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## Copper Partitioning in CO<sub>2</sub>-Bearing Melt-Vapor-Brine Systems

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Analysis of fluid and melt inclusions from arc-related intrusions and porphyry copper deposits (PCD) reveal that many fluid inclusions from PCD are typically characterized by  $X_{CO2} < 0.10$ , which is lower than that found in volatile phases exsolved from shallow (e.g., 5 to 10 km), arc magmas, in general ( $X_{CO2}$  up to order ~ 0.45). This disparity remains to be resolved.

The efficiency with which copper can be removed from arc magmas into exsolving volatile phases is a function of the competition between crystalline phases ( $\pm$  liquid sulphides), and the exsolving vapor  $\pm$  brine. Experiments in melt-vapor-brine systems permit the investigation of the partitioning of copper between silicate melts and volatile phases under magmatic conditions. However, the effect of CO<sub>2</sub> on melt-volatile phase equilibria relevant to the formation of PCD has remained unconstrained. In this study, the partitioning of copper in CO<sub>2</sub>-bearing, sulfur-free and sulfur-bearing, experiments may provide additional insights into copper partitioning and the generation of PCD.

We present results from experiments performed at 800 °C and 100 MPa in CO2-bearing, sulfur-free and sulfur-bearing melt-vaporbrine systems with  $X_{CO2}$  (bulk vapor  $\pm$  brine) = 0.10 and 0.38. The compositions of vapor and brine inclusions and run-product glasses were used as proxies for the compositions of the magmatic phases. The salinities of vapor inclusions that nucleated clathrate (CO<sub>2</sub>  $\pm$ H<sub>2</sub>S clathrate) upon cooling were determined via Raman analysis and microthermometry [1]. The partitioning of copper between brine and vapor  $(D^{b/v}_{Cu}(\pm 2\sigma))$  increases from 25(±6) to 100 (±30) for sulfurfree experiments and from  $11(\pm 3)$  to  $95(\pm 23)$  for sulfur-bearing experiments, as  $X_{CO2}$  is increased from 0.10 to 0.38. The partitioning of copper between vapor and melt increases with the addition of sulfur at  $X_{CO2} = 0.10$ :  $(D^{v/m}_{Cu}(\pm 2\sigma)) = 9.6(\pm 3.3)$  (sulfurfree, metaluminous melt); 18(±8) (sulfur-bearing, peralkaline melt); and 30(±11) (sulfur-bearing, metaluminous melt). These values are to be contrasted with  $(D^{v/m}_{Cu}(\pm 2\sigma)) = 2(\pm 0.8)$  at  $X_{CO2} = 0.38$  (the effect of sulfur cannot be distinguished at this mole fraction of CO<sub>2</sub>). These data demonstrate that changes in the salinity of the vapor and brine, which are controlled by changes in X<sub>CO2</sub>, play a major role in controlling copper partitioning in sulfur-free, CO2bearing systems. Sulfur-bearing experiments demonstrate that magmatic vapors are enriched in copper in the presence of sulfur at low X<sub>CO2</sub>. However, the enrichment of copper in the magmatic vapor is suppressed for sulfur-bearing systems at high X<sub>CO2</sub>. These data indicate that the efficient removal of copper from silicate melts into vapor  $\pm$  brine is mitigated by high concentrations of CO<sub>2</sub>. Furthermore, the poisoning effect of CO2 is more pronounced for sulfur-bearing volatile phases. As a result, high concentrations of CO<sub>2</sub> may play a negative role in the formation of PCD.

[1] Fall et al. (2011) *Geochimica et Cosmochimica Acta* **75**, 951-964.