

## Elevated magma fluxes deliver high-Cu magmas to the upper crust

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DOI:  
[10.1130/G47562.1](https://doi.org/10.1130/G47562.1)

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*Document Version*  
Peer reviewed version

*Citation for published version (Harvard):*  
Cox, D, Watt, S, Jenner, FE, Hastie, A, Hammond, SJ & Kunz, BE 2020, 'Elevated magma fluxes deliver high-Cu magmas to the upper crust', *Geology*, vol. 48, no. 10, pp. 957-960. <https://doi.org/10.1130/G47562.1>

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**Title: Elevated magma fluxes deliver high-Cu magmas to the upper crust**

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**ABSTRACT**

Porphyry Cu-Au ore deposits are globally associated with convergent margins. However, controls on the processing and distribution of the chalcophile elements (e.g., Cu) during convergent margin magmatism remain disputed. Here, we show that magmas feeding many Chilean stratovolcanoes fractionate high-Cu/Ag

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sulfides early in their crustal evolution. These magmas show evidence of lower-crustal garnet and amphibole crystallisation, and their degree of sulfide fractionation and Cu depletion increase with both crustal thickness and the extent of garnet fractionation. However, samples from a small proportion of volcanoes with elevated eruptive fluxes depart from this Cu-depleting trend, instead erupting Cu-rich magmas. This implies that at these atypical sites, elevated magma productivity and crustal throughput, potentially facilitated by ‘pathways’ exploiting major crustal fault systems, enables rapid magma transit, avoiding lower-crustal Cu-depleting sulfide fractionation and potentially playing an important role in porphyry ore genesis.

## INTRODUCTION

Porphyry ore deposits are enriched in chalcophile metals (e.g., Cu, Ag) and are most frequently associated with areas above continental subduction zones (Sillitoe, 2010). The processes responsible for generating such deposits, formed in close association with upper-crustal arc-magmatic systems, are debated (Wilkinson, 2013; Blundy et al., 2015; Lee and Tang, 2020). At oceanic island arcs, initial increases in magma Cu content are observed during crystallisation of hydrous magmas, until magnetite fractionation causes a decrease in magma  $fO_2$ , triggers sulfide fractionation and results in an abrupt decrease in magma Cu content (Jenner et al., 2010). Conversely, evolving continental arc magmas achieve sulfide saturation in the lower crust prior to magnetite crystallisation (Lee et al., 2012; Chiaradia, 2014; Georgatou et al., 2018; Cox et al., 2019). Earlier sulfide saturation during continental arc magmatism is attributed to either (1) pressure and temperature controls on sulfide stability (Jenner, 2017; Cox et al., 2019), and/or (2) garnet crystallisation (Cox

et al., 2019; Lee and Tang, 2020). In Model 1, pressure and/or temperature effects enhance sulfide stability, permitting high- $fO_2$  magmas to fractionate sulfides near the base of the crust. In Model 2, lower-crustal garnet fractionation promotes sulfide saturation by depleting a magma in FeO, a consequence of the dependence of sulfur solubility on magma FeO content (O'Neill and Mavrogenes, 2002). However, the preferential uptake of  $Fe^{2+}$  relative to  $Fe^{3+}$  suggests that extensive lower-crustal garnet fractionation would eventually increase magma  $fO_2$  and therefore sulfur solubility (Lee and Tang, 2020). Lee and Tang (2020) suggest this garnet-driven auto-oxidation re-dissolves entrained sulfides, releasing Cu into the magma, which eventually partitions into magmatic fluids.

Both models suggest sulfides crystallise in the lower continental crust, forming Cu-rich cumulates, consistent with the Cu and Cu/Ag-depleted nature of the upper continental crust (Jenner, 2017; Chen et al., 2020). However, Model 2 provides a mechanism to transport ‘trapped’ Cu to upper crustal levels, a necessary step in porphyry ore formation (Lee and Tang, 2020). As garnet fractionation is restricted to magmas crystallising at high-pressures at the base of the continental crust (Alonso-Perez et al., 2009), Model 2 has been used to explain the dominance of porphyry Cu deposits at continental rather than oceanic arcs (Lee and Tang, 2020). An alternative, yet untested model involves magma ascent rapid enough to avoid substantial sulfide fractionation in the lower crust and therefore circumvent the need to identify a mechanism to rework and transport lower-crustal Cu-rich resources to upper-crustal levels (Jenner, 2017).

