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Vapor-liquid partitioning of metals at hydrothermal conditions

G. S. POKROVSKI¹, J. ROUX² AND J-C. HARICHOURY¹

¹Géochimie: Transferts et Mécanismes, LMTG, 38 rue des 36 Ponts, 31400 Toulouse, France (gleb@lmtg.ups-tlse.fr)

²IPGP-UMR7047, Physique des Minéraux et des Magmas, 4 place Jussieu, T14/3 75252 Paris cedex 05, France (roux@ipgp.jussieu.fr)

It has long been recognized that boiling and vapor-brine separation commonly occur in magmatic - hydrothermal systems and may affect ore deposition. Until recently however, few informations were available about the role of the vapor phase in ore metal transport and distribution. Recent fluid inclusion studies of a variety of magmatic-hydrothermal Sn-Mo-Cu±Au deposits have demonstrated a contrasting distribution between H₂O-HCl±H₂S vapor and NaCl-rich brine for different metals: As, Cu, and sometimes Sb and Au, significantly enrich the vapor phase, in contrast to other metals that preferentially concentrate into the brine [1,2].

In an attempt to interpret these surprising fractionations, we measured vapor-liquid partition coefficients for As, Sb, Cu, Ag, Zn, Fe and silica at the two-phase equilibrium curve of the system H₂O-NaCl±HCl. Experiments were conducted at 350, 400 and 450°C using Ti-alloy rigid autoclaves and flexible-cell reactors (Coretest), both allowing sampling of the vapor or/and liquid phase during the experiment.

Results show that Fe(II), Cu(I), Zn and Ag, whose liquid-phase speciation is entirely dominated by chloride complexes, form neutral chloride species in the vapor phase, with partition coefficients ($K = m_{\text{vapor}}/m_{\text{liquid}}$) similar to those for NaCl (10^{-4} - 10^{-1} , depending on temperature and NaCl content). As(III), Sb(III) and Si(IV) form hydroxide complexes in moderately acid vapor ($m_{\text{HCl}} < 0.1$), similar to their dominant aqueous species, with K increasing from ~0.01 to 0.1-0.5 in the following order: Sb-Si-As. In more acid vapor, Sb partition coefficients increase significantly thus implying the formation of SbCl₃(g) or similar species.

Vapor-liquid partition coefficients for all studied metals can be described in a wide temperature range using a simple relationship as a function of the vapor-to-liquid density ratio [3]. Our data can account for the preferential partitioning of As and, in some cases, Sb into the vapor phase as observed in the fluid inclusions from high-temperature (400-700°C) magmatic-hydrothermal deposits [1,2]. Our measurements for Zn, Ag, Fe also compare favorably with natural observations. However, our experiments do not explain the strong copper enrichment in vapor-like inclusions ($K_{\text{Cu}} \sim 10$), and thus may indicate the existence of other vapor species for Cu. Studies of the influence of sulfur and redox potential on vapor-liquid partitioning of metals are in progress.

References

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Vapour transport of metals in Cu-Au porphyry-epithermal systems

A. E. WILLIAMS-JONES, A. MIGDISOV AND S.M. ARCHIBALD

McGill University, Earth & Planetary Sciences, Canada (willyj@eps.mcgill.ca)

Although fluid inclusion studies suggest that the vapour phase may play an important role in transporting copper and gold in porphyry-epithermal systems, theoretical models based on volatility calculations indicate that the solubility of these metals is negligible in the vapour phase. However, these models ignore the potentially important contributions of solvation processes, i.e., interactions between the volatilized species and water vapor, to the transport properties of the latter. In view of this, and the importance of chlorine in porphyry-epithermal systems, we conducted experiments designed to determine the solubility of copper and gold in HCl-bearing water vapor at elevated temperatures. These experiments showed that the solubility of these metals in the vapor is orders of magnitude greater than that predicted theoretically, which we attribute to the formation of hydrated gaseous metal chloride species. However, the solubility of both metals is retrograde over the ranges of temperatures investigated (280-320 °C; 300-360 °C), due, we believe, to a decrease in hydration number with increasing temperature. It may therefore be questioned whether meaningful concentrations of copper and gold can be transported as hydrated chloride complexes at the conditions typically encountered in porphyry systems. In order to address this question, we have carried out preliminary calculations designed to extrapolate our experimental data to the much higher temperatures, chlorinities and vapour pressures of such systems. These calculations show that at 600 °C, a chlorinity equivalent to 2 wt.% equivalent NaCl and a pressure of 500 bars, the solubilities of Cu and Au in the vapour phase are 2 wt. % and 10 ppb, respectively. Significantly, the Cu concentration, although very approximate, is quite similar to that reported recently from LAM ICP-MS analyses of vapour-rich fluid inclusions. The Au concentration is substantially lower. However, concentrations of both metals are more than sufficient to form Cu-Au porphyry-epithermal ore deposits in geologically reasonable periods of time based on idealized model calculations using HCl fluxes from active volcanoes. This study demonstrates that the formation of hydrated metal chloride species is a major factor controlling copper and gold solubility in natural hydrothermal vapours. However, it does not rule out the possibility that species involving other gases may further enhance solubility or even be the dominant control on solubility. On the contrary, the study emphasises the very superficial level of our current understanding of hydrothermal vapour transport of metals and the need to extend experiments to mixtures of H₂O with other gases, notably H₂S.