



# How to make porphyry copper deposits

Cin-Ty A. Lee<sup>\*</sup>, Ming Tang

Department of Earth, Environmental and Planetary Sciences, Rice University, Houston, TX, USA

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## ABSTRACT

Much of the world's economic copper resources are hosted in porphyry copper deposits (PCDs), shallow level magmatic intrusions associated mostly with thick (> 45 km) magmatic arcs, such as mature island arcs and continental arcs. However, a well-known, but unresolved paradox, is that arc magmas traversing thick crust, particularly in continental arcs, are generally depleted in Cu whereas in island arcs, where PCDs are less common, magmas become enriched in Cu. Here, we show that the formation of PCDs requires a complex sequence of intra-crustal magmatic processes, from the lower crust to the upper crust. PCDs form when the crust becomes thick (> 45 km) enough to crystallize garnet. Garnet fractionation depletes Fe from the magma, which drives sulfide segregation and removal of most of the magma's Cu into the lower crust, leaving only small amounts of Cu in the residual magma to make PCDs. However, because garnet is depleted in ferric iron, the remaining Fe in the magma becomes progressively oxidized, which eventually oxidizes sulfide to sulfate, thereby releasing sulfide bound Cu from the magma into solution. This auto-oxidation of the magma, made possible by deep-seated garnet fractionation, increases the ability of endogenic magmatic fluids to self-scavenge Cu from large volumes of otherwise Cu-poor magmas and then transport and concentrate Cu to the tops of magmatic bodies. Examination of the occurrence of PCDs in the central Andes shows that ore formation occurs when continental arcs reach their maximum thickness (> 60 km), just before the termination of magmatism.

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## 1. Introduction

Copper (Cu) is one of many “mineral” resources needed to support the world's increasing needs for energy production, storage and transport. Because background concentrations of Cu at the Earth's surface are typically less than 30 ppm (Rudnick and Gao, 2003), economically viable extraction can only come from ore deposits, highly localized regions of the Earth, where a sequence of mysterious geologic processes conspire to enrich rocks in metals by orders of magnitude (Hedenquist and Lowenstern, 1994). Most economic Cu deposits are found in porphyry magmatic systems, km-scale magmatic bodies characterized by silicic compositions and a distinctive porphyritic texture in which large (cm-scale) euhedral feldspar phenocrysts sit within a fine-grained groundmass (Sillitoe, 2010). The Cu ore itself is confined to localized cupolas or wallrock near the tops of these porphyritic bodies. Cu concentrations in these cupolas can reach up to 1–3 wt.%, equivalent to an enrichment of 10,000 times that of background concentrations (Sillitoe, 2010).

Like most ore deposits, porphyry copper deposits (PCDs) are rare, but they exhibit spatiotemporal patterns of distribution and

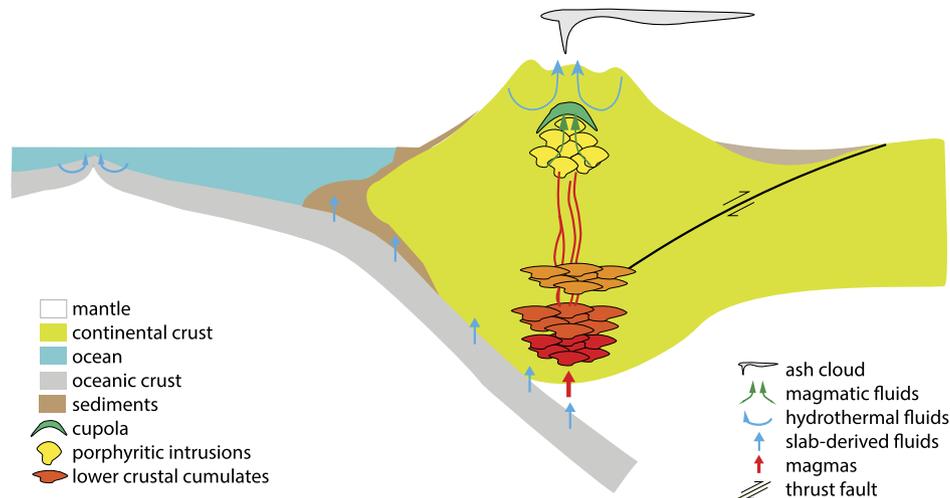
geochemical signatures that may hint at their origins. They represent shallow level intrusives (2–5 km) (Sillitoe, 2010), not too shallow that they erupt and not too deep that they do not degas (Fig. 1). On a global scale, they are almost exclusively found in magmatic arcs associated with subduction zones, not in extensional or intraplate settings. But even within arcs, they tend to be associated with continental arcs, where oceanic lithosphere subducts beneath continental lithosphere and where the magmatic arc crust is thick (35–80 km) (Kesler, 1997; Sillitoe, 1972; Sinclair, 2007) (Fig. 2). Where arc crust is thin (< 25 km), as in most island arcs, they are less common. Magmas hosting PCDs have also been shown to be strongly associated with high Sr/Y ratios (Chiaradia et al., 2012; Kay and Mpodozis, 2001; Loucks, 2014), which is most likely controlled by the involvement of garnet or amphibole in the generation of these magmas, but whether high Sr/Y ratios are imparted by the subducting slab or by intracrustal differentiation is debated (Lee et al., 2006, 2007; Macpherson et al., 2006; Moya, 2009; Sun et al., 2011).

## 2. Hypotheses for the formation of porphyry copper deposits

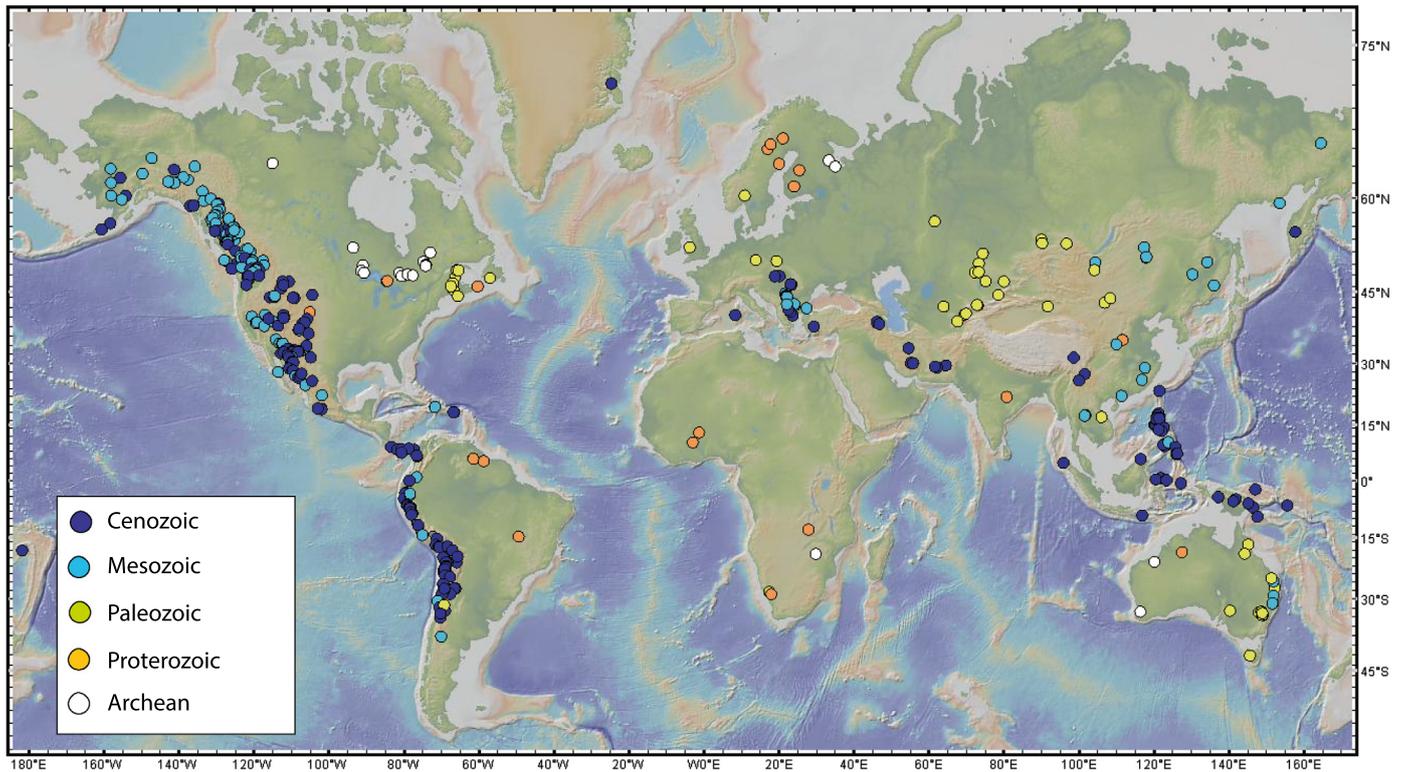
Making a PCD clearly involves a sequence of events wherein Cu is first mobilized, then scavenged from the source rock and finally immobilized to concentrate the metals into an enriched

<sup>\*</sup> Corresponding author.

E-mail address: ctleee@rice.edu (C.-T.A. Lee).