Here, we present major and trace element data [see Supplementary Materials] for volcanic rocks from several Pliocene-Holocene stratovolcanoes (Apagado, Hornopirén Villarrica, Quetrupillán, Lanín, San Pedro, Ollagüe) situated

along the Chilean segments of the Andean Volcanic Arc, South America (Fig. 1). We show that magmas ascending through thick ( $\geq 70$  km) crust fractionate a greater proportion of garnet and sulfide at the base of the continental crust than those transiting thinner ( $\leq 40$  km) crust. Thus, extensive garnet fractionation appears to enhance sulfide stability and Cu-depletion. We also identify instances where garnet and Cu-depleting sulfide fractionation appears minimal, specifically at locations of high magma flux.

## RESULTS AND DISCUSSION

Copper concentrations and Cu/Ag of continental arc stratovolcanoes in Ecuador (Georgatou et al., 2018) and at Antuco Volcano, Chile (Cox et al., 2019) show positive trends with MgO, replicated here by our new Cu and Cu/Ag data for several Chilean stratovolcanoes (Fig. 2a, b). The decrease in Cu and Cu/Ag with decreasing MgO suggests removal of sulfides from many Chilean stratovolcano magmas across their entire compositional range (Cox et al., 2019). This is in contrast to oceanic arc-like magmas erupting through thinner crust (e.g., Manus Basin magmas, Fig. 2), which show sulfide saturation at later stages of differentiation ( $\sim 3$  wt.% MgO), where sharp decreases in Cu and Cu/Ag coincide with the onset of magnetite fractionation (Jenner et al., 2010). Many of the primitive (high-MgO) Chilean stratovolcano samples have lower Cu/Ag relative to the global mid-ocean ridge basalt (MORB) array, suggesting that most magmas have been affected by some degree of sulfide removal in the lower continental crust, prior to ascent (Cox et al., 2019). This interpretation is consistent with the high-Cu/Ag nature of continental arc cumulates (Chen et al., 2020). Samples from Villarrica are an exception, having elevated Cu and Cu/Ag relative to other Chilean magmas and showing trends comparable to the low-pressure Manus Basin suite.

Unlike Manus Basin magmas, all our Chilean samples show evidence for garnet fractionation, having  $(\text{Dy/Yb})_N$  ratios  $>1$  (Fig. 3a). ‘Shape coefficients’ [cf. O’Neill (2016)] are used to further evaluate the linear slope ( $\lambda_1$ ) and curvature ( $\lambda_2$ ) of normalised rare earth element patterns (Fig. 3b; see Supplementary Materials for discussion). The bulk of the Chilean stratovolcano dataset clusters tightly within a narrow range of  $\lambda_1$  (5 to 11) and at slightly higher values at a given  $\lambda_2$  than the MORB array and Manus Basin suite. These differences are consistent with garnet fractionation (Fig. 3a) from the Chilean magmas. Both Ollagüe and San Pedro stratovolcanoes erupt through extremely thick continental crust ( $\geq 70$  km) and display stronger garnet [i.e., higher  $\lambda_1$  and  $(\text{Dy/Yb})_N$ ; Fig. 3] and sulfide fractionation signatures than Chilean magmas erupting through thinner crust (i.e.,  $<40$  km). We suggest the strength of garnet and sulfide fractionation signatures at Ollagüe and San Pedro reflect differences in crustal thicknesses, which across their Pliocene-Holocene life cycle are unlikely to have differed significantly from those observed today (Mamani et al., 2010). Positive correlations between  $(\text{Dy/Yb})_N$  and  $\text{Dy/Dy}^*$  across our Chilean datasets suggest amphibole crystallisation followed garnet removal (Fig. 3a) at lower-crustal depths. Indeed, experimental studies have demonstrated that at  $\geq 1.2$  GPa ( $\geq 40$  km) garnet crystallises first at high temperatures ( $1000^\circ\text{C}$ ), followed by clinopyroxene and amphibole fractionation (Alonso-Perez et al., 2009).

