples appear to either be sulfide under-
579 saturated or fractionate a smaller percentage of sulfide melt during differentiation
580 compared to 'typical' MORB. Consequently, these samples were not considered to be
581 representative of the typical behaviour of the CSE during the petrogenesis of MORB
582 and were filtered from the dataset prior to calculating the slopes and the primitive-
583 and evolved-MORB compositions.

584

585 Data fitting

586 The slopes, b , by which the log-mean content of a given element, $[M]$, changes with
587 $[MgO]$, that is, $d(\log[M])/d[MgO]$, and the predicted abundances of $\log[M]_{10}$ at
588 $[MgO] = 10$ (average primitive-MORB) and $\log[MgO]_{7.6}$ at $[MgO] = 7.6$ (average
589 erupted MORB) were obtained from the least squares best-fit to the Equation:

590

591
$$\log[M]_{10} = \log [M]_o + b([MgO]-10) \quad (E1a)$$

592

593
$$\log[M]_{7.6} = \log [M]_o + b([MgO]-7.6) \quad (E1b)$$

594

595 respectively, where logarithms are to the base 10. The parental MORB and evolved
596 MORB compositions converted back to ‘normal’ numbers are presented in
597 Supplementary Table 1, together with the corresponding slopes.

598

599 The standard error of the slope, S_b , is calculated using:

600

601
$$s(\log[M])/\sqrt{\sum([MgO] - \overline{[MgO]})^2} \quad (E2)$$

602

603 Where $s(\log[M])$ is the standard error of the regression (termed ‘variability’ by
604 O’Neill and Jenner^{33, 34}), given by:

605

606
$$s(\log[M]) = \sqrt{(\sum(\log[M] - \log[M]_o - b [MgO])^2)/(n-2)} \quad (E3)$$

607

608 There is a systematic increase in $s(b)$ and $s(\log[M])$ with decreasing slope
609 (Supplementary Table 1 and O’Neill and Jenner³³, their Figure 3), because variability

610 in erupted MORB compositions, inherited during both mantle and crustal processes,
611 increases with incompatibility (see Refs.^{33, 34}, for detailed discussion). The elevated
612 $s(b)$ and $s(\log[M])$ for Re, Pt, Au, As and Sb can be attributed to the low contents of
613 each of these elements (near limits of detection) and/or interferences on each mass
614 during LA-ICP-MS analysis (see^{13, 51, 52}).

615

616 The standard error of $\log[M]_{7.6}$ is calculated using:

617

$$618 \quad s(\log[M]_{7.6}) = s(\log[M]) \times \sqrt{(1/n + (7.6 - [\overline{\text{MgO}}])^2) / \sum([\text{MgO}] - [\overline{\text{MgO}}])^2)}$$

619

$$620 \quad (E4)$$

621 and likewise for $s(\log[M]_{10})$. Each of the equations listed above can be calculated
622 using the Excel LINEST function. Uncertainties in $[M]_{7.6}$ were calculated using:

623

$$624 \quad s[M]_{7.6} = \ln(10) \times [M]_{7.6} \times s(\log[M]_{7.6}) \quad (E5)$$

625

626 and likewise for $s[M]_{10}$, and are presented in Supplementary Table S1.

627

628 **References**

- 629 51. Jenner, F.E. & O'Neill, H.S.C. Major and trace analysis of basaltic glasses by
630 laser-ablation ICP-MS. *Geochemistry geophysics geosystems* **13**, Q03003
631 (2012).
- 632 52. Jenner, F.E., Holden, P., Mavrogenes, J.A., O'Neill, H.S.C. & Allen, C.
633 Determination of Selenium Concentrations in NIST SRM 610, 612, 614 and

- 634 Geological Glass Reference Materials using the Electron Probe, LA-ICP-MS
635 and SHRIMP II. *Geostandards and Geoanalytical Research* **33**, 309-317.