

Response

The genetic association between magnetite–hematite and porphyry copper deposits: Reply to Pokrovski

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Received 23 May 2013; accepted in revised form 28 July 2013; available online 9 August 2013

Porphyry mineralization is a very complicated process with hundreds of different possible reactions. Sun et al. (2013) presented only several combined important reaction equations in order to make the paper more straightforward. Our response to Pokrovski's comment provides us with an opportunity to better explain the controlling factors and reactions of porphyry mineralization. The most important thing for understanding porphyry mineralization is that both magmas and fluids are involved in porphyry mineralization processes. Hydrothermal processes at temperatures between 550–350 °C are the most important for the final porphyry Cu mineralization (Sillitoe, 2010). Most of the reactions occurred in fluids and/or during fluid/rock interactions, which is not fully considered by Pokrovski (2013) and many others when discussing reactions responsible for porphyry mineralization (Zajacz et al., 2011, 2012). It must always be considered that reactions proposed may not mimic geological observations.

Hematite–magnetite intergrowths are common in essentially all large porphyry Cu–Au deposits (Sillitoe, 2010; Sun et al., 2013). This has puzzled us for a while, because the ferrous/ferric ratio of magmas are usually much higher than that of magnetite, therefore the crystallization of magnetite would further increase the ferrous/ferric ratio and correspondingly tend to lower the oxidation fugacity of the parental magmas, under the same physical–chemical

conditions (Sun et al., 2004; Liang et al., 2009; Jenner et al., 2010). This is true for magmatic process when the pH value does not change much. After struggling with this problem for some time, we realized that the formation and further oxidation of magnetite are responsible for sulfate reduction controlled by pH, which is the key process for the final mineralization.

It has long been recognized that magmas with high oxygen fugacity favors porphyry Cu mineralization (Ballard et al., 2002; Mungall, 2002; Liang et al., 2006, 2009; Sillitoe, 1997, 2010; Sun et al., 2010, 2011, 2012a,b; Zhang et al., 2013). Elements that exist in variable oxidation states and present in sufficient abundances to affect the redox state of the porphyry mineralization system, e.g., C, H and S, all establish oxygen fugacity lower than the HM buffer under standard conditions (Fig. 1) (Mungall, 2002). In contrast to FMQ, HM oxygen buffers (Fig. 1, Eqs. (3 and 4)), sulfur-related redox reactions are sensitive to pH and concentrations of species involved (Eqs. (1) and (5)), i.e., the oxidation potential of sulfate increases with decreasing pH values and H₂S/H₂SO₄ (Eq. (1)). To catch up with progress in sulfur studies, we used the logfO₂ versus pH diagram for sulfur speciation of Pokrovski and Dubrovinsky (2011) to explain the effects of magnetite–hematite intergrowth on porphyry mineralization and the mechanism behind it (Sun et al., 2013). Although it is claimed that the trisulfur S₃[−] ion has been demonstrated to be the dominant sulfur species at temperatures between 250–450 °C, pressures between 5–35 kbar and pH of 1–7, and is more stable at higher temperatures (Pokrovski and Dubrovinsky, 2011),

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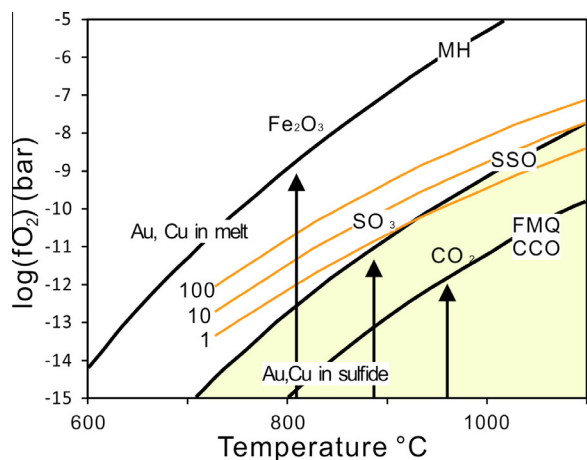
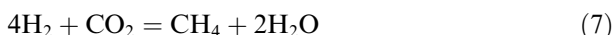


Fig. 1. Oxygen buffers in $\log(fO_2)$ versus temperature (Matthews et al., 1994; Mungall, 2002). SSO—sulfide–sulfur oxide buffer (Eq. (1): $H_2S + 2O_2 = H_2SO_4$); CCO—carbon dioxide–carbon oxide buffer (Eq. (2): $CO_{2(\text{fluid})} = C_{(\text{gr})} + O_{2(\text{fluid})}$); FMQ—fayalite–magnetite–quartz oxygen buffer (Eq. (3): $3Fe_2SiO_4 + O_2 = 2Fe_3O_4 + 3SiO_2$); MH—magnetite–hematite oxygen buffer (Eq. (4): $4Fe_3O_4 + O_2 = 6Fe_2O_3$). Hematite–magnetite buffer is higher than SSO buffer and 1, 10, 100: H_2S-SO_2 (Eq. (5): $2H_2S + 3O_2 = 2H_2O + 2SO_2$) at 4 kbar, with SO_2/H_2S ratios of 1, 10 and 100, respectively.