Ollagüe and San Pedro, with the strongest garnet signatures, have the lowest Cu/Ag of the studied stratovolcanoes (Fig. 2). Thus, garnet fractionation appears to enhance crystalline sulfide fractionation and consequently, would result in the formation of more extensive sulfide cumulates at the base of thicker compared to thinner continental crust. Remobilisation of this Cu-rich reservoir could potentially

account for the occurrence of some of the world’s largest porphyry Cu deposits in areas where the continental crust is thick and garnet fractionation is extensive. However, contrary to the model presented by Lee and Tang (2020), our data suggests that garnet fractionation does not appear to provide a sufficient enough increase in magma  $fO_2$  to re-dissolve sulfides. This is likely because the sulfide stability field extends beyond the  $fO_2$  range of magmas fractionating under lower-crustal pressure and temperature conditions (Matjuschkin et al., 2016; Nash et al., 2019). Thus, secondary mechanisms, such as injection of anomalously high  $fO_2$  and/or sulfide undersaturated magmas, would be required to mobilise this deep Cu reservoir.

Similarities in Cu and Cu/Ag systematics between Villarrica and Manus Basin suites (Fig. 2) suggests that the Villarrica magmas achieved sulfide saturation following low-pressure magnetite fractionation and later in their evolutionary history (i.e., at lower MgO) than the other Chilean stratovolcano magmas. Samples from Villarrica show the least evidence of deep garnet fractionation among all our studied volcanoes, which contrasts with nearby samples erupting through similarly thick crust (Quetrupillán, Lanín). This implies fractionation of Villarrica magmas at mid- to upper-crustal pressures, where magnetite rather than garnet is stable (Matjuschkin et al., 2016). Thus, in contrast with the other Chilean stratovolcanoes, Villarrica magmas must have ascended rapidly enough to limit the effects of concomitant garnet and sulfide fractionation in the lower crust [i.e., before melt temperatures decreased to the 1000°C required for garnet fractionation (Alonso-Perez et al., 2009)].

Although uncommon, ‘Villarrica-type’ trends are not unique across Chile, with many samples from Llaima and the Puyehue–Cordon Caulle Volcanic Complex

[PCCVC; Fig. 2a, S2] showing similar Cu enrichments (data from GeoROC database). At Villarrica, this appears to be a strongly localised effect; Quetrupillán and Lanín, part of the same across-arc volcanic chain, show no Cu-enrichment (Fig. 2). Significantly, Villarrica and Llaima are the most active volcanic systems in the Southern Volcanic Zone (SVZ), based on historical records [64 and 50 eruptions since AD 1800, respectively (Global Volcanism Program, 2013)], while the PCCVC has also erupted several times in this period. Moreover, all three systems are characterised by an elevated eruptive flux, having volumes well in excess of 300 km<sup>3</sup>, the largest among all volcanoes in the SVZ, and considerably greater than the average edifice volume (100 km<sup>3</sup>) (Volker et al., 2011). This suggests a link between high levels of magma productivity and conditions promoting rapid crustal ascent and the transport of high-Cu magmas to upper-crustal levels.

## **PORPHYRY ORE FORMATION**

Higher degrees of mantle melting, consistent with geophysical evidence for elevated slab-fluid release beneath Villarrica and Llaima (Dzierma et al., 2012) and their high eruption rates, may facilitate their rapid magma ascent. A high magmatic flux may maintain elevated lower-crustal temperatures, preserving an open ‘pathway’ through the lower crust and assisting rapid magma ascent, limiting the effects of magma stalling and storage on fractionation processes. Rapid magma ascent, limiting high temperature garnet fractionation (~1000°C) at the base of the continental crust, is potentially also facilitated by major fault systems [e.g., Liquiñe-Ofqui Fault Zone (LOFZ); Fig. 1], which are associated with many economic porphyry Cu deposits in northern Chile (Sillitoe, 2010). However, several Chilean volcanoes on the LOFZ show Cu depletions (e.g., Yate, Hornopirén, Lonquimay), so fault-related transport alone is insufficient to explain the ascent of Cu-rich magmas.



Our new data identify an atypical scenario, contrasting with the usual chalcophile element cycle at continental arcs (i.e., formation of Cu-rich cumulates in the lower crust), that allows Cu-rich magmas to ascend to upper-crustal levels. Following ascent, processes inhibited in the lowermost continental crust may exploit the excess Cu in the system. For example, low-pressure S degassing causes sulfide undersaturation, destabilises sulfides and leads to melt Cu enrichment (Reekie et al., 2019). Hence, S-degassing during crystallisation of magmas with ‘Villarrica-style’ low-pressure signatures might dissolve entrained sulfides, crystallised following magnetite fractionation [see also Wilkinson (2013) and Blundy et al. (2015) for additional mechanisms that could exploit low-pressure sulfide cumulates and aid ore formation]. Consequently, late-stage exsolved magmatic fluids might be enriched in Cu compared to those exsolved from typical continental arc magmas, which may enhance the ore-forming process.

