



Experiment title: Effect of sulfur radicals on molybdenite solubility and influence of dissolved silica on molybdenum ion pairing with sodium in sulfur-free hydrothermal fluids

Experiment number:
ES-1050

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Report:

Knowledge of Mo speciation in hydrothermal fluids is a key to understand the formation of its deposits. We used the in situ synchrotron XAS method to investigate Mo solubility and its speciation in aqueous solutions in equilibrium with MoO₂ (tugarinovite), MoO₃ (molybdite), and MoS₂ (molybdenite) at 300°C and 500 bar.

Table 1. Experimental systems studied at 300°C and 500 bar

Initial solid phase (s)	Solution composition, <i>m</i> – mol/kg solution	Solid glued (+) or not (-)
MoO ₂	H ₂ O	+
MoO ₃	H ₂ O	+
MoO ₃	H ₂ O	-
MoO ₃	0.50 <i>m</i> H ₂ O ₂	-
MoO ₂	0.96 <i>m</i> NaOH, November 2021	-
MoO ₃	0.96 <i>m</i> NaOH	-
MoO ₂ + SiO ₂ (quartz)	0.96 <i>m</i> NaOH	+
MoS ₂	1.00 <i>m</i> Na ₂ S ₂ O ₃ and 0.30 <i>m</i> KOH	+
	0.90 <i>m</i> Na ₂ S ₂ O ₃ and 0.28 <i>m</i> HCl	+
	1.00 <i>m</i> NaHS	+
	1.00 <i>m</i> C ₂ H ₅ NS	+

Compared to our previous experiment (Nov. 2021), temperature repartitor made of Mo has been replaced with that made of Cu in the autoclave, which improved the XAS detection limit for Mo by a factor of 100 (from 50 to 0.5 ppm Mo). Unfortunately, the new device lacked Be foils to shield the heat from the Cu sleeve and suffered from temperature gradients within the graphite cell. The resulting fluid convection caused flotation of MoS₂ crystals in solution during heating. As a result, we had to hold our solid phase attached to the lower piston of the cell using a cyanoacrylate glue. For future experiments the Cu repartitor will be equipped with Be foils to reduce the temperature gradient. As was checked, such Be foils do not generate detectable Mo signal.

In 2 experiments with MoO₃(s) and water (with or without the glue, Fig. 1), we observed a combined reducing effect of the carbon glassy cell and the glue: Mo concentrations in solution first sharply increased upon heating, then decreased more slowly with time (Fig. 1), likely reaching a steady state at about 0.0004 *m* Mo, which likely corresponds to the solubility of the MoO₂(s) solid phase identified at the end of both runs. Another run with MoO₃(s) had more oxidizing conditions by adding 0.5 *m* H₂O₂ in the cell. The use of H₂O₂ eliminated the MoO₃(s) reduction and allowed to reach a steady state solubility of 0.01 *m* Mo. The black line labeled “MoO₃-H₂O₂ ex situ” (Fig.1) refers to the Mo solubility in 0.5 *m* H₂O₂ solution obtained from the quench

experiment in Ti autoclave. Work is in progress to determine the exact chemical speciation of Mo in water which was found to be different in equilibrium with $\text{MoO}_3(\text{s})$ and $\text{MoO}_2(\text{s})$ (Fig. 2).

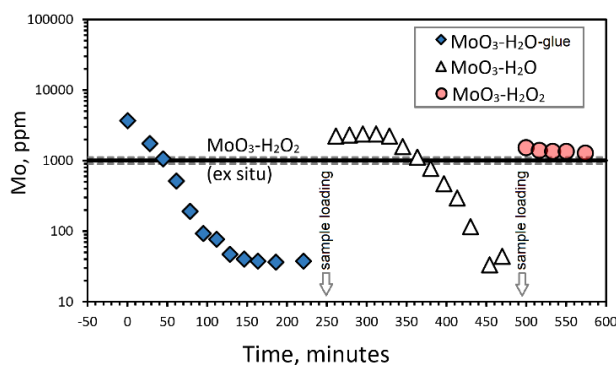


Fig. 1. Concentration of Mo as a function of time in experiments with $\text{MoO}_3(\text{s})$ and water (300°C , 500 bar).