the published figure was applicable at 350 °C and 5 kbar, which is slightly lower in temperature and higher in pressure than optimal porphyry mineralization conditions. We therefore wrote to Professor Pokrovski, asking whether it is indeed applicable under higher temperatures and lower pressures. Professor Pokrovski kindly replied with a positive answer and a diagram at 450 °C and 5 kbar (not published), which is quite similar to that under lower temperatures. We therefore used the diagram at 350 °C and 5 kbar (Pokrovski and Dubrovinsky, 2011) to explain our model. While the diagram used in Sun et al. (2013) was an iron free system (Pokrovski and Dubrovinsky, 2011; Pokrovski, 2013), this is of no consequence because Fe reacts with S^{2-} forming pyrite, H_2 and H^+ (Eq. (6)) (Heinrich, 1990), such that it promotes sulfate reduction and further elevates the oxidation potential of sulfate. Therefore, as shown by Eqs. (1) and (6), whether S_3^{2-} is stable or not has no influence on our conclusion. The oxidation potential of sulfate increases during its reduction as a result of decreasing pH and H_2S/H_2SO_4 (or S_3^{2-}/H_2SO_4), which eventually reaches the HM buffer. For the same reason, the basic concepts of the phase diagram emphasized by Pokrovski (2013) are irrelevant to our model.

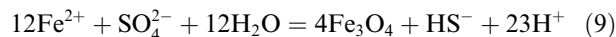


H_2 tends to escape from the porphyry system during degassing or infiltration, and may also further react with CO_2 and/or O_2 (Eqs. (7) and (8)).



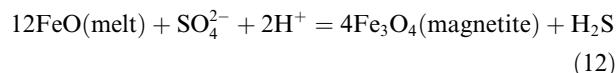
Pokrovski (2013) claims that the reactions listed in (Sun et al., 2013) do not allow any definite constraint on the evolution of redox or pH conditions during porphyry deposit

formation. However, all those reactions are combinations of 2 or more reactions. This also explains the apparent large number of electron transferred in these reactions (Sun et al., 2013). For example, Eq. (9) is a combination of two reactions (Eqs. (10) and (11)):



Oxygen is divided out when Eqs. (10) and (11) are combined. This does not mean that those reactions have no control on redox conditions. Given that the oxygen fugacity of the FMQ buffer is much lower than that of the SSO reaction line at near-neutral condition (Fig. 1), the oxygen fugacity of the system is mainly controlled by SSO (Eq. (1)) before ferrous iron is consumed, i.e., the redox is controlled by the oxidation potential of sulfate (Eq. (11)), which increases with decreasing pH values. This is dramatically different for magmatic processes. Under magmatic conditions, pH does not change much. Crystallization of magnetite converts sulfate to sulfide, and lowers the oxygen fugacity of the system (Sun et al., 2004; Liang et al., 2009; Jenner et al., 2010). A similar process has been proposed to explain sulfate reduction during porphyry mineralization. In contrast to magmatic processes, pH value plays a big role in controlling the oxidation potential of sulfate during hydrothermal activities, i.e., the pH value decreases during sulfate reduction by magnetite, which elevated the oxidation potential of sulfate (Sun et al., 2013). Once ferrous iron concentration is lowered enough by magnetite crystallization, the oxygen fugacity is controlled by the magnetite–hematite buffer (Eq. (4)), which does not change with pH. When both sulfate– S_3^{2-} and hematite–magnetite buffers are active, the reactions occur near the intersection of HM and sulfate reduction lines. Note that although sulfate reduction lines change with relative activity ratios of species evolved, the slope, and thus the trend, does not change.

For the formation of magnetite, Pokrovski (2013) proposes an alternative reaction (Eq. (12)), and suggests that protons are consumed upon magnetite formation and there is thus a decrease in acidity (i.e., an increase in pH) in the melt and the resulting exsolved fluid:



We would note that the magmatic system is complicated, while most readers prefer simplified reactions. We feel that the problem with the scheme proposed by Pokrovski is that he used oxides (FeO) to react with acid (H_2SO_4), and this certainly lowers the acidity. However, such a proposal is misleading. For the following reasons, we believe this reaction is inappropriate for porphyry mineralization. (1) Ferrous iron is mainly present in silicate minerals (salt, instead of oxide) in magmas and as $FeCl_2$ in co-existing magmatic fluids, but not FeO. The fluid phase is more reactive and important for porphyry mineralization, i.e., no fluids, no porphyry. “In many porphyry Cu deposits, it is fluid cooling over the ~550 to 350 °C range, assisted

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