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

**DR. MARIA A. KOKH, PHD**, 1,2, STEPHAN KLEMM1, CHRISTIAN SCHMIDT3, JEAN-LOUIS HAZEMANN4, DENIS TESTEMALE4, DR. CLÉMENT LASKAR5,6, DR. MANUELA BORCHERT1,7, ELENA F. BAZARKINA8,9,10, CHRISTOPH MOELLER2, GLEB POKROVSKI11 AND MAX WILKE2

1 Institut für Mineralogie - WWU
2 Universität Potsdam
3 Deutsches GeoForschungsZentrum (GFZ)
4 Institut Néel - CNRS - Univ Grenoble Alpes - FAME beamline - European Synchrotron Radiation Facility
5 Laboratoire de Génie Chimique - CNRS - Univ Toulouse III - INP
6 Géosciences Environnement Toulouse - CNRS - Univ Toulouse III - IRD - CNES - OMP
7 Deutsches Elektronen-Synchrotron, Hamburg
8 Institut Néel - CNRS
9 The Rossendorf Beamline - European Synchrotron Radiation Facility
10 Helmholtz-Zentrum Dresden–Rossendorf e. V., Institute of Resource Ecology
11 Géosciences Environnement Toulouse - CNRS - Université Toulouse III

Presenting Author: koh@uni-potsdam.de

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 ($\text{HMoO}_4^{−}$, $\text{MoO}_4^{2−}$) and their ion pairs with alkalis (e.g., $\text{NaHMoO}_4^{0}$, $\text{KHMoO}_4^{0}$) in S- and Cl-poor fluids, oxy-chloride species ($\text{MoO}_m\text{Cl}_{8-2m+n}^{6-2m+n}$) in strongly acidic saline fluids, and thiomolybdate complexes (e.g., $\text{MoS}_2^{−}$, $\text{MoS}_2^{0}$) in reduced H$_2$S-bearing fluids and vapors [1-6]. However, these available data are unable to account for the massive transport of Mo in porphyry-related fluids and vapors 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, $S_3^{•−}$, which is predicted to be abundant in sulfate-sulfide H$_2$S/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 $S_3^{•−}$-rich aqueous solutions at 300 °C and 500 bar. We found that Mo can be efficiently transported by $S_3^{•−}$-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 $S_3^{•−}$ 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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