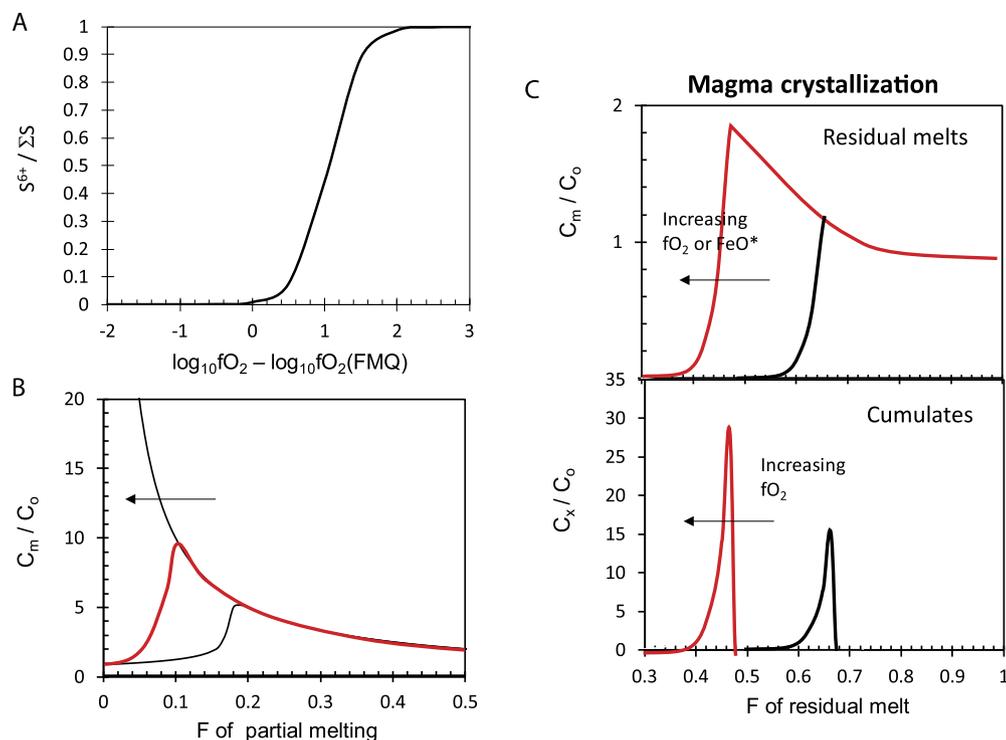
**Fig. 1.** Schematic of an ocean-continent subduction zone (“continental arc”) denoting areas in which ore-forming elements are mobilized, transported and enriched. Here, the arc crust is thick (> 45 km). Porphyry copper deposits (PCDs) represent shallow level intrusions (2–5 km) in the crust. Mineralization of Cu ores tend to occur at the tops of porphyry systems in cupolas. Possible regimes where Cu may be mobilized include hydrothermal circulation at mid-ocean ridge centers, dehydration or melting of the subducting slab, and late stage scavenging by magmatic fluids (green arrows). Formation of deep crustal cumulates, if sulfide-saturated, has the potential of removing and sequestering chalcophile elements like Cu deep in the crust. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)



**Fig. 2.** Occurrence of porphyry copper deposits (PCDs) through time. All were formed in the magmatic arcs associated with subduction zones, but there is a preference for regions of thick arc crust (> 35 km), such as continental arcs and mature island arcs. The majority are Mesozoic and Cenozoic in age due to preservation bias from the cumulative effects of erosion. Data from Sinclair (2007).

reservoir (Wilkinson, 2013). Key to understanding Cu’s behavior is understanding the behavior of S. Cu, a chalcophile element, strongly partitions into sulfide minerals, where S is in the  $-2$  (FeS) or  $-1$  state (FeS<sub>2</sub>) (Kiseeva and Wood, 2013; Li et al., 1996; Ripley et al., 2002). Cu is incompatible in most of the common silicate phases (Le Roux et al., 2015; Lee et al., 2012; Liu et al., 2014; Reekie et al., 2019). Under highly oxidizing conditions, wherein the dominant speciation of S is sulfate (S<sup>6+</sup>), sulfide is destabilized and Cu is efficiently transported into the melt or fluid phase (Jugo et al., 2005; Lee et al., 2012) (Fig. 3). Under con-

ditions reducing enough to stabilize sulfide species, Cu will be retained in sulfide minerals if the system is sulfide saturated (Fig. 3b). Removing Cu from a sulfide-bearing source requires melting degrees high enough to exhaust sulfide or conditions oxidizing enough to destabilize sulfide (Ding and Dasgupta, 2017; Lee et al., 2012). Similarly, when a magma reaches sulfide saturation, Cu is efficiently removed from the melt, resulting in Cu-rich cumulates (Fig. 3c). Of course, these are generalized behaviors as there are a number of complicating factors. For example, high degree melting (> 20%) will exhaust sulfide and make Cu incom-



**Fig. 3.** Generalized behavior of S and chalcophile elements during melting and crystallization. A) Sulfur speciation in basaltic melt as a function of oxygen fugacity in  $\log_{10}$  units relative the fayalite–magnetite–quartz (FMQ) buffer (Jugo et al., 2010). B) Concentration of a chalcophile element in a primary mantle melt (equilibrium batch melt) as a function of degree of melting ( $F$ ) of a peridotite with 200 ppm S and a chalcophile element partition coefficient between melt and sulfide of  $\sim 1000$ . The chalcophile element is depleted in the melt before sulfide exhaustion, but after sulfide exhaustion, the chalcophile element behaves perfectly incompatibly. Point of sulfide exhaustion depends on solubility of S in the melt, which is enhanced at high  $fO_2$  or high FeO content of melt. C) Behavior of a chalcophile element during crystallization of a magma ( $F$  represents residual melt fraction). Top panel shows the evolution of the melt and the bottom panel represents evolution of the complementary crystal cumulates. Before sulfide saturation, the chalcophile element concentration in melt increases like an incompatible element. Once sulfide saturates, chalcophile elements are rapidly depleted from the melt. Corresponding cumulates are sulfide-free before sulfide saturation, but when sulfide saturates, cumulates experience an abrupt increase in chalcophile element concentration. Increasing  $fO_2$  or  $FeO^*$  of the melt delays sulfide saturation. Decreasing  $fO_2$  or  $FeO^*$  by any number of mechanisms (Jenner et al., 2010) will thus promote sulfide saturation.  $C_x$  = cumulate composition,  $C_m$  = melt composition, and  $C^0$  = bulk composition of system. Calculations are meant to be schematic given uncertainties in sulfide solubility and S speciation as well as uncertainties in T and P of melting or crystallization. The above figures should be used only as a general guide to the behavior of S and chalcophile elements (Lee et al., 2012) as many additional factors make it challenging to develop unique models (melting degree, source composition, and effects of pressure, temperature, water and melt composition on S solubility and speciation).

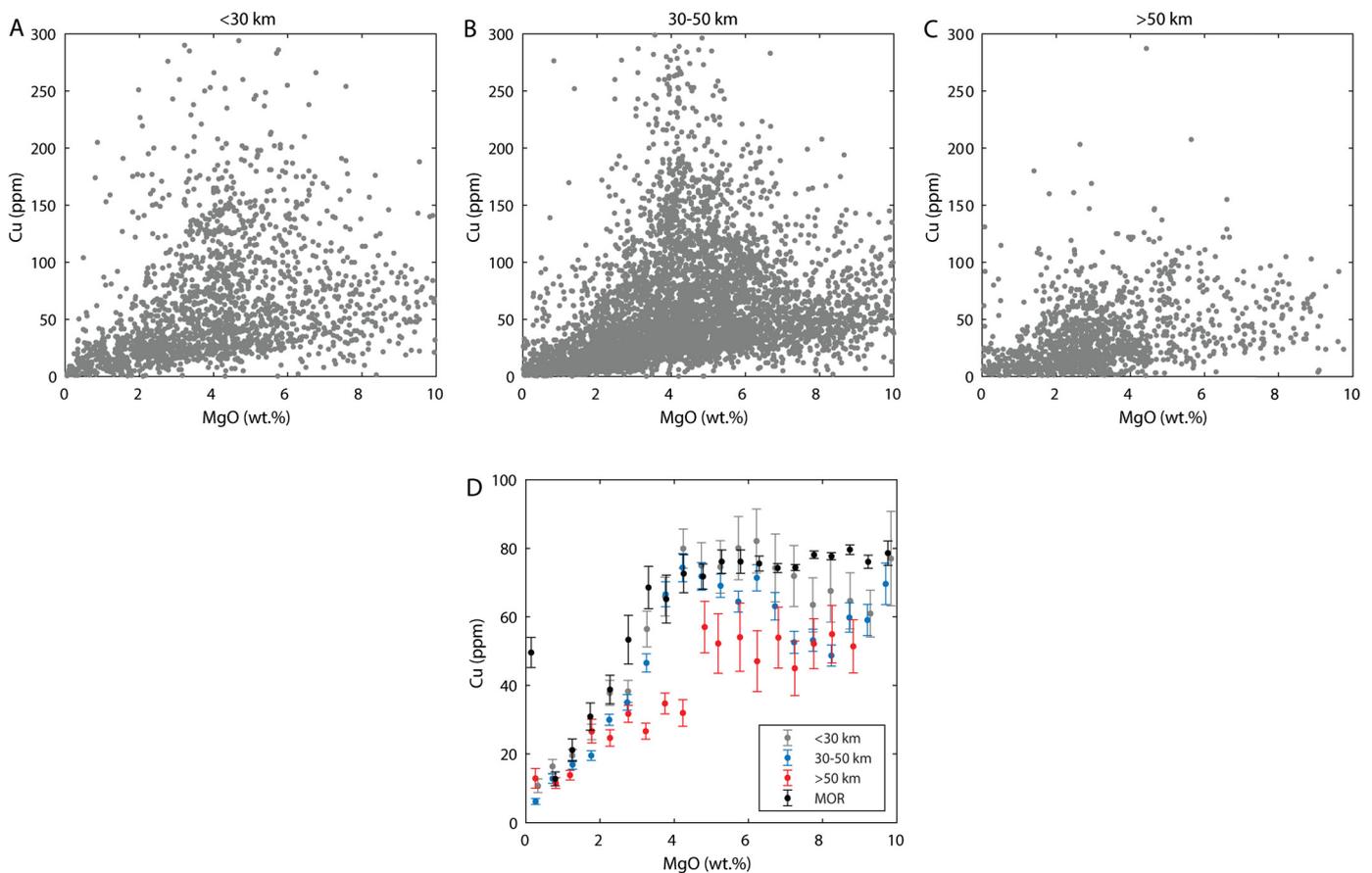
patible, regardless of oxygen fugacity. Source composition may also play a role. Finally, pressure, temperature, water content and melt composition can control solubility and speciation in ways that are not yet fully resolved.

