

The Solubility of Silver in Magmatic Fluids

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Silver mineralization can occur in magmatic-hydrothermal systems, including porphyry and epithermal-type deposits. During the ascent and solidification of magmas in upper crustal reservoirs, crystallization and decompression leads to the exsolution of a low-density fluid phase. This low-density fluid, containing water, sulfur, carbon, chlorine and metals, is considered the primary control of metal extraction from the magma and subsequent precipitation in the country rock. The focus of this study is to assess the physiochemical controls on the solubility of Ag in these low-density, magmatic fluids. High-pressure-temperature experiments are used to determine the effect of various species (NaCl, KCl, LiCl, CaCl₂, SO₂, H₂S) on the solubility of Ag and to identify the dominant complexes of Ag at 900°C, 200 MPa and an oxygen fugacity of 0.5 log units below the Ni-NiO buffer. An Au₉₇Ag₂Cu₁ alloy was used as capsule material, which imposes an Ag activity of 0.005. The experiments were conducted in rapid-quench, Mo-Hf carbide, externally-heated, pressure vessel assemblies and the subsequent volatile phases were sampled through the *in-situ* entrapment of synthetic fluid inclusions in fractured quartz chips. Laser-ablation inductively coupled plasma mass spectrometry was used to analyze the fluid inclusions. The results demonstrate that, in an alkali-chloride water system, the log Ag solubility linearly increases as a function of NaCl and with NaCl and HCl at a 1:1 ratio. When adding HCl to replace NaCl in the system, maintaining cCl=1m, the apparent solubility of Ag reaches a maximum (432±123 ug/g) at equal NaCl and HCl concentrations (0.5m). The solubility of Ag then decreases towards two end-members (1m NaCl and 1m HCl) following a parabolic function. This implies the presence of NaAgCl₂ or Na₂AgCl₃ complexes in the fluid. The addition of H₂S to the system significantly impacts Ag solubility, especially when combined with NaCl or KCl in the fluid. In this case, the results alternatively indicate the presence of (Na,K)Ag(HS)₂ and (Na,K)AgHSCl complexes. It is interpreted that although some Ag can be extracted from mafic melts by exsolving sulfur-rich fluids, it is more likely that most Ag is degassed from magmas at a later stage, when the residual melt becomes felsic, which leads to the generation of chloride-rich fluids.