As the pattern of elevated Cu concentrations is only observed at a small number of stratovolcanoes in the Chilean Andes, it could explain the sporadic and restricted distribution of porphyry ore deposits in the region. However, it is the thicker crust of the Central Andes that hosts many of the largest porphyry Cu deposits (Sillitoe, 2010), rather than the thinner crust of the Southern Andes. This could be because ore deposits, possibly forming beneath sites such as Villarrica today, are yet to be exposed. Additionally, the lack of ‘Villarrica-type’ Cu trends observed at currently-active stratovolcanoes in Central/Northern Chile may also partly reflect sampling bias in available datasets; most of our samples were collected from southern Chile and datasets including Cu analyses for central and northern Chile volcanoes are scant in the literature. Alternatively, the possibility remains that reworking of the more substantive Cu-rich cumulates at the base of the thickest crust

in Chile is still required to explain the dominance of porphyries in these regions (e.g., through injection of anomalously sulfide undersaturated magmas, which would assimilate pre-existing sulfides). Regardless, we identify a mechanism to transport high-Cu magmas to the upper crust – rapid magma ascent rates. Together with the greater volume of magmas and therefore volume of Cu at sites of elevated magmatic fluxes, Villarrica-style magmatism might play a key role in enhancing ore formation.

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282

283 **Figure captions:**

284 **Fig. 1.** Map showing the location of the Chilean stratovolcanoes investigated in the  
285 current study, Moho depth (red text) (Tassara and Echaurren, 2012), subducting slab  
286 age and Nazca Plate velocity (Stern, 2004). LOFZ: Liquiñe-Ofqui Fault Zone;

PCCVC: Puyehue – Cordon Caulle Volcanic Complex. Maps constructed using the Generic Mapping Tool (Wessel et al., 2019).

**Fig. 2.** Select bivariate plots of the Chilean stratovolcano datasets. Cu (a) and Cu/Ag (b) continually decrease with MgO (black arrows) in the continental arc stratovolcano datasets [including at Antuco; C19: data from Cox et al. (2019)]. This differs to the trend observed (blue arrows) in the Manus Basin sample suite [data from J12: Jenner et al. (2012)], where both Cu and Cu/Ag increase to a ~3 wt% MgO maximum before they plummet due to magnetite fractionation induced sulfide saturation [the onset of magnetite fractionation is identified by a sudden drop in the total Fe contents of the Manus Basin suite at ~4 wt.% MgO (panel c)]. Samples from Villarrica, and most analyses from Llaima and the Puyehue – Cordon Caulle Volcanic Complex (PCCVC) (data for all Chilean stratovolcanoes sourced from the GeoROC database, <http://georoc.mpch-mainz.gwdg.de/georoc>: accessed 25/01/20), have Cu contents elevated relative to other Chilean and Ecuadorian [data from G18: Georgatou et al. (2018)] stratovolcanoes and the global mid-ocean ridge basalt (MORB) array [J12] at a given MgO. Filtered Cu and MgO from the GeoROC Databases are collated in Supplementary Material S3. Ag analyses are unavailable from Llaima and PCCVC.

**Fig. 3.** Rare earth element (REE) systematics of the Chilean stratovolcano datasets. (a)  $(\text{Dy}/\text{Yb})_N$  versus  $\text{Dy}/\text{Dy}^*$ , after Davidson et al. (2012) . All samples show evidence of an initial stage of garnet fractionation prior to more extensive amphibole fractionation, most strongly developed for volcanoes on thickest crust, and most

weakly for Villarrica (the Manus Basin oceanic-crust samples show no evidence of garnet fractionation). Insets represent the expected REE patterns in each quadrant. (b) ‘Shape coefficients’, defined by O’Neill (2016);  $\lambda_1$ : linear slope of the REE pattern,  $\lambda_2$ : curvature of the REE pattern (outlined in Supplementary Materials). The red dashed tramlines highlight the field defined by mid-ocean ridge basalts (MORB) [data from Jenner and O’Neill (2012)]. Ocean island basalt (OIB; Hawaii) data are plotted to exemplify the offset related to garnet fractionation [data from Feigenson et al. (2003)]. The vectors ‘Amph fract.’ and ‘Grt fract.’ highlight expected fractionation trends for amphibole and garnet, respectively. 25 – 40 km and >70 km denote the thickness of the continental crust on which the stratovolcanoes are sat. C19: data for Antuco stratovolcano from Cox et al. (2019); J12: data for the Manus Basin (MB) magmas from Jenner et al. (2012).

