An experimental study of the solubility and speciation of MoO₃(s) in hydrothermal fluids at temperatures up to 350 °C

L.B. SHANG^{1,2}*, A.E. WILLIAMS-JONES², X.S. WANG^{1,2},

A. TIMOFEEV², R.Z. HU¹, X.B. BI¹

¹ State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China (*shanglinbo@vip.gyig.ac.cn)

² Department of Earth & Planetary Sciences, McGill University, 3450 University Street, Montreal, QC H3A 0E8, Canada

Previous studies have concluded that Mo is present mainly as $HMoO_4^-$ and $MoO_4^{2^-}$ in aqueous fluids at high temperature. However, as the fluids in porphyry systems are characterised by high salinity (> 2 m NaCl), some researchers have proposed that species involving either Cl or Na may also play an important role in the formation of porphyry Mo and Mo-Cu deposits. Here, we report results of a study designed to improve our understanding of the transport and deposition of Mo in NaCl-bearing hydrothermal systems.

The study involved measuring the solubility of MoO₃(s) in NaCl-H₂O fluids at 250, 300 and 350 °C and saturated water vapor pressure in Batch-type experiments using titanium autocalves. The results of these experiments showed that the solubility of MoO₃(s) increases with both temperature and salinity. At low salinity, the solubility of MoO₃(s) is independent of NaCl concentration and the dominant species is HMoO₄, whereas at higher salinity, Mo concentration increases with increasing NaCl content, suggesting that Mo forms complexes involving Cl⁻ or Na⁺. We conducted additional experiments with sodium triflate to decide between these posibilities. The concentration of Mo in the sodium triflate solutions produced the same dependency on solute concentration as with the NaCl solutions, showing that Mo forms ion pairs with Na⁺. Based on the approximately 1:1 dependence of the logarithm of Mo solubility on the logarithm of NaCl concentration and pH, we interpret the solubility of Mo to have been controlled by the the following reactions:

 $MoO_3(s) + H_2O + Na^+ = NaHMoO_4^0 + H^+$ (1)

the values of the logarithms of the equilibrium constants for Reaction 1 are -3.40 \pm 0.11, -3.25 \pm 0.19 and -2.97 \pm 0.09 at 250, 300 and 350 °C, respectively.

These data indicte that NaHMoO₄⁰ is the dominant Mo species in porphyry Mo ore-forming hydrothermal systems. They also predict Mo concentrations in the fluids very similar to those observed in fluid inclusions.