Redox conditions dictate the fate of sulfur at the magmatic-hydrothermal transition

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Sulfur plays an essential role in magmatic-hydrothermal ore genesis. It serves as a ligand for ore metals in high-temperature fluids, it is responsible for acid rock alteration and sulfide ore mineral precipitation. Indeed, porphyry-type copper deposits are even larger positive geochemical anomalies in the Earth's crust for sulfur than for copper. Therefore, understanding sulfur partitioning during silicate melt - aqueous fluid and vapor - liquid immiscibility is critical for better understanding of porphyry ore genesis.

We conducted high pressure (*P*) - temperature (*T*) experiments to assess the effect of the redox state of sulfur on its vapor/liquid partition coefficient. Experiments were conducted at $T = 650$ and $900\ ^{o}C$ and $P = 90 - 180$ MPa. We imposed fO_2 either 1 log unit below or 1.8 log unit above that of the Ni-NiO buffer, ensuring the presence of dominantly reduced or oxidized sulfur species in the fluid, respectively. Co-existing vapor and liquid phases were trapped in the form of synthetic fluid inclusions in quartz, fractured *in situ* during the experiments. The concentration of sulfur in the vapor and liquid (brine) inclusions was later determined by LA-ICP-MS. The results show that the oxidation state of sulfur strongly affects its partitioning between vapor and liquid. At low fO_2, sulfur shows strong preference for the vapor phase with vapor/liquid partition coefficients [D_S(vap/liq)] above 4. On the other hand, at oxidizing conditions, little fractionation of S was observed between vapor and liquid with D_S(vap/liq)]≈1. The surprisingly strong partitioning of S into the liquid phase is consistent with the results of a separate set of experiments that were conducted to assess the solubility of anhydrite in high-*T* fluids. These showed an exponential increase of anhydrite solubility with increasing fluid salinity and pointed to the stability of alkali sulfate species in the liquid phase.

Our results imply that a significant amount of sulfur may either be extracted from magmas as sulfate species by magmatic brines, or will partition into brines that condense from supercritical fluids. These brines may later precipitate anhydrite during cooling without causing acid alteration. Therefore, it is possible to directly co-precipitate copper-rich sulfides and anhydrite from high-temperature brines in the potassic alteration zone of porphyry deposits.