



## Review

## Porphyry deposits and oxidized magmas



Weidong Sun<sup>a,\*</sup>, Rui-fang Huang<sup>b,c</sup>, He Li<sup>a</sup>, Yong-bin Hu<sup>a,c</sup>, Chan-chan Zhang<sup>a,c</sup>, Sai-jun Sun<sup>a,c</sup>,  
Li-peng Zhang<sup>a,c</sup>, Xing Ding<sup>b</sup>, Cong-ying Li<sup>a</sup>, Robert E. Zartman<sup>a</sup>, Ming-xing Ling<sup>b</sup>

<sup>a</sup> CAS Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 511 Kehua Street, Wushan, Guangzhou 510640, China

<sup>b</sup> State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 511 Kehua Street, Wushan, Guangzhou 510640, China

<sup>c</sup> University of the Chinese Academy of Sciences, Beijing 100049, China

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## ABSTRACT

Porphyry deposits supply most of the world's Cu and Mo resources. Over 90% of the porphyry deposits are found at convergent margins, especially above active subduction zones, with much fewer occurrences at post-collisional or other tectonic settings. Porphyry Cu–(Mo)–(Au) deposits are essentially magmatic–hydrothermal systems, which are generally initiated by injection of oxidized magmas saturated with metal-rich aqueous fluids, i.e., the parental magmas need to be water rich and oxidized with most of the sulfur appearing as sulfate in the magma. Sulfur is the most important geosolvent that controls the behavior of Cu and other chalcophile elements, due to high partition coefficients of chalcophile elements between sulfide and silicate melts. Small amount of residual sulfides can hold a large amount of Cu. Therefore, it is essential to eliminate residual sulfides to get high Cu contents in magmas for the formation of porphyry deposits. Sulfate ( $\text{SO}_4^{2-}$ ) is over 10 times more soluble than sulfide ( $\text{S}^{2-}$ ), and thus the solubility of sulfur depends strongly on sulfur speciation, which in turn depends on oxygen fugacities. The magic number of oxygen fugacity is  $\log f_{\text{O}_2} > \text{FMQ} + 2$  (i.e.,  $\Delta\text{FMQ} + 2$ ), where FMQ is the fayalite–magnetite–quartz oxygen buffer. Most of the sulfur in magmas is present as sulfate at oxygen fugacities higher than  $\Delta\text{FMQ} + 2$ . Correspondingly, the solubility of sulfur increases from ~1000 ppm up to >1 wt.%. Oxidation promotes the destruction of sulfides in the magma source, and thereby increases initial chalcophile element concentrations, forming sulfur-undersaturated magmas that can further assimilate sulfides during ascent. Copper, Mo and Au act as incompatible elements in sulfide undersaturated magmas, leading to high chalcophile element concentrations in evolved magmas. The final porphyry mineralization is controlled by sulfate reduction, which is usually initiated by magnetite crystallization, accompanied by decreasing pH and correspondingly increasing oxidation potential of sulfate. Hematite forms once sulfate reduction lowers the pH sufficiently, driving the oxidation potential of sulfate up to the hematite–magnetite oxygen fugacity (HM) buffer, which is  $-\Delta\text{FMQ} + 4$ . Given that ferrous iron is the most important reductant that is responsible for sulfate reduction during porphyry mineralization, the highest oxygen fugacity favorable for porphyry mineralization is the HM buffer. In addition to the oxidation of ferrous iron during the crystallization of magnetite and hematite, reducing wallrock may also contribute to sulfate reduction and mineralization. Nevertheless, porphyry deposits are usually mineralized in the whole upper portion of the pluton, whereas interactions with country rocks are generally restricted at the interface, therefore assimilation of reducing sediments is not likely to be a decisive controlling process. Degassing of oxidized gases has also been proposed as a major process that is responsible for sulfate reduction. Degassing, however, is not likely to be a main process in porphyry mineralization that occurs at 2–4 km depths in the upper crust. Sulfide formed during sulfate reduction is efficiently scavenged by aqueous fluids, which transports metals to shallower depths, i.e., the top of the porphyry and superjacent wallrock. According to traditional views, sulfide saturation and segregation during magma evolution is not favorable for the formation of porphyry Cu  $\pm$  Au  $\pm$  Mo deposits. This is the main difference between porphyry deposits and Ni–Cu sulfide deposits. Nevertheless, in places with thick sections of reducing sediments, e.g., the western North America, sulfide saturation and segregation may occur during evolution of the magma, forming Cu-rich cumulates at the base of plutons. These Cu-rich sulfides may evolve into porphyry mineralization or even control the ore-forming process. Their contribution depends heavily on subsequent oxidation, i.e., a major contribution can be expected only when the sulfide cumulates are oxidized to sulfate, liberating the chalcophile elements. Sulfate reduction and ferrous Fe oxidation form  $\text{H}^+$ , which dramatically lowers the pH values of ore-forming fluids and causes pervasive alteration zones in porphyry Cu deposits. The amount of  $\text{H}^+$  released during mineralization and the alkali content in the porphyry together control the intensity of alterations. In principle,  $\text{H}_2$  and methane