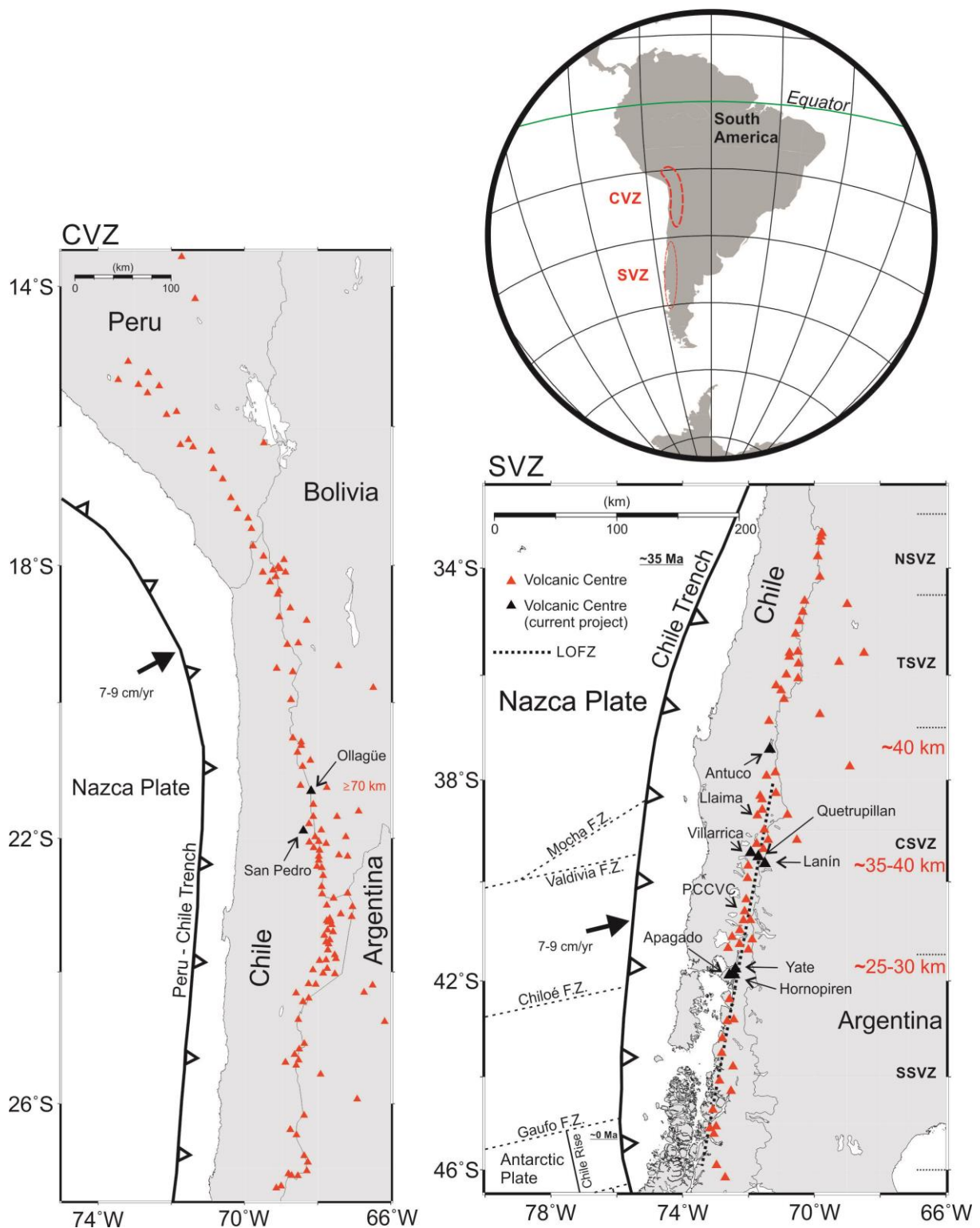
## **Acknowledgments:**

We thank Alvaro Amigo Ramos, Ginevra Chelli and David Cavell for fieldwork assistance and Iain McDonald (Cardiff University) and Lin Marvin-Dorland (University of Leicester) for laboratory support. We acknowledge funding for this work from the Natural Environment Research Council (NERC): NE/M000427/1 (Mantle volatiles: processes, reservoirs & fluxes), NE/M010848/1 [SoS Tellurium & Selenium Cycling & Supply ] and NE/P017045/1 [From Arc Magmas to Ore Systems]. All data are presented in the main manuscript or Supplementary Materials. Gerald Dickens (Editor) and three anonymous reviewers are thanked for their thorough and constructive comments during review, which greatly improved the manuscript.