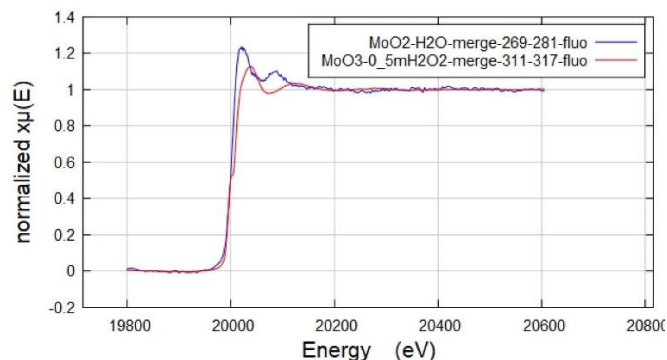


Fig 2. In situ XAS spectra at the Mo K-edge from experiments in water in equilibrium with $\text{MoO}_2(\text{s})$ (blue) and $\text{MoO}_3(\text{s})$ (red) at 300°C and 500 bar .

In 1 m NaOH solutions, Mo K-edge XANES spectra are similar to that of the 0.05 m Na_2MoO_4 solution at 25°C in which Mo is known to be in the form of tetrahedral $\text{Mo}^{\text{VI}}\text{O}_4$ complexes. Fourier transforms of the EXAFS spectra from this experiment do not show any evidence of Na^+ that might be expected to be present in the second coordination shell of Mo. The Mo concentrations in solution increase with time in the run started with $\text{MoO}_2(\text{s})$ (blue points), and slightly decrease with time for the run started with $\text{MoO}_3(\text{s})$ (red points) (Fig. 3). As in the case of runs in water, the carbon-glassy cell likely reacts with $\text{MoO}_3(\text{s})$ by partially reducing it to $\text{MoO}_2(\text{s})$. The measured Mo concentrations in the $\text{MoO}_2(\text{s})$ run in 1 m NaOH are pretty close to those predicted at equilibrium with the $\text{MoO}_2(\text{s})$ phase (dashed blue line). In contrast, Mo concentrations measured in the $\text{MoO}_3(\text{s})$ run are 10 times lower than those predicted in equilibrium with the $\text{MoO}_3(\text{s})$ phase, but are much closer to those predicted in equilibrium with $\text{MoO}_2(\text{s})$ and carbon. Such inconsistent trends may be due to combined effects of redox kinetics with the cell material depending of the initial system composition and differences in the experimental temperature between the MoO_2 -runs (using heat shielding) and MoO_3 -runs (without heat shielding) that may cause inhomogeneous temperature distribution across the experimental chamber. The presence of quartz in the experimental system with $\text{MoO}_2(\text{s})$ in 1 m NaOH decreased the Mo solubility at 300°C and 500 bar by a factor of 10 (0.20 m Mo in SiO_2 -free vs 0.025 m in SiO_2 -bearing run), which is likely due to the less alkaline pH caused by the dissolution of quartz.

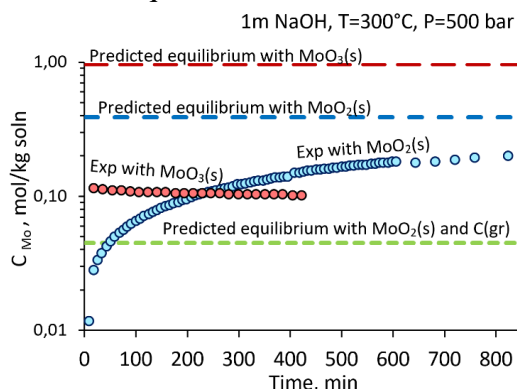


Fig.3. Comparison between the measured Mo concentrations and equilibrium thermodynamic calculations assuming MoO_4^{2-} to be the major aqueous complex (Shock et al., 1997, GCA 61, 907–950).

In sulfur-bearing runs with $\text{C}_2\text{H}_5\text{NS}$, $\text{MoS}_2(\text{s})$ solubility was found to be below the detection limit. Runs with thiosulfate and NaHS showed a few ppm of dissolved Mo. At the same time, the available data on OH-Cl-S complexes predict negligibly small ($<100\text{ ppb}$) Mo concentrations under our conditions. The obtained results are in good agreement with our experiments in the Coretest reactor and batch autoclaves for NaHS and $\text{Na}_2\text{S}_2\text{O}_3$ -HCl solutions, but are 10 times lower in $\text{Na}_2\text{S}_2\text{O}_3$ -NaOH solutions. This might be due to slow reactions rates in sulfate-sulfide solutions at alkaline pH. The spectra obtained in sulfur-bearing systems are very similar to those of the solid reference $(\text{NH}_4)_2\text{MoS}_4$, in which Mo is tetrahedrally coordinated with 4 S atoms. Work is in progress to identify the species and to quantitatively assess the role of the HS^- versus S_3^{2-} ligands in Mo complexation in hydrothermal fluids.