\* Corresponding author.

E-mail address: [weidongsun@gig.ac.cn](mailto:weidongsun@gig.ac.cn) (W. Sun).

form during the final mineralization process of porphyry deposits, but are mostly oxidized by ferric Fe during subsequent processes. Some of the reduced gases, however, may survive the highly oxidizing environment to escape from the system, or even to get trapped in fluid inclusions. Therefore, small amount of reduced gases in fluid inclusions cannot argue against the oxidized feature of the magmas. Reduced magmas are not favorable for porphyry mineralization. Reduced porphyry deposits so far reported are just mineralization that has either been reduced in host rock away from the causative porphyry or through assimilation of reducing components during emplacement.

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## 1. Introduction

Porphyry deposits are hosts to one of the most important economic mineral associations (Cooke et al., 2005; Halter et al., 2005; Heinrich et al., 2004; Mutschler et al., 2010; Sillitoe, 2010), accounting for ~80% Cu and ~95% Mo of the world's total reserves. It is also an important resource of Au, Ag, Zn, Sn and W. Most porphyry deposits are found above active subduction zones (Fig. 1) (e.g., Chiaradia, 2014; Chiaradia et al., 2012; Gonzalez-Partida et al., 2003; Hedenquist et al., 1998; Kesler, 1997; Lee, 2014; Richards, 1999, 2013; Sillitoe, 2010; Sun et al., 2011; Wilkinson, 2013), with a few occurrences at post-collisional or other tectonic settings (Sillitoe, 2010), e.g., porphyry Mo deposits in the eastern Qinling orogenic belt (Chen, 2013; Li et al., 2012a; N. Li et al., 2013) and, arguably porphyry Cu–Mo deposits in Gangdese belt on the south Tibetan Plateau (Hou et al., 2009; Qu et al., 2004; Xiao et al., 2012) and some porphyry Cu deposits in Iran (Calagari, 2003; Castillo, 2006; Haschke et al., 2010; Shafiei et al., 2009).

The consensus is that most of the porphyry Cu ± Mo ± Au systems are initiated by injection of oxidized adakitic magma saturated with aqueous fluids that are S- and metal-rich, i.e., the parental magmas must be water rich and oxidized (e.g., Ballard et al., 2002; Burnham and Ohmoto, 1980; Garrido et al., 2002; Imai, 2002; Liang et al., 2006; Mungall, 2002; Sillitoe, 2010; Stern et al., 2007; Sun et al., 2013b). It is, however, still controversial as regards to: why high oxygen fugacity is favorable for the mineralization of porphyry deposits, how oxidized the magma could be, whether adakitic magma is essential for porphyry mineralization or whether the porphyry deposits can be associated with normal arc rocks (Fig. 2), and why the pure porphyry Mo deposits are also closely associated with highly oxidized magmas.

Copper, Au and Mo are chalcophile elements, which are strongly controlled by the behavior and speciation of sulfur. Therefore, the less the quantity of residual sulfide, the higher the initial Cu contents in primary magmas (Fig. 3) (Lee et al., 2012; Sun et al., 2004a, 2013b). Experiments show that sulfate is much more soluble than sulfide in magmas

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