Most hypotheses for the origin of PCDs can be broadly categorized as source or differentiation driven (Fig. 1). In source driven scenarios, parental magmas from the deep crust, lithospheric mantle, mantle wedge or subducting slab are thought to be enriched in Cu from the outset. Proposed mechanisms of generating Cu-rich magmas include partial melting of subducted oceanic crust (Sun et al., 2010, 2011), metasomatized continental lithospheric mantle (Richards, 2009; Rielli et al., 2018), arc lower crust or fluid-modified mantle wedge (Hattori and Keith, 2001; Lee et al., 2012; Richards, 2009). In these hypotheses, the effects of magmatic differentiation and shallow level processes are of secondary importance. In contrast, in differentiation driven scenarios, parental magmas need not be enriched in Cu, but widespread scavenging of mid-crustal to shallow level plutons followed by efficient trapping and concentration of the mobilized Cu into a localized reservoir (ore) is required (Henley et al., 2015; Kay and Mpodozis, 2001; Sillitoe, 2010; Wilkinson, 2013). For all of these hypotheses, oxidizing conditions are thought to be important in mobilizing Cu, but the origin of such oxidation is still unclear. Few of these hypotheses, in their current form, can explain why PCDs occur mostly in continental arcs.

### 3. The paradoxes of copper

Cu displays intriguing behavior in arcs. First, the Cu contents of primitive arc magmas ( $MgO > 6$  wt.%) in both continental and island arcs are not only similar to each other but also to ocean floor basalts (e.g., Mid-ocean Ridge Basalts) (Lee et al., 2012), suggesting minimal contribution of Cu from subducting slabs (Fig. 4). These similarities also suggest that the redox conditions in subarc mantle cannot be significantly different from that beneath mid-ocean ridge spreading centers. If subarc mantle were more oxidizing, sulfide would be more efficiently consumed during melting, resulting in much higher Cu contents in the magmas. These similarities in redox conditions are perplexing because nearly all erupted arc lavas (Carmichael, 1991; Cottrell and Kelley, 2011) and PCDs themselves (Ballard et al., 2002) are more oxidized than typical seafloor basalts. Are the parental magmas of PCDs oxidized from the outset or do they undergo oxidation during differentiation?

Another intriguing observation pertains to the compositions of arc magmas as they differentiate and evolve (Chiaradia, 2014; Lee et al., 2012) (Figs. 4 and 5). Continental arc magmas become Cu-depleted while most island arcs become Cu-enriched. PCDs are thus associated with magmas depleted in Cu (i.e., barren in Cu), but island arc magmas with relatively higher Cu content generally do not have PCDs. This divergence in the behavior of Cu during differentiation is undoubtedly attributed to differences in the behavior of sulfur: sulfide saturation in the case of Cu depletion and suppression of sulfide saturation in the case of Cu



**Fig. 4.** Copper concentrations as a function of MgO in modern arcs built on thin (< 30 km, A), normal (30–50 km, B) and thick (> 50 km, C) crust. Island arcs are thin and continental arcs are generally thick. The arc samples examined here are volcanic rocks of Pleistocene to Holocene ages. Shown in D are MgO-binned (bin size = 0.5 wt.%) average Cu concentrations in mid ocean ridge settings (MOR) and arcs of thin, normal and thick crust. Arc data are from Farner and Lee (2017) and MOR data are from Jenner et al., 2010).

enrichment (Ding and Dasgupta, 2017). What controls the timing of sulfide saturation are pressure, temperature, oxygen fugacity, and magma water and iron content. While there may be variations in initial oxygen fugacity, the variations are too small to play a dominant role (Kelley and Cottrell, 2009; Lee et al., 2005). Enhanced stability of sulfide at high pressure may also play a role (Cox et al., 2019; Matjuschkin et al., 2016). However, the most important factor might be how Fe evolves because sulfide solubility strongly correlates with magma FeO (Li and Ripley, 2005; O’neill and Mavrogenes, 2002). Why the behavior of Fe might be controlled by crustal thickness is unclear.

#### 4. Thick (continental) versus thin (island) arcs

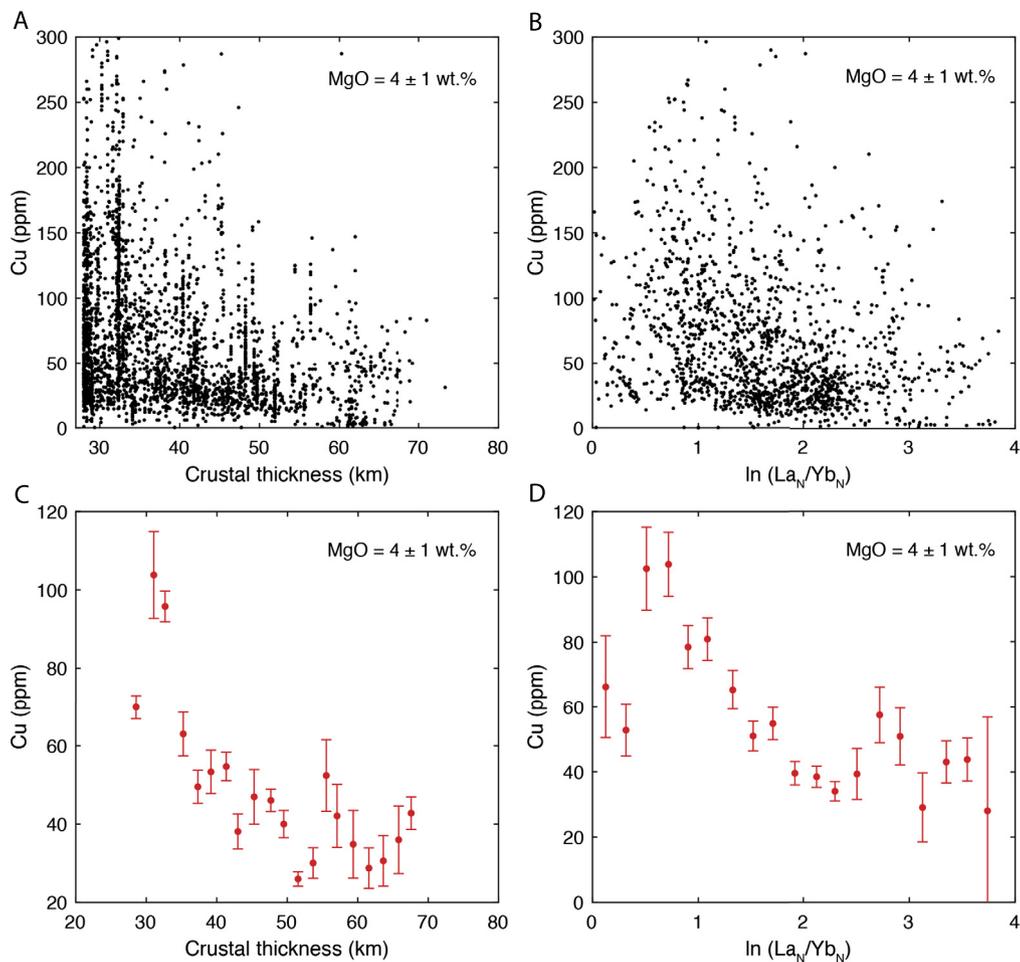
##### 4.1. The iron divergence

Arc magmas built on medium to thick crust undergo early Fe depletion, whereas arc magmas built on the thin crust (typically island arc) and/or on the ocean floor first enrich in Fe before undergoing Fe depletion (Miyashiro, 1974; Zimmer et al., 2010). The early Fe-depleting series is commonly referred to as the calc-alkaline differentiation series and the early Fe-enriching trend as the tholeiitic series (Zimmer et al., 2010). What causes this divergence in Fe content between the two arc environments is debated, but pressure of differentiation and crustal thickness appear to play a role. Fe-depletion is clearly more pronounced in the thick crust (> 50 km) characteristic of mature island arcs and continental arcs; Fe-enrichment is almost never seen in continental arcs (Farner and Lee, 2017). Consistent with a pressure and crustal thickness effect is that Fe content in cumulates increases with

crustal thickness, complementary to the decreasing magmatic Fe content with crustal thickness (Chin et al., 2018). This divergence in the behavior of Fe is important to understanding Cu’s behavior. Sulfide solubility increases with FeO content, thus Fe-depleting magmatic series should deplete in Cu, consistent with the low Cu contents of continental arc magmas (Lee et al., 2012). In contrast, sulfide saturation may be delayed in Fe-enriching magmatic series, allowing Cu to increase as seen in island arc magmatic suites. Again, consistent with this line of logic is the fact that deep crustal cumulates from continental arcs contain sulfide and have the high concentrations of Cu needed to complement the Cu-depleted nature of continental arc magmas (Jenner, 2017; Lee et al., 2012) (Fig. 6). The cause of Fe depletion has been widely thought to be driven by magnetite ( $\text{Fe}_3\text{O}_4$ ) fractionation (Berndt et al., 2004; Zimmer et al., 2010). However, magnetite has a 2:1 ratio of ferric to ferrous Fe, which should drive reduction of the magma (Jenner et al., 2010), inconsistent with the fact that arc lavas, particularly in thick or continental arcs, are oxidized by the time they rise to the surface. The solution to this dilemma is to invoke a fractionating phase that simultaneously depletes the magma of Fe and oxidizes what remains of the Fe in the residual magma. This phase must also be favored at high pressures in order to explain the systematic variations of the degree of Fe depletion with crustal thickness.

