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Copper Partitioning in CO_2-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 (± liquid sulphides), and the exsolving vapor ± 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_2 on melt-volatile phase equilibria relevant to the formation of PCD has remained unconstrained. In this study, the partitioning of copper in CO_2-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 ^{o}C and 100 MPa in CO_2-bearing, sulfur-free and sulfur-bearing melt-vapor-brine systems with X_{CO2} (bulk vapor ± 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_2 ± H_2S 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 sulfur-free experiments and from 11(±3) to 95(±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(±3.3) (sulfur-free, 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(±0.8) at $X_{CO2} = 0.38$ (the effect of sulfur cannot be distinguished at this mole fraction of CO_2). These data demonstrate that changes in the salinity of the vapor and brine, which are controlled by changes in X_{CO2}, play a major role in controlling copper partitioning in sulfur-free, CO_2-bearing systems. Sulfur-bearing experiments demonstrate that magmatic vapors are enriched in copper in the presence of sulfur at low X_{CO2}. However, the enrichment of copper in the magmatic vapor is suppressed for sulfur-bearing systems at high X_{CO2}. These data indicate that the efficient removal of copper from silicate melts into vapor ± brine is mitigated by high concentrations of CO_2. Furthermore, the poisoning effect of CO_2 is more pronounced for sulfur-bearing volatile phases. As a result, high concentrations of CO_2 may play a negative role in the formation of PCD.

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