

# The role of $S_3^{\bullet-}$ in molybdenum transport by hydrothermal fluids revealed by in situ X-ray absorption spectroscopy

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Knowledge of the chemical speciation of molybdenum under hydrothermal conditions is a key to understanding the formation of porphyry deposits, which are the primary economic source of molybdenum. Previous studies have revealed various Mo complexes including (hydrogen)molybdate ions ( $HMoO_4^-$ ,  $MoO_4^{2-}$ ) and their ion pairs with alkalis (e.g.,  $NaHMoO_4^0$ ,  $KHMoO_4^0$ ) in S and Cl-poor fluids, oxy-chloride species ( $MoO_mCl_n^{(6-2m-n)-}$ ) in strongly acidic saline fluids, and thio-molybdate complexes (e.g.,  $MoS_4^{2-}$ ,  $MoOS_2^0$ ) in reduced  $H_2S$ -bearing fluids and vapors [1-6]. However, these available data are unable to account for the massive transport of Mo in porphyry-related fluids revealed by fluid inclusion analyses demonstrating 100s ppm of Mo (e.g., [7]). A potential missing ligand for Mo may be the trisulfur radical ion,  $S_3^{\bullet-}$ , which is predicted to be abundant in sulfate-sulfide  $H_2S/SO_4^{2-}$  rich acidic-to-neutral porphyry-like fluids.

We performed *in situ* X-ray absorption spectroscopy (XAS) measurements at the Mo K-edge (20.0 keV) in a hydrothermal autoclave available at BM30 of ESRF synchrotron [8] to study the molybdenite solubility in model  $S_3^{\bullet-}$  rich aqueous solutions at 300 °C and 500 bar. We found that Mo can be efficiently transported by  $S_3^{\bullet-}$ -bearing fluids at concentrations of several ppm, whereas the available data on OH-Cl-S complexes predict

negligibly small Mo concentrations at our conditions (<0.01-0.1 ppm). Work is in progress to extend the experiments to a wider *T-P*-composition range of porphyry fluids and to quantitatively assess the role of  $S_3^{\bullet-}$  in Mo transport by geological fluids. Another goal of this research is to revise thermodynamic properties of other Mo aqueous complexes.

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