##### 4.2. Thick crust, garnet and auto-oxidation

Garnet has recently been suggested as the key fractionating phase in driving early Fe-depletion in arc magmas traversing thick

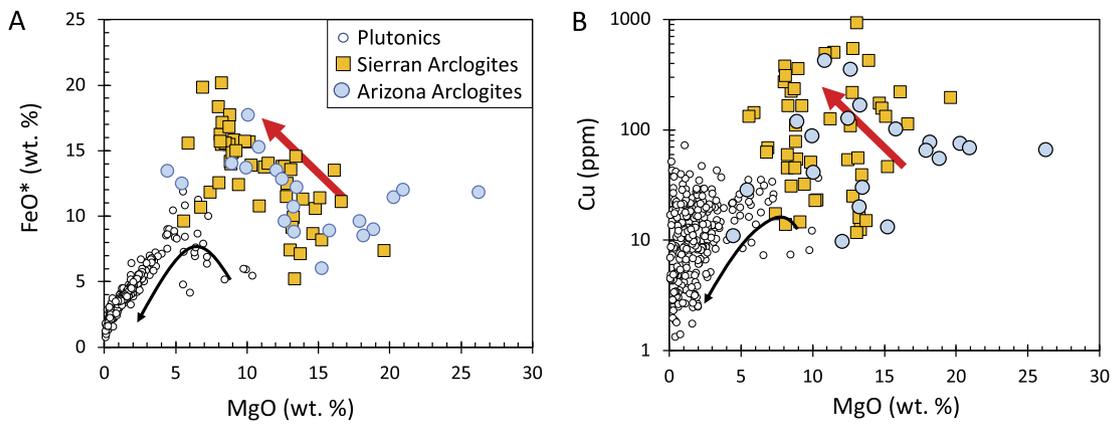


**Fig. 5.** Copper concentrations in modern arc magmas with  $4 \pm 1$  wt.% MgO as functions of crustal thickness (A) and natural logarithm of La/Yb, the latter normalized to chondrite (McDonough and Sun, 1995). (C) and (D) same as (A) and (B) respectively, but represent averages (1 standard error) of for a given crustal thickness interval. Crustal thickness is calculated from elevation assuming Airy isostasy following the methods in Lee et al. (2015) and Farner and Lee (2017). Data represent spatial averages over  $1 \text{ km}^2$  area to prevent sampling bias. Data are from compilation of Farner and Lee (2017) and available in Supplementary Table 1.

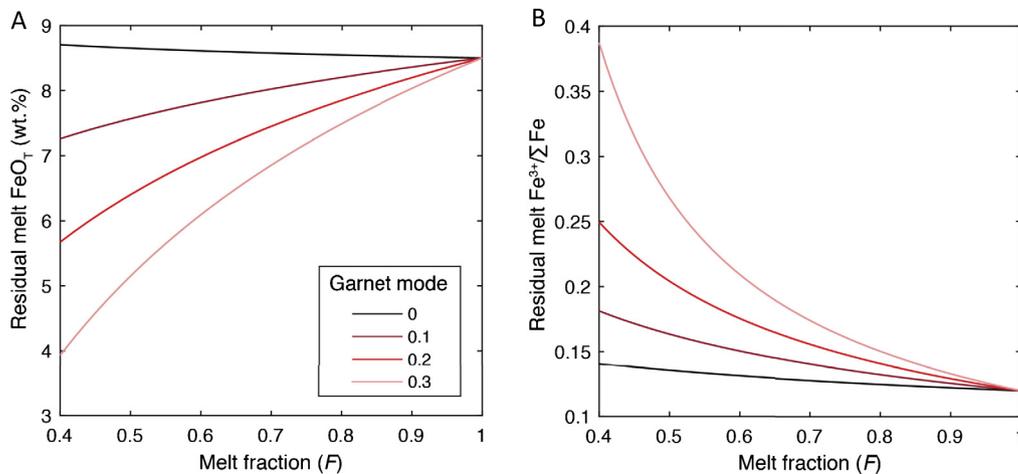
crust (Tang et al., 2018, 2019a). Magmatic garnet is enriched in Fe but poor in ferric iron component (Tang et al., 2019b), so garnet fractionation can do what magnetite cannot: oxidize and deplete in total Fe (Fig. 7). Both high pressures and hydrous conditions stabilize garnet, hence garnet fractionation is favored in subduction zones where the arc crust is thick ( $> 45$  km). Magnetite is still responsible for driving late Fe depletion in the tholeiitic series, but magnetite stability decreases substantially above  $\sim 1$  GPa, giving forth to rutile as the Ti-bearing phase and garnet as the dominant Fe bearing phase (Matjuschkin et al., 2016; Tang et al., 2019a). Garnet driven oxidation provides a simple explanation for why Fe depletion (and Cu depletion) and oxidation typify continental arc magmas, but rarely island arcs and never mid-ocean ridge settings. Indeed, only deep crustal cumulates from continental arc settings have the necessary high Fe contents to drive Fe depletion (Chin et al., 2018; Lee et al., 2006, 2007). Continental arc cumulates are represented by garnet pyroxenites (arclogites), many with high ( $> 50\%$ ) garnet mode and high Fe (Fig. 6). Arclogites indeed have the high Cu contents (hosted in magmatic sulfide) needed to balance the Cu-depleted nature of continental arc magmas as evidenced by arc cumulates from Arizona and California, USA (Lee et al., 2012) (Fig. 6). Recently, it has also been shown that arclogites have the high Nb/Ta ratios needed to balance the low Nb/Ta signatures of continental arc magmas and continental crust in general (Tang et al., 2019a). These high Nb/Ta ratios in the arclogites are controlled by magmatic rutile, which is also favored at high pressures like garnet (Tang et al., 2019a). In sum-

mary, all the geochemical observations indicate that a critical step in generating continental arc magmas is the formation of thick arc crust. The importance of thick arc crust has been suggested before, but in such studies, crustal thickening was invoked to drive metamorphic dehydration of amphiboles, resulting in the release of metal mobilizing fluids (Kay and Mpodozis, 2001). Here, we suggest that thick crust is critical because it forces deep-seated crystallization of garnet-bearing cumulates, which in turn drives oxidation, eventually making Cu available.

We thus propose that garnet-driven oxidation, favored at deep crustal levels ( $> 45$  km), is a necessary first step in priming the conditions to make PCDs. By the time magmas have become felsic and risen higher in the crust, they are oxidized enough to convert sulfide to more oxidized forms of sulfur, such as sulfate ( $\text{SO}_4^{2-}$ ) or  $\text{SO}_2$ . When magmas stall at shallow depths and cool, saturation in a free fluid phase composed of water or  $\text{CO}_2$ , combined with oxidizing conditions, mobilizes Cu from the entire pluton. We propose that these fluids are transported to the top of the pluton, where the contact with the colder country rocks serves as an efficient fluid trap (e.g., cupola), leading to the immobilization and concentration of Cu into an ore deposit (Fig. 8). Reaction of fluids with Ca-rich minerals (plagioclase or carbonates in country rock) could cause disproportionation of  $\text{SO}_2$  to sulfate and sulfide, the former precipitating as anhydrite and the latter as chalcopyrite (Henley et al., 2015).



**Fig. 6.** FeO\* (as total Fe) and Cu in Cretaceous–Paleogene arclogite xenoliths sampled from beneath the Sierra Nevada batholith (Lee et al., 2006, 2012) and in western Arizona (Chin et al., 2018; Erdman et al., 2016) compared to Cretaceous continental arc plutonic rock compositions (as represented by the Peninsular Ranges batholith in southern California Lee et al., 2007). Note that FeO- and Cu-depleted nature of evolved plutonic rocks can be explained by eventual fractionation of FeO- and Cu-rich arclogites. Arrows represent differentiation trends (black = magma; red = arclogite cumulates).



