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Response

Magnetite–hematite, oxygen fugacity, adakite and porphyry copper deposits: Reply to Richards

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We thank Richards (2013) for the comment, which provides us a chance to better explain our concept and model. Porphyry Cu deposits are closely associated with oxidized adakitic magmas, the connection behind these association is still in debate.

1. The title of Sun et al. (2013) is based on the observation that sulfate is the dominant S species in the parental magma, but sulfides are dominant in porphyry deposits. Richards claims that sulfide-dominant porphyry deposits are more oxidized than their sulfate-dominant parental magmas, which does not make sense. The S^{6+}/S_{total} ratio is sensitive to oxygen fugacity (Matthews et al., 1994; Metrich and Clocchiatti, 1996; Jugo et al., 2005). The porphyry Cu system (both parental magmas and deposits) is rich in sulfur, such that its oxygen fugacity is usually controlled by sulfur speciation. Sulfate is the dominant sulfur species in magmas but is very rare in sulfide ores, with scarce isolated anhydrite inclusions. We take this as a clear sign that parental magmas are much more oxidized than the ore bodies. We also would like to point out that the magnetite–pyrite boundary lies above the SO_2–H_2S (not sulfate) boundary at temperatures higher than 650 °C, which is much higher than the mineralization temperature. More importantly, both magnetite, pyrite are solid states, whereas SO_2 and H_2S are not, such that the SO_2–H_2S boundary assumes 1 unit concentrations of both species.

When talking about the mechanism of porphyry mineralization, we are dealing with three things, parental magmas, ore bodies and the linkage between them (mineralization process). In general, the redox reactions of Fe and S are the key controlling factors of porphyry Cu deposits (Sun et al., 2004, 2013; Liang et al., 2009). The most optimal oxygen fugacity of parental magmas is higher than ΔFMQ+2 (Mungall, 2002), such that there is sufficient sulfate in the magmas to obtain high initial Cu contents, and lower than the HM buffer to maintain ferrous iron for the reduction of sulfate during the mineralization process (Sun et al., 2013). As discussed in detail in Sun et al. (2013), the oxidation potential of sulfate increases with decreasing pH during the mineralization process, which eventually reaches the HM buffer (Sun et al., 2013). We would like to point out also that the hematite-magnetite assemblage is quite common in porphyry systems, which has also been reported by many others, including (Sillitoe, 2010). Nevertheless, the pH values increase during alterations that consume H^+, consequently, the oxidation potential of sulfate decreases. The very low S^{6+}/S_{total} ratio in porphyry ore bodies (sulfide rich) indicates oxygen fugacity much lower than the FMQ buffer. Nevertheless, the reac-

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tions among solid minerals are very slow once fluids dried out. This explains the coexistence of minerals that formed under very different oxygen fugacities.

2. Richards misunderstood previous papers (Pokrovski and Dubrovinsky, 2011; Sun et al., 2013). The sulfur speciation is controlled by physicochemical conditions. S_3^- was shown as the dominant sulfur species by Raman spectroscopy at 25° to 450 °C and 0.5 to 3.5 GPa and $1 < pH < 7$ (Pokrovski and Dubrovinsky, 2011). Sulfate, however, is more abundant at higher pH and oxygen fugacities (Fig. 3 of Pokrovski and Dubrovinsky, 2011), especially in fluids under pressures of 0.3–1.0 GPa and temperatures up to 700 °C (Ni and Keppler, 2012). Note, the lines separating the domains of two neighboring species correspond to the concentration ratio 1:1 of these species in solution.

