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| | Experiment title: Influence of dissolved silica on molybdenum ion pairing with sodium in hydrothermal fluids | Experiment number: 1278 |
| Beamline: | Date of experiment: from: 6/06/2023 to: 12/06/2023 | Date of report: 27/10/2023 |
| Shifts: | Local contact(s): Jean-Louis Hazemann, Isabelle Kieffer | <i>Received at ESRF:</i> 01/10/2023 |

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Report:

The experiment was planned, first, to study the molybdenum speciation in Si-rich hydrothermal fluids and, second, to improve our knowledge of Mo speciation in S-rich fluids that we investigated during our previous experiment in ESRF (ES-1050). The temperature and pressure (*TP*) conditions of our experiments were 300-350°C and 500 bar, respectively.

Here we performed 8 autoclave experiments for the following chemical systems:

- exp. 1 MoS₂ (cr) dissolution in 1 M NaHS, pH_{25°C} = 7.73
 - exp. 2 MoS₂ (cr) dissolution in 1 m Na₂S₂O₃ + 0.3 m NaOH, pH_{25°C} = 13.0
 - exp. 3 MoS₂ (cr) dissolution in 0.8 m Na₂S₂O₃, pH_{25°C} = 6.44
 - exp. 4a Solution 78 ppm Mo ; (NH₄)₂MoS₄ dissolved in 1 M NaHS, pH_{25°C} = 8.15
 - exp. 4b Solution 71 ppm Mo ; (NH₄)₂MoS₄ dissolved in 1 M NaHS + NaOH, pH_{23°C} = 12.51
 - exp. 5 MoS₂ (cr) dissolution in 1 m S, 0.4 m NaOH, pH_{calc.300°C} = 5
 - exp. 6 MoO₂ (cr) and quartz dissolution in 0.1 m B(OH)₃ + 0.05 m NaOH, pH_{23°C} = 9.17
 - exp.7 Solution 150 ppm Mo ; Na₂MoO₄ dissolved in H₂O + NS3 glass, (Na₂Si₃O₇ 22.4 wt%, 0.86 mol/kg soln), the NS3 glass dissolved completely during the experiment
- here M – mol/L, m – mol/kg soln

Further, additional and good quality spectra of solid reference materials were collected: (NH₄)₂MoS₄, (NH₄)₂Mo₃S₁₃, (NH₄)₂Mo₂S₁₂, K₂MoS₄, MoOS₂.

During ES-1050 we glued the molybdenite to lower piston to prevent flotation during convection of fluid. We omitted the glueing this time to completely exclude any potential interaction of cyanoacrilate from the glue with the metal of interest in our experimental solutions. Consequently, at 350°C we faced the problem of floatation of molybdenite crystals in our experimental solution due to convection induced by the thermal gradient in the carbon glassy cell. This problem can be solved in future by a better shielding of the furnace using beryllium foil.

The sulfur-bearing standard solutions have similar spectra at ambient conditions (Fig. 1, left) but demonstrate various behavior with heating (Fig. 1, right). The standard solution with 1M NaHS + NaOH matrix demonstrated reversible changes in Mo speciation after heating and cooling back to room conditions, whereas the Mo standard solution in 1M NaHS matrix is not stable at high *TP* causing molybdenite precipitation, probably on the wall of the glassy carbon cell in the area where the beam is (Fig. 1, right).

