

The effect of sulfur on vapor-liquid partitioning of metals in hydrothermal systems: An experimental batch-reactor study

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Despite the growing geological evidence that the vapor phase formed through boiling of magmatic ore-bearing fluids can selectively concentrate and transport metals, the physical-chemical mechanisms that control the metal vapor-liquid fractionation remain poorly known. In particular, the recent experiments and models on metal vapor-liquid partitioning in sulfur-free water-salt-acid systems [1] fail to explain the strong enrichments of the vapor phase by chalcophile metals like Cu and Au, as inferred from fluid inclusion studies of magmatic-hydrothermal Sn-Mo-Cu-Au deposits. It was suggested that complexing of Cu and Au with reduced sulfur might account for their enhanced volatility.

To quantify the role of sulfur in the vapor-phase transport of metals, we have recently initiated a systematic experimental study of equilibrium vapor-liquid partitioning of different metals in the system H₂O-NaCl-KCl-HCl-H₂S-SO₂. Our measurements were conducted at 350 and 450°C using Ti-alloy rigid autoclaves and flexible-cell reactors, both allowing sampling of the vapor and liquid during the run.

First results show that As, Sb and Fe vapor-liquid distribution is not affected by the presence of sulfur, in agreement with the formation of hydroxide and/or chloride species in both phases [1]. In the presence of 0.1-0.5 m S (H₂S±SO₂) in the vapor, Zn vapor-liquid partition coefficients ($K=m_{\text{vapor}}/m_{\text{liquid}}$) increase by an order of magnitude in comparison with a sulfur-free system, but still remain largely in favor of the liquid. Cu, Ag and Au partitioning into the vapor increases by a factor of 100 at acidic conditions ($K\sim 0.01$ at 350°C, 0.1-1.0 at 450°C), but is almost similar to that found in S-free systems at neutral pH. This may be explained by the predominance, in the liquid phase at acid pH, of neutral sulfide (e.g., AuHS⁰, Au(H₂S)HS⁰) or mixed sulfite-sulfide complexes which are more volatile than the negatively charged di-hydrosulfide species dominant at neutral pH (e.g., Au(HS)₂⁻). Thus, the fluid acidity which determines the liquid-phase speciation of both sulfur and chalcophile metals, may exert important control on the metal partitioning into the vapor phase in S-rich systems.

References

[1] Pokrovski G.S., Roux J., and Harrichoury J-C. (2005) *Geology* **33**, 657-660.