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The Effect of Sulfur on the Partitioning between Vapor-Aqueous Phase of Metals and Metalloids in the Formation of Ore Deposits

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1 Introduction

In the magmatic-hydrothermal and epithermal ore deposits, even the MVT and Carlin-type gold deposits, sulfur is required for the precipitation of the economically important sulfide minerals, and is also an essential ligand in metal-transporting fluids, enhancing the solubility of metals like Cu, Au by formation of stable metal-sulfide complexes in subcritical aqueous solutions (Seo, 2009). Thus, sulfur has an obvious effect on the transportation of some metals and metalloids and the generation of ore deposits.

However, the previous geological models of ore deposits formation thought that the metals were transported by aqueous fluid and metals concentrated in the dense liquid phase, ignoring the metal vapor phase transport, and assumed that boiling just promotes the partitioning of volatiles (e.g., H₂, H₂S, CO₂) from the aqueous solution to the vapor, resulting in changes of pH, redox potential, ligand concentration and, consequently, further effecting the mineral solubility in the liquid phase.

Recent advances in both high-temperature experimental techniques that can get the dates about the solubility of metal mineral and vapor-liquid equilibrium distribution coefficients ($K_m = m_{\text{vapor}}/m_{\text{liquid}}$) on the conditions of nature, and micro-analytical tools for studies of fluid inclusions with which can measure the major and trace element concentrations in coexisting high-density brine (H₂O-NaCl) and low density vapor (H₂O-HCl-H₂S±CO₂) inclusions in nature samples from a variety of magmatic-hydrothermal ore deposits have substantially changed this classical point of view.

2 Effect of Sulfur on Vapor-Liquid Partitioning

The research on natural inclusions from the Mole granite Yankee Lode ore, porphyry Cu-Au, epithermal Au ore, and the Skarn-type deposits show that spectacular enrichments in Cu, Au, and, in some cases As, Sb and Bi, of the vapor phase compared to other metals (e.g., Zn, Fe, Ag, Mn, W, Sn, Pb) which preferentially concentrate in the dense chloride-rich solution.

The growing evidence reveal that some metals like Cu, Au will partition into the vapor phase generated by magma degassing and ore fluid boiling under magmatic-hydrothermal conditions, which result in the vapor fluid can selectively concentrate and transport metals.

In sulfur-free systems, the vapor-liquid distribution patterns of metals and metalloids result from combined effects of 1) Fluid density. A lot of experiments and analysis of fluid inclusion demonstrate that the vapor-liquid distribution of elements obeys simple relationships involving the densities of the coexisting vapor and liquid phases (Pokrovski, 2013); 2) HCl content. the partitioning coefficients of As, Zn, Cu, Fe, Ag are independent of the HCl vapor phase content. Antimony partitioning is not affected by the presence of a moderate HCl content (< 0.1 wt% HCl in vapor), but at higher HCl concentrations Sb is enriched in the vapor (Pokrovski et al. 2005a, 2008b); 3) liquid-phase metal speciation. The identity and stability of their dominant species in the liquid phase should influence their partitioning in the vapor, in general, the charged speciation is less weaker volatility than the neutral complex.

Systematic experiments to investigate the effect of sulfur ligands on metal vapor-liquid partitioning in model

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H₂O-S-NaCl-KCl-NaOH systems at temperatures from 350 to 500 °C demonstrate that the vapor-liquid equilibrium distribution coefficients of As, Sb, Zn, Fe, Pb, Ag are less than 1, and are not significantly affected by the presence of geologically common sulfur concentrations. However, the distribution coefficients of Cu, Au, and Pt are more than 1, and partitioning of Cu, Au, and Pt into the vapor increases by a factor of 100 in comparison to the S-free water-salt system. Thus, Cu, Au, and Pt will partition into vapor phase due to formation of volatile neutral complexes with reduced sulfur (Pokrovski, 2008a).

Volatiles are the key agent for the enrichment of metals like Cu, Au in the vapors phase in the magmatic-hydrothermal ore deposits. Experimental determinations of gold solubilities in the magmatic volatile phases show that gold hydrosulfide complexes will supersede gold chloride complexes, and the stability of gold hydrosulfide complexes is greatly increased by the presence of minute concentrations of KCl or NaCl (Zajacz, 2010). On the contrary, the predominated ligand complex with Au in sulfur-free systems is chlorine, maybe the hydroxide (Zajacz, 2010; Pokrovski, 2013; et al)

Co-genetic brine and vapor inclusions from magmatic-hydrothermal ore deposits and granitic intrusions show that S, Cu and Au are highly enriched in vapor-like fluids, demonstrating that the low salinity, S-rich fluids are the key agent for the formation of porphyry copper and epithermal gold deposits (Seo, 2009).

The effects of sulfur on the partitioning into vapor-phase and transport by vapor of metal and metalloids are combined effects of 1) the metal complex with reduced

sulfur ligands result in the formation of volatile species; 2) the changes in the metal-S complex from charged speciation to neutral speciation in the coexisting liquid phase as a function of S content, CO₂, pH, temperature, pressure; 3) solute-solvent interactions in both phases.

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