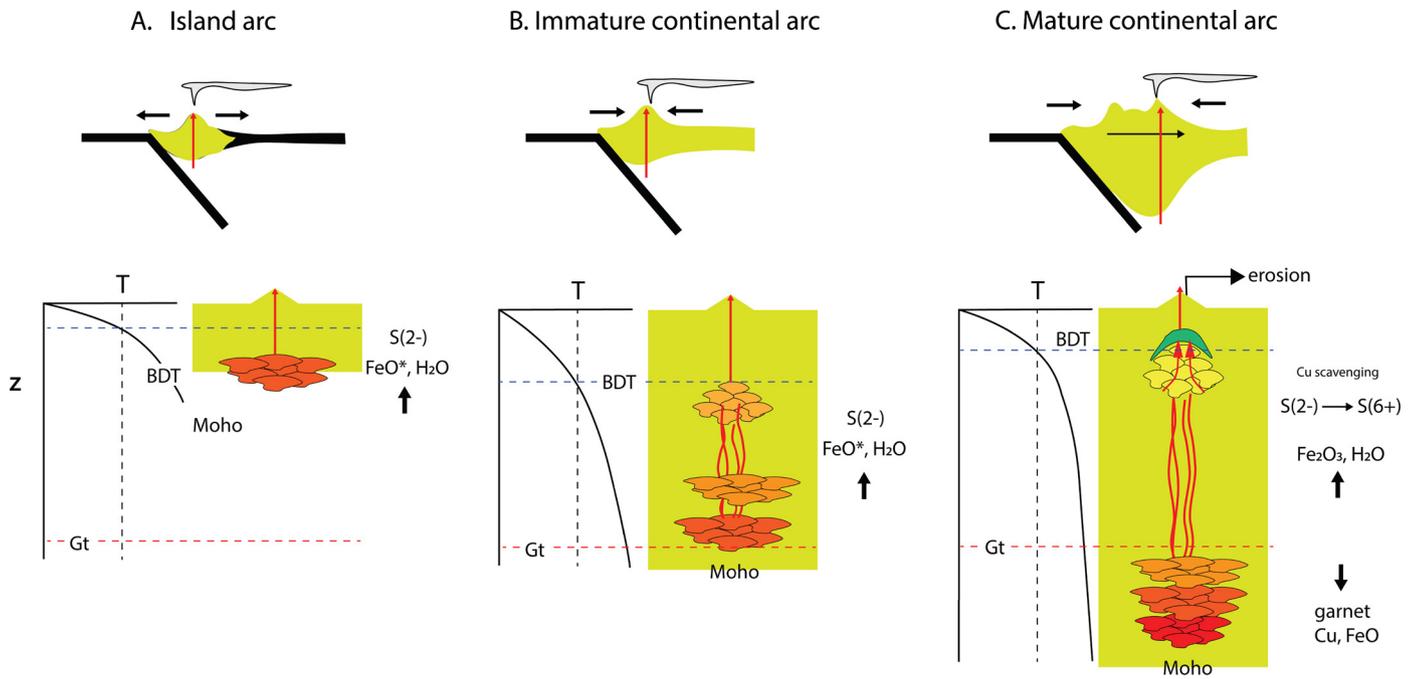
**Fig. 7.** Effect of garnet fractionation on the residual magma's iron content (as total FeO\*) and the proportion of iron in the system that is ferric (molar  $\text{Fe}^{3+}/\Sigma\text{Fe}$ ).  $F$  represents residual melt fraction. Because arclogite garnets are enriched in FeO but low in ferric iron proportion ( $\text{Fe}^{3+}/\Sigma\text{Fe} < 0.1$ ), fractionation of garnet results in depletion in total iron (FeO\*) but increasing oxidation of residual iron (Tang et al., 2018; Tang et al., 2019b). Calculations were done for garnet-clinopyroxene assemblages, assuming 0–0.3 garnet modes and 0–50% total Fe depletion through garnet fractionation after 60% crystal fractionation. Non-garnet phases have a bulk  $D(\text{Fe}^{2+})$  and  $D(\text{Fe}^{3+})$  of 1 and 0.8, respectively. The Fe-rich arclogites in Fig. 6 typically have greater than 50% garnet.

## 5. Porphyry copper deposits in the framework of the evolution of an arc

Our proposed mechanism for PCD generation is consistent with their intimate association with thick arcs. Our hypothesis allows us to predict when ores are most likely to form during the evolution of an arc: the greatest oxidizing power and propensity for scavenging Cu occurs when garnet begins to crystallize. To test this prediction, we looked to the central Andes, an active continental arc, to compare geochemical/geochronological data of magmas to the frequency of PCDs (Sinclair, 2007) (Fig. 9). Over the last 80 My, there were two segments of magmatism in the central Andes (17–27 °S): between 30–80 Mya (million years ago) and from 20 Mya to the present (Haschke et al., 2006; Kay et al., 2014; Mpodozis and Cornejo, 2012). Each magmatic segment was characterized by tectonic shortening and magmatic inflation during which a well-defined arc magmatic front gradually migrated away from the trench (Fig. 10a). Rearward migration of the arc from the trench eventually culminated in cessation in magmatism, followed by a  $\sim 10$  My amagmatic gap between the two magmatic segments.

Concomitant with rearward migration of the arc front are increases in Tb/Yb and Sr/Y ratios as well as in initial  $^{87}\text{Sr}/^{86}\text{Sr}$

(Fig. 10b–d) (Haschke and Gunther, 2003; Haschke et al., 2006). High Tb/Yb and Sr/Y ratios reflect garnet fractionation owing to the compatible behavior of Yb and Y in garnet while high initial Sr reflects increasing crustal contamination. An increase in Tb/Yb and Sr/Y suggests that the average pressures of magmatic differentiation must be increasing, which has been shown to also indicate increasing thickness of the arc crust (Chapman et al., 2015; Chiaradia, 2015; Farner and Lee, 2017). Although rearward migration of the arc front is often attributed to a decrease in the angle of subduction (e.g., shallowing dip; Haschke et al., 2006), a simpler explanation is that progressive thickening of the arc crust by magmatic inflation/underplating and tectonic shortening gradually forces the hot part of the mantle wedge to migrate away from the trench (Dickinson, 1973; Karlstrom et al., 2014). This tectono-magmatic thickening of the arc crust is a distinct feature of continental arcs. By contrast, the upper plate in island arcs is in extension, preventing upper plate thickening and resulting in a stationary arc relative to the trench (Karlstrom et al., 2014). Crustal thickening in continental arcs also forces the hot mantle wedge to greater depths, eventually to depths too deep to generate melts, terminating magmatism. Xenolith studies of continental arc crust confirm that the arc crust can grow to thickness of 60–90 km, resulting in direct impingement of the arc lithosphere



**Fig. 8.** Evolution of an arc as represented by schematic crustal columns and temperature–depth ( $z$ ) profiles through the crust. A) Island arc stage when crust is thin ( $< 25$  km). If the upper plate is in extension, a thin arc crust is developed. Average pressures of intracrustal differentiation are low and insufficient to stabilize garnet. Because the crust is in extension, heat flow is high and geotherms are advected upwards, resulting in a shallow brittle ductile transition (BDT). Combination of stress state and shallow BDT causes residence time of magmas in the crust to be low and allows magmas to readily breach the surface and erupt. B) Immature continental arc stage (25–35 km). Upper plate is under compression, which deepens early intracrustal differentiation as well as upper crustal magmatic differentiation. Thickening also causes geotherm depression, which deepens the BDT, further frustrating eruption and development of shallow level magma bodies. C) Mature continental arc stage ( $> 45$  km). As arc crust becomes thicker, magmatic arc front migrates away from the trench and pressure of initial intracrustal differentiation becomes sufficient to stabilize garnet. Thermal incubation by the passage of magmas elevates geotherms, while erosion (enhanced by the high elevations), causes further shallowing of the BDT. Consequently, later stage magmas are allowed to emplace shallowly and generate porphyries. Garnet fractionation removes Fe from the residual magma, causing a decrease in S solubility, which in causes sulfide segregation and sequestration of Cu into lower crustal cumulates. Residual magmas become more oxidized, increasing Cu scavenging power of the magma. At shallow levels, degassing releases the oxidized magmatic fluids, which then migrate from the entire magma body and concentrate near the top, forming a Cu-enriched cupola. In thin arcs, residual magma does not oxidize. Cumulates are not Fe-enriched.

against the cold subducting slab and terminating magmatism (Chin et al., 2015). Re-initiation of magmatism requires that the thick arc crust be thinned, perhaps by foundering of dense arclogites back into the mantle.

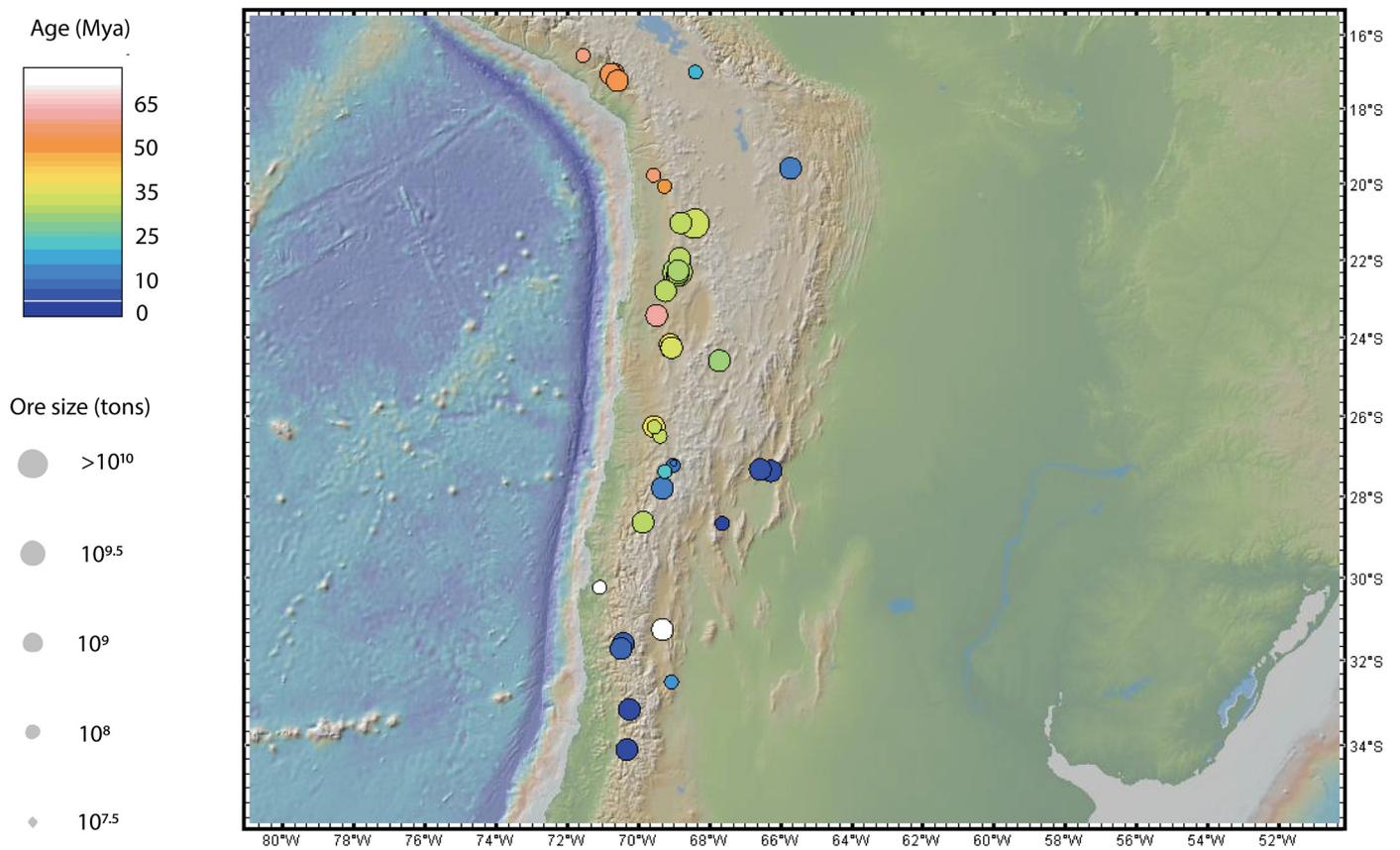
In Fig. 10, we have superimposed the frequency of PCDs in the central Andes on the temporal trends in geochemistry and arc front position using data from Sinclair (2007) and Haschke et al. (2006). PCDs appear to occur only during the very last stages of the 30–80 Mya magmatic segment, in particular, when the arc crust reaches its maximum thickness (as inferred by Tb/Yb ratios) and just before magmatism terminates. We do not see many PCDs in the 20–0 Mya segment, but we attribute this to the fact that any recently formed PCDs have yet to be exhumed. Previous studies have suggested that PCDs are generated by subsequent re-melting of the Cu-rich arc cumulates (arclogites) (Lee et al., 2012). However, the great thickness of arc crust needed to generate arclogites leaves little room for a hot mantle wedge to provide the necessary heat to re-melt the lower crust (Karlstrom et al., 2014). Extension-driven decompression of the lower crust might be the only mechanism by which arclogites can be significantly re-melted (Richards, 2009), but when continental arcs approach their maximum thickness, they are generally being tectonically thickened rather than thinned (Haschke and Gunther, 2003; Jiang et al., 2015; Kay and Mpodozis, 2001). Post-delamination asthenospheric upwelling has been suggested as a means of re-melting the lower crust (Richards, 2009), but not if the Cu-rich arclogites are also delaminated (Haschke et al., 2010; Lee et al., 2012). In any case, termination of the magmatic gap and re-initiation of arc magmatism would likely represent the aftermath of delamination (DeCelles