Richards argues that SO_2 is the principal form of sulfur in magmatic volatile phases and the disproportionation of aqueous SO_2 upon cooling forms “coprecipitation” of magnetite with sulfide and anhydrite. The references cited by (Richards, 2013) are all about hydrothermal systems. Sulfur behaves differently in porphyry systems under much higher pressures. High-pressure experiments show that sulfate is the dominant sulfur species in magmas under high oxygen fugacity, with some sulfite (S^{4+}) (Jugo, 2009; Jugo et al., 2010). High concentrations of SO_2 are observed in volatile phases (Einaudi et al., 2003; Heinrich, 2005). Therefore, the dominant reaction among sulfur species is more likely to go opposite to the direction proposed by Richards (2013), i.e., sulfide reacts with sulfate, forming SO_2 (Eq. (1)). Moreover, H_2S tends to react with SO_2, forming S (Eq. (2)). Note, native S is abundant in volcanic craters, but is not reported in any porphyry deposits, yet. For the same reasons, the reactions 2 and 3 of Richards (2013) are not likely to be the main reactions that are responsible to the final mineralization, either.

$$H_2S + 3H_2SO_4 = 4SO_2 + 4H_2O_2 \quad (1)$$

$$H_2S + SO_2 = 3S + 2H_2O \quad (2)$$

3. Richards criticized that reactions (1, 2, 4) of Sun et al. (2013) because they are all very high positively charged. This is a misunderstanding. These reactions were all ionic equations, simplified to make it more straightforward. The apparent positive charge is actually balanced by Cl^- and other anions, which are not shown in these reactions.
4. Richards and Kerrich set “MgO normally <3 wt percent” as a criterion, but they set “Mg number ≈0.5” as well (Richards and Kerrich, 2007), which is a far tighter constraint than the former and was the main point of dissent of Sun et al., (2013). In other words, the word “normally” does not make much difference. Furthermore, as discussed in Sun et al., (2013), they also set up Ni, Cr criteria that go towards the opposite fractionation directions.

Richards further claims that slab melts react with overlying mantle through open system AFC-type processes, such that it is very difficult to infer source processes from geochemical data. This is very surprising to us. Essentially all magmas experience AFC-type processes, as do adakites. The slab-melting model is supported by high-pressure experiments (Rapp and Watson, 1995; Rapp et al., 1999). More importantly, reactions of adakite with surrounding mantle peridotite and crusts tend to erase the unique characteristics of adakite. In other words, adakites may be changed to normal arc rocks through AFC-type processes (Sun et al., 2012a). Therefore, adakitic characteristics are indeed original.

5. Richards argues that the partition coefficients of Cu between amphibole and magmas vary dramatically from 0.05 to 16 or if only newer data were used, from 0.49 to 1.8 (GERM). This gives us an opportunity to clarify. Richards attributed the formation of adakite to amphibole crystallization (Richards and Kerrich, 2007). We argued that amphibole cannot explain the association between porphyry Cu deposits and adakites (Sun et al., 2011, 2012a,b, 2013). Partition coefficient values lower than 1 are either for basaltic andesite or for rhyolite, whereas it is compatible in amphibole for andesite (up to 16, GERM). Adakite with porphyry Cu deposits are mostly andesite, therefore amphibole is not favorable for Cu mineralization (Sun et al., 2011, 2012b).
6. Richards argued that high water contents is responsible to Cu mineralization (Richards and Kerrich, 2007; Richards, 2012). We don’t think this is the case, because subduction of younger oceanic crusts has much (e.g., Chile) more porphyry deposits, whereas subduction of older oceanic crusts has much fewer (e.g., Japan) (Sun et al., 2012b). This time he changed his mind and argued that “most of the hydration occurred near the mid-ocean ridges” based on the distribution of hydrothermal activities. This argument is inconsistent with the observation that older oceanic crust is systematically more altered and wetter than young oceanic crust. The effects of oxygen fugacity on porphyry mineralization has been discussed in detail in Sun et al. (2011, 2013).

Our main disagreement with Richards (2013) focuses on the linkage between adakite and porphyry copper mineralization. Adakite was originally proposed to represent slab melts with characteristic high Sr/Y ratios (Defant and Drummond, 1990). It has long been recognized that most