

Sulfur Anomalies and Porphyry Copper Deposits in Their Early Stage of Formation

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Sulfur solubility and sulfur speciation are two key factors that control the transport of chalcophile elements and formation of magmatic ore deposits. Reduced sulfur occurs in the form of sulfide (typically FeS) and its presence is not conducive to the formation of porphyry copper deposits (PCD), as it tends to remove Cu from the evolving silicate melt. The subsequent formation of Cu-rich sulfides scattered in low concentration throughout a deep magmatic body will not produce an economic deposit. In contrast, oxidized sulfur is 3-5 times more soluble in silicate melts and crystallizes in the form of anhydrite as magma becomes S-oversaturated. Because Cu does not partition into anhydrite, it remains an incompatible element, and can be concentrated in late-stage processes. Thus, the process of sulfur oxidation opens a window for the formation of Cu-Au-enriched sulfur anomalies, highly desirable to the mining industry. This oxidation mechanism has been the focus of much research in the last few decades including possible links to regional tectonic settings for the purposes of prospecting.

The speciation of sulfur is mostly controlled by the overall oxidation state of the magma, which is commonly expressed in $\Delta\log f_{O_2}$ units relative to FMQ, where FMQ is fayalite-magnetite-quartz oxygen buffer. Recent studies suggest that transition from S^{2-} to S^{6+} (sulfide to sulfate) takes place in the oxygen fugacity (f_{O_2}) range from ΔFMQ 0 to +2 at 1000°C and 2 kbar (~5 km depth). Consequently, full oxidation of sulfur and formation of anhydrite is usually expected at ΔFMQ +2 or higher. In this study we explore this window of oxidation at much higher pressures of 10 and 15 kbar, corresponding to 30 and 45 km depth, simulating the lower crustal differentiation environment. High-pressure piston cylinder experiments were carried out using synthetic basaltic andesite from Laguna del Maule, Chile. The starting composition was doped with S (3000 ppm), Cl (1500 ppm) and 5.5 wt % H_2O representing typical concentrations for hydrous arc magmas. 1.5 wt % carbon was added by reaction of $Ca(OH)_2$ with air. Experimental temperatures ranged from 850° to 950°C and oxygen fugacity from ΔFMQ -0.5 to +5.5, controlled using the new solid oxygen buffer technique.

Results show a strong f_{O_2} control over phase relations. As a consequence, reduced experiments at ΔFMQ -0.5 and +1 exhibit 1-3 wt % higher concentrations of Al_2O_3 and CaO in the melt compared to more oxidized experiments owing to suppressed plagioclase crystallization. Pyrrhotite (FeS) was stable at f_{O_2} up to ΔFMQ +3, and S-solubility rapidly increases at ΔFMQ +3, suggesting the presence of additional S^{6+} component in the melt. The anhydrite stability field (sulfate only) was reached at ΔFMQ +5. This demonstrates that the S^{2-} to S^{6+} transitions at 10 and 15 kbar require a higher level of oxidation than reported for 2 kbar. Such oxidized conditions appear to be unrealistic for the deep sub-arc environment and support the model of PCD formation due magma mixing rather than from a single magmatic event.