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335 Figure 1

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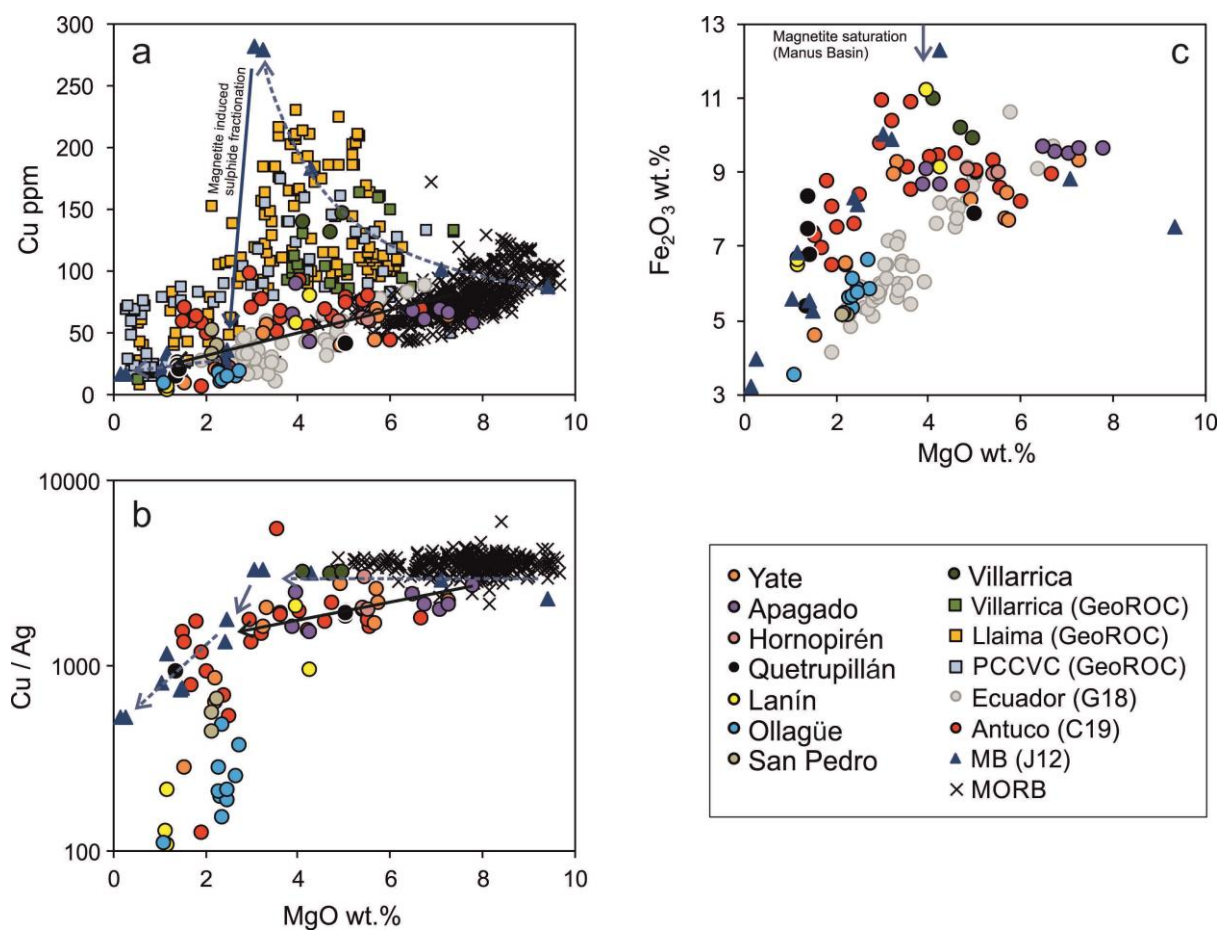


'Elevated magma fluxes deliver high-Cu magmas to the upper crust'

338 Figure 2

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'Elevated magma fluxes deliver high-Cu magmas to the upper crust'

341 Figure 3

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