et al., 2009), hence the PCDs likely predate any hypothetical delamination event.

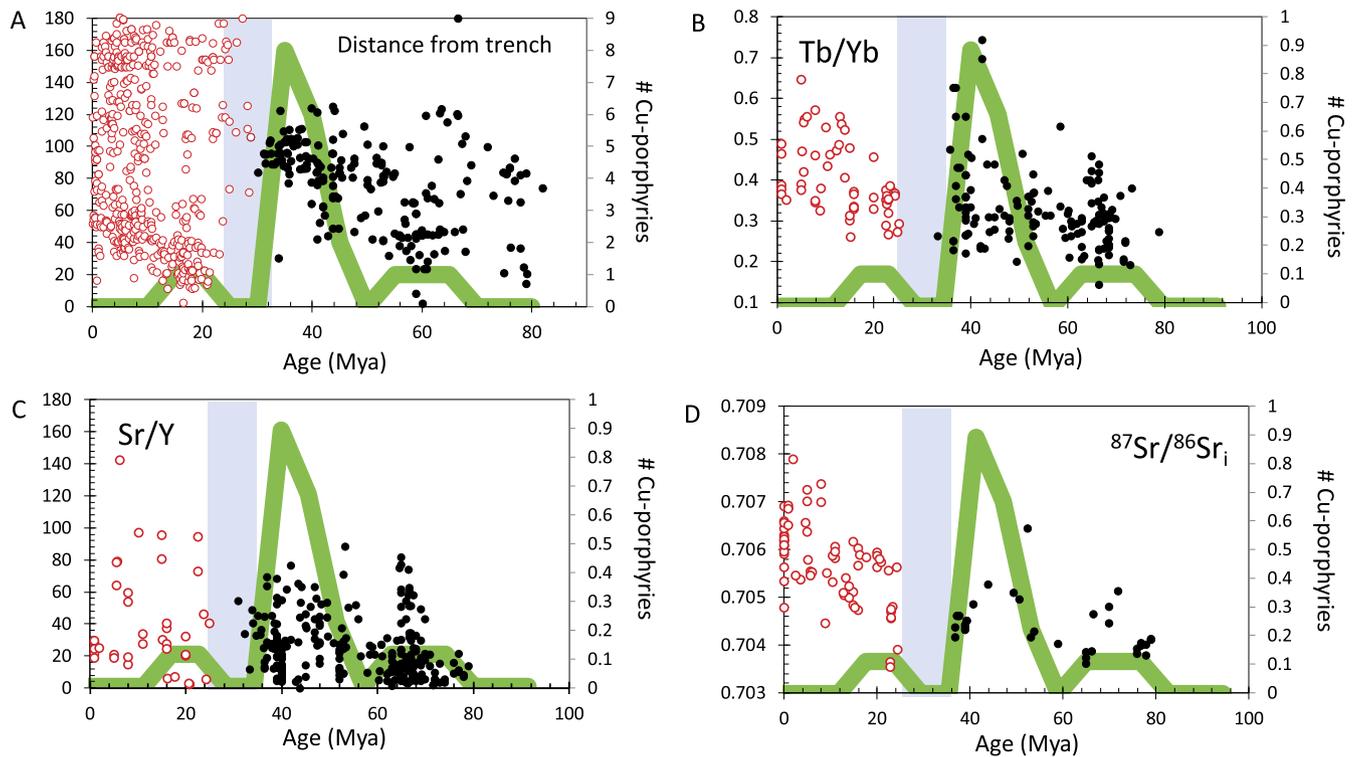
## 6. Evolution of magma emplacement depths with arc maturation

Although crustal thickening, garnet fractionation and subsequent auto-oxidation are necessary to form PCDs, large volumes of otherwise Cu-depleted plutonic material must be tapped to achieve the 1000-fold enrichment of Cu to form the cupola ore. Magmas must exsolve oxidized fluids, which are then mobilized from large volumes of the magma, followed by transport and focusing into a reservoir (cupola). How these processes occur is beyond our current scope. Nonetheless, we touch on one relevant question: what are the conditions for exsolving the fluids, which can mobilize this available Cu?

Assuming that relevant magmas are all hydrous to begin with, the important factor may be where magmas stall and exsolve fluids. Should magmas breach the Earth's surface, there may be insufficient time for any fluids to scavenge, and metals would be lost to eruption (Edmonds et al., 2018). Should magmas stall at depth ( $> 10$  km), such as in the middle crust or deeper, fluid saturation may not occur (volatile solubility increases with pressure). Crustal thickness and stress state likely play a role in controlling the depths at which magmas are emplaced. In extensional arcs or when the crust is thin, magmas may traverse the crust too quickly and erupt (Fig. 8). However, in compressional and thick arcs, magmas initially stall at depths (as evidenced by high Tb/Yb and Sr/Y ratios) too deep to generate significant fluid exsolution, and yet PCDs are formed when arcs reach their maximum thickness. We are thus left with the question of what controls the emplacement



**Fig. 9.** PCDs in the central Andes color coded for age. Size of circles represents total tonnage (metric tons) of Cu ore. Data from Sinclair (2007) (see Supplemental Table 2).



**Fig. 10.** Physical and geochemical evolution of arc magmas in the central Andes between 17–27 °S. A) Relative distance of arc magmas from trench (km) as a function of time (Mya = million years ago) (left hand vertical axis). Two magmatic intervals were identified (denoted by red and black) separated by a ~10 My magmatic window (gray vertical bar). In each segment, distance is referenced to the location of the front at the beginning of each magmatic segment. Green curve represents frequency of porphyry copper deposits (right hand vertical axis). B) Tb/Yb of magmas versus age. High Tb/Yb reflects garnet fractionation. C) Sr/Y of magmas versus age. High Sr/Y reflects garnet fractionation. D) Initial  $^{87}\text{Sr}/^{86}\text{Sr}_i$  of magmas versus age. High values indicate increased crustal assimilation. Data are from compilation by Haschke and Gunther (2003), Haschke et al. (2006) (see Supplemental Table 3).

depths of the evolved, felsic magmas after they rise from the lower crust?

One potential factor may be the depth of the brittle–ductile transition (BDT). The BDT is sensitive to the thermal state of the crust so its depth should evolve as the arc matures (Fig. 8). For example, although thickening will drive deeper differentiation, the BDT would be expected to shallow with arc maturity due to the warming caused by accumulated magmatism. Magmatic and tectonic thickening should also lead to rapid erosion (Jiang and Lee, 2017), with erosion serving to advect heat upwards, further shallowing the BDT (Cao et al., 2019). Thus, with arc maturation, shallow level emplacement of magmas may become more favorable even as the depth of initial differentiation deepens. We note that the high elevations associated with crustal thickening might also drive orographic precipitation, initiating meteoric hydrothermal systems, which would cool the crust (and pluton) and limit continued erosion-induced shallowing of the BDT. The BDT-shallowing effects of erosion and magmatism combined with the BDT-deepening effects of hydrothermal circulation could result in a characteristic depth of late stage magmatic emplacement (Cao et al., 2019). More work is necessary to evaluate the effects of all these processes, but we speculate that the ideal conditions for PCD formation occur when the arc crust exceeds a critical thickness and is still magmatically and tectonically active.

## 7. Additional questions

One additional factor that may be important is the concentration and makeup of the volatile phase ( $H_2O$  or  $CO_2$  dominated). As large amounts of fluids are needed to scavenge Cu from such large volumes of plutons, high volatile contents are needed, but how much and from where such volatiles derive is an open question. Are continental arc magmas more volatile-rich to begin with than island arc magmas, and if so, why? Alternatively, can processes like magmatic recharge, which are favored in the lower crust, further concentrate volatiles such that magmas traversing thick crust are more volatile-rich (Lee et al., 2014)? The release of large amounts of fluids may be key to developing porphyritic textures as fluids enhance crystal growth rates (Nabelek et al., 2010). However, subsequent escape of these fluids to the surrounding country rock would increase the solidus of the magma, causing freezing, rapid nucleation and the formation of a fine-grained groundmass. Detailed studies on the kinetics of porphyritic textures may go far in elucidating the timing and rates of fluid release, shedding light on the final stages of Cu ore formation.

Timescales of fluid transport are also important. Presumably, fluid release and migration occur during the last stages of magma crystallization. To what extent does fluid scavenging and transport occur while the pluton is still above its solidus? How much sub-solidus transport occurs? Are cupolas fed from one large magma body or are they formed incrementally over the lifespans of many small plutons (Schöpa et al., 2017)? It will also be important to better understand the nature of the fluid transport pathways. For example, are the transport pathways represented by a fracture network, and if so, what is the density and geometry of the network? How and when is the fracture network generated within the pluton? These questions are similar to those being asked of how large volumes of crystal-poor silicic magmas can be extracted from a crystal mush and erupt (Bachmann and Bergantz, 2004).

Finally, although our model can explain the correlation of PCDs in continental arcs with the development of thick arc crust, PCDs do exist in some island arcs, such as the Philippines, Papua New Guinea, Panama and accreted island arc terranes in British Columbia, central Asia and eastern Australia (Sinclair, 2007). Our model at face value may not be able to explain these occurrences, suggesting other “roads” to Cu mineralization in arc systems. How-

ever, we note that in nearly all of these island arc cases, the PCDs are associated with high Sr/Y magmas (so-called adakitic signature). If these island arcs were not thick enough to generate arclogite cumulates, the high Sr/Y may reflect partial melting of eclogitized slab. While geologically different from our model, slab melting would ultimately have the same petrogenetic effect as our model because garnet in the residue would drive oxidation. Whether these occurrences of PCDs in island arcs are due to slab melting will remain a fruitful area of research. We note that some studies have suggested that high Sr/Y in island arcs, while rare, may very well be explained by the formation of deep-seated cumulates (Macpherson et al., 2006). Thus, even though island arcs are generally thin, it is possible that certain segments temporarily evolve into crust thick enough to stabilize garnet, and it is then that PCDs in island arcs can form.

## 8. Conclusions

In summary, other than the presence of magmatic water, which necessitates PCDs to be associated with subduction zones, there is little unusual about the deep source regions or parental magmas from which PCDs derive. Instead, the formation of PCDs requires a unique set of intra-crustal processes, from the lower crust to the upper crust, to align during magmatic differentiation. Thick crust in arcs (common in continental arcs and rare in island arcs) promotes garnet fractionation, which simultaneously drives depletion of the magma in total Fe and preferential enrichment in ferric Fe. Fe depletion facilitates sulfide segregation, which in turn sequesters most of the magma’s Cu into the lower crust. Paradoxically, but now well understood, it is from these evolved Cu-poor magmas that Cu porphyries subsequently derive. Garnet fractionation drives oxidation of the residual magma, releasing Cu from sulfides into solution and increasing the ability of endogenic magmatic fluids to self-scavenge and transport Cu from otherwise Cu-poor plutons to the tops of the plutons. The lower crust of arcs, however, remains the largest repository of Cu, but such Cu never makes it to the surface and may even be permanently lost from the crust if lower crustal foundering into the mantle occurs.

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## Appendix A. Supplementary material

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.epsl.2019.115868>.

## References

- Bachmann, O., Bergantz, G.W., 2004. On the origin of crystal-poor rhyolites: extracted from batholithic crystal mushes. *J. Petrol.* 45, 1565–1582.
- Ballard, J.R., Palin, M.J., Campbell, I.H., 2002. Relative oxidation states of magmas inferred from Ce (IV)/Ce (III) in zircon: application to porphyry copper deposits of northern Chile. *Contrib. Mineral. Petrol.* 144, 347–364.
- Berndt, J., Koepke, J., Holtz, F., 2004. An experimental investigation of the influence of water and oxygen fugacity on differentiation of MORB at 200 MPa. *J. Petrol.* 46, 135–167.

- Cao, W., Lee, C.-T.A., Yang, J., Zuza, A.V., 2019. Hydrothermal circulation cools continental crust under exhumation. *Earth Planet. Sci. Lett.* 515, 248–259.
- Carmichael, I.S.E., 1991. The redox states of basic and silicic magmas: a reflection of their source regions? *Contrib. Mineral. Petrol.* 106, 129–141.
- Chapman, J.B., Ducea, M.N., DeCelles, P.G., Profeta, L., 2015. Tracking changes in crustal thickness during orogenic evolution with Sr/Y: an example from the North American Cordillera. *Geology* 43, 919–922.
- Chiaradia, M., 2014. Copper enrichment in arc magmas controlled by overriding plate thickness. *Nat. Geosci.* 7, 43.
- Chiaradia, M., 2015. Crustal thickness control on Sr/Y signatures of recent arc magmas: an Earth scale perspective. *Sci. Rep.* 5, 8115.
- Chiaradia, M., Ulianov, A., Kouzmanov, K., Beate, B., 2012. Why large porphyry Cu deposits like high Sr/Y magmas? *Sci. Rep.* 2, 685.
- Chin, E., Lee, C., Blichert-Toft, J., 2015. Growth of upper plate lithosphere controls tempo of arc magmatism: constraints from Al-diffusion kinetics and coupled Lu–Hf and Sm–Nd chronology. *Geochem. Perspect. Lett.*
- Chin, E.J., Shimizu, K., Bybee, G.M., Erdman, M.E., 2018. On the development of the calc-alkaline and tholeiitic magma series: a deep crustal cumulate perspective. *Earth Planet. Sci. Lett.* 482, 277–287.
- Cottrell, E., Kelley, K.A., 2011. The oxidation state of Fe in MORB glasses and the oxygen fugacity of the upper mantle. *Earth Planet. Sci. Lett.* 305, 270–282.
- Cox, D., Watt, S.F., Jenner, F.E., Hastie, A.R., Hammond, S.J., 2019. Chalcophile element processing beneath a continental arc stratovolcano. *Earth Planet. Sci. Lett.* 522, 1–11.
- DeCelles, P.G., Ducea, M.N., Kapp, P., Zandt, G., 2009. Cyclicity in Cordilleran orogenic systems. *Nat. Geosci.* 2, 251.
- Dickinson, W.R., 1973. Widths of modern arc-trench gaps proportional to past duration of igneous activity in associated magmatic arcs. *J. Geophys. Res.* 78, 3376–3389.
- Ding, S., Dasgupta, R., 2017. The fate of sulfide during decompression melting of peridotite—implications for sulfur inventory of the MORB-source depleted upper mantle. *Earth Planet. Sci. Lett.* 459, 183–195.
- Edmonds, M., Mather, T.A., Liu, E.J., 2018. A distinct metal fingerprint in arc volcanic emissions. *Nat. Geosci.* 11, 790.
- Erdman, M.E., Lee, C.-T.A., Levander, A., Jiang, H., 2016. Role of arc magmatism and lower crustal foundering in controlling elevation history of the Nevadaplano and Colorado Plateau: a case study of pyroxenitic lower crust from central Arizona, USA. *Earth Planet. Sci. Lett.* 439, 48–57.
- Farner, M.J., Lee, C.-T.A., 2017. Effects of crustal thickness on magmatic differentiation in subduction zone volcanism: a global study. *Earth Planet. Sci. Lett.* 470, 96–107.
- Haschke, M., Ahmadian, J., Murata, M., McDonald, I., 2010. Copper mineralization prevented by arc-root delamination during Alpine–Himalayan collision in central Iran. *Econ. Geol.* 105, 855–865.
- Haschke, M., Gunther, A., 2003. Balancing crustal thickening in arcs by tectonic vs. magmatic means. *Geology* 31, 933–936.
- Haschke, M., Günther, A., Melnick, D., Ehtler, H., Reutter, K.-J., Scheuber, E., Oncken, O., 2006. Central and southern Andean tectonic evolution inferred from arc magmatism. In: *The Andes*. Springer, pp. 337–353.
- Hattori, K.H., Keith, J.D., 2001. Contribution of mafic melt to porphyry copper mineralization: evidence from Mount Pinatubo, Philippines, and Bingham Canyon, Utah, USA. *Miner. Depos.* 36, 799–806.
- Hedenquist, J.W., Lowenstern, J.B., 1994. The role of magmas in the formation of hydrothermal ore deposits. *Nature* 370, 519.
- Henley, R.W., King, P.L., Wykes, J.L., Renggli, C.J., Brink, F.J., Clark, D.A., Troitzsch, U., 2015. Porphyry copper deposit formation by sub-volcanic sulphur dioxide flux and chemisorption. *Nat. Geosci.* 8, 210.
- Jenner, F.E., 2017. Cumulate causes for the low contents of sulfide-loving elements in the continental crust. *Nat. Geosci.* 10, 524.
- Jenner, F.E., O'Neill, H.S.C., Arculus, R.J., Mavrogenes, J.A., 2010. The magnetite crisis in the evolution of arc-related magmas and the initial concentration of Au, Ag and Cu. *J. Petrol.* 51, 2445–2464.
- Jiang, H., Lee, C.-T.A., 2017. Coupled magmatism–erosion in continental arcs: reconstructing the history of the Cretaceous Peninsular Ranges batholith, southern California through detrital hornblende barometry in forearc sediments. *Earth Planet. Sci. Lett.* 472, 69–81.
- Jiang, H., Lee, C.-T.A., Morgan, J.K., Ross, C.H., 2015. Geochemistry and thermodynamics of an earthquake: a case study of pseudotachylites within mylonitic granitoid. *Earth Planet. Sci. Lett.* 430, 235–248.
- Jugo, P.J., Luth, R.W., Richards, J.P., 2005. Experimental data on the speciation of sulfur as a function of oxygen fugacity in basaltic melts. *Geochim. Cosmochim. Acta* 69, 497–503.
- Jugo, P.J., Wilke, M., Botcharnikov, R.E., 2010. Sulfur K-edge XANES analysis of natural and synthetic basaltic glasses: implications for S speciation and S content as function of oxygen fugacity. *Geochim. Cosmochim. Acta* 74, 5926–5938.
- Karlstrom, L., Lee, C.T., Manga, M., 2014. The role of magmatically driven lithospheric thickening on arc front migration. *Geochem. Geophys. Geosyst.* 15, 2655–2675.
- Kay, S.M., Mpodozis, C., 2001. Central Andean ore deposits linked to evolving shallow subduction systems and thickening crust. *GSA Today* 11, 4–9.
- Kay, S.M., Mpodozis, C., Gardeweg, M., 2014. Magma sources and tectonic setting of Central Andean andesites (25.5–28 S) related to crustal thickening, forearc subduction erosion and delamination. *Geol. Soc. (Lond.) Spec. Publ.* 385, 303–334.
- Kelley, K.A., Cottrell, E., 2009. Water and the oxidation state of subduction zone magmas. *Science* 325, 605–607.
- Kesler, S.E., 1997. Metallogenic evolution of convergent margins: selected ore deposit models. *Ore Geol. Rev.* 12, 153–171.
- Kiseeva, E.S., Wood, B.J., 2013. A simple model for chalcophile element partitioning between sulphide and silicate liquids with geochemical applications. *Earth Planet. Sci. Lett.* 383, 68–81.
- Le Roux, V., Dasgupta, R., Lee, C.-T.A., 2015. Recommended mineral–melt partition coefficients for FRTEs (Cu), Ga, and Ge during mantle melting. *Am. Mineral.* 100, 2533–2544.
- Lee, C.-T., Leeman, W.P., Canil, D., Li, Z.-X.A., 2005. Similar V/Sc systematics in MORB and arc basalts: implications for the oxygen fugacities of their mantle source regions. *J. Petrol.* 46, 2313–2336.
- Lee, C.-T.A., Cheng, X., Horodyskyj, U., 2006. The development and refinement of continental arcs by primary basaltic magmatism, garnet pyroxenite accumulation, basaltic recharge and delamination: insights from the Sierra Nevada, California. *Contrib. Mineral. Petrol.* 151, 222–242.
- Lee, C.-T.A., Lee, T.C., Wu, C.-T., 2014. Modeling the compositional evolution of recharging, evacuating, and fractionating (REFC) magma chambers: implications for differentiation of arc magmas. *Geochim. Cosmochim. Acta* 143, 8–22.
- 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 systematics in arc magmas and implications for crust–mantle differentiation. *Science* 336, 64–68.
- Lee, C.-T.A., Morton, D.M., Kistler, R.W., Baird, A.K., 2007. Petrology and tectonics of Phanerozoic continent formation: from island arcs to accretion and continental arc magmatism. *Earth Planet. Sci. Lett.* 263, 370–387.
- Lee, C.-T.A., Thurner, S., Paterson, S., Cao, W., 2015. The rise and fall of continental arcs: interplays between magmatism, uplift, weathering, and climate. *Earth Planet. Sci. Lett.* 425, 105–119.
- Li, C., Barnes, S.-J., Makovicky, E., Rose-Hansen, J., Makovicky, M., 1996. Partitioning of nickel, copper, iridium, rhenium, platinum, and palladium between monosulfide solid solution and sulfide liquid: effects of composition and temperature. *Geochim. Cosmochim. Acta* 60, 1231–1238.
- Li, C., Ripley, E.M., 2005. Empirical equations to predict the sulfur content of mafic magmas at sulfide saturation and applications to magmatic sulfide deposits. *Miner. Depos.* 40, 218–230.
- Liu, X., Xiong, X., Audétat, A., Li, Y., Song, M., Li, L., Sun, W., Ding, X., 2014. Partitioning of copper between olivine, orthopyroxene, clinopyroxene, spinel, garnet and silicate melts at upper mantle conditions. *Geochim. Cosmochim. Acta* 125, 1–22.
- Loucks, R., 2014. Distinctive composition of copper–ore-forming arc magmas. *Aust. J. Earth Sci.* 61, 5–16.
- Macpherson, C.G., Dreher, S.T., Thirlwall, M.F., 2006. Adakites without slab melting: high pressure differentiation of island arc magma, Mindanao, the Philippines. *Earth Planet. Sci. Lett.* 243, 581–593.
- Matjuschkin, V., Blundy, J.D., Brooker, R.A., 2016. The effect of pressure on sulphur speciation in mid-to deep-crustal arc magmas and implications for the formation of porphyry copper deposits. *Contrib. Mineral. Petrol.* 171, 66.
- McDonough, W.F., Sun, S.-S., 1995. The composition of the Earth. *Chem. Geol.* 120, 223–253.
- Miyashiro, A., 1974. Volcanic rock series in island arcs and active continental margins. *Am. J. Sci.* 274, 321–355.
- Moyen, J.-F., 2009. High Sr/Y and La/Yb ratios: the meaning of the “adakitic signature”. *Lithos* 112, 556–574.
- Mpodozis, C., Cornejo, P., 2012. Cenozoic tectonics and porphyry copper systems of the Chilean Andes. In: *Society of Economic Geologists Special Publication*, vol. 16, pp. 329–360.
- Nabelek, P.I., Whittington, A.G., Sirbescu, M.-L.C., 2010. The role of H<sub>2</sub>O in rapid emplacement and crystallization of granite pegmatites: resolving the paradox of large crystals in highly undercooled melts. *Contrib. Mineral. Petrol.* 160, 313–325.
- O'Neill, H.S.C., Mavrogenes, J.A., 2002. The sulfide capacity and the sulfur content at sulfide saturation of silicate melts at 1400 C and 1 bar. *J. Petrol.* 43, 1049–1087.
- Reekie, C., Jenner, F., Smythe, D., Hauri, E., Bullock, E., Williams, H., 2019. Sulfide resorption during crustal ascent and degassing of oceanic plateau basalts. *Nat. Commun.* 10, 82.
- Richards, J.P., 2009. Postsubduction porphyry Cu–Au and epithermal Au deposits: products of remelting of subduction-modified lithosphere. *Geology* 37, 247–250.
- Rielli, A., Tomkins, A.G., Nebel, O., Raveggi, M., Jeon, H., Martin, L., Ávila, J.N., 2018. Sulfur isotope and PGE systematics of metasomatized mantle wedge. *Earth Planet. Sci. Lett.* 497, 181–192.
- Ripley, E.M., Brophy, J.G., Li, C., 2002. Copper solubility in a basaltic melt and sulfide liquid/silicate melt partition coefficients of Cu and Fe. *Geochim. Cosmochim. Acta* 66, 2791–2800.
- Rudnick, R.L., Gao, S., 2003. Composition of the continental crust. *Treatise Geochem.* 3, 659.

- Schöpa, A., Annen, C., Dilles, J.H., Sparks, R.S.J., Blundy, J.D., 2017. Magma emplacement rates and porphyry copper deposits: thermal modeling of the Yerington Batholith, Nevada. *Econ. Geol.* 112, 1653–1672.
- Sillitoe, R.H., 1972. A plate tectonic model for the origin of porphyry copper deposits. *Econ. Geol.* 67, 184–197.
- Sillitoe, R.H., 2010. Porphyry copper systems. *Econ. Geol.* 105, 3–41.
- Sinclair, W., 2007. Porphyry deposits. In: *Mineral Deposits of Canada: A Synthesis of Major Deposit-Types, District Metallogeny, the Evolution of Geological Provinces, and Exploration Methods*. In: Geological Association of Canada, Mineral Deposits Division, Special Publication, vol. 5, pp. 223–243.
- Sun, W., Ling, M., Yang, X., Fan, W., Ding, X., Liang, H., 2010. Ridge subduction and porphyry copper–gold mineralization: an overview. *Sci. China Earth Sci.* 53, 475–484.
- Sun, W., Zhang, H., Ling, M.-X., Ding, X., Chung, S.-L., Zhou, J., Yang, X.-Y., Fan, W., 2011. The genetic association of adakites and Cu–Au ore deposits. *Int. Geol. Rev.* 53, 691–703.
- Tang, M., Erdman, M., Eldridge, G., Lee, C.-T.A., 2018. The redox “filter” beneath magmatic orogens and the formation of continental crust. *Sci. Adv.* 4, eaar4444.
- Tang, M., Lee, C.-T.A., Chen, K., Erdman, M., Costin, G., Jiang, H., 2019a. Nb/Ta systematics in arc magma differentiation and the role of arclogites in continent formation. *Nat. Commun.* 10, 235.
- Tang, M., Lee, C.-T.A., Costin, G., Höfer, H.E., 2019b. Recycling reduced iron at the base of magmatic orogens. *Earth Planet. Sci. Lett.* 528, 115827.
- Wilkinson, J.J., 2013. Triggers for the formation of porphyry ore deposits in magmatic arcs. *Nat. Geosci.* 6, 917.
- Zimmer, M.M., Plank, T., Hauri, E.H., Yogodzinski, G.M., Stelling, P., Larsen, J., Singer, B., Jicha, B., Mandeville, C., Nye, C.J., 2010. The role of water in generating the calc-alkaline trend: new volatile data for Aleutian magmas and a new tholeiitic index. *J. Petrol.* 51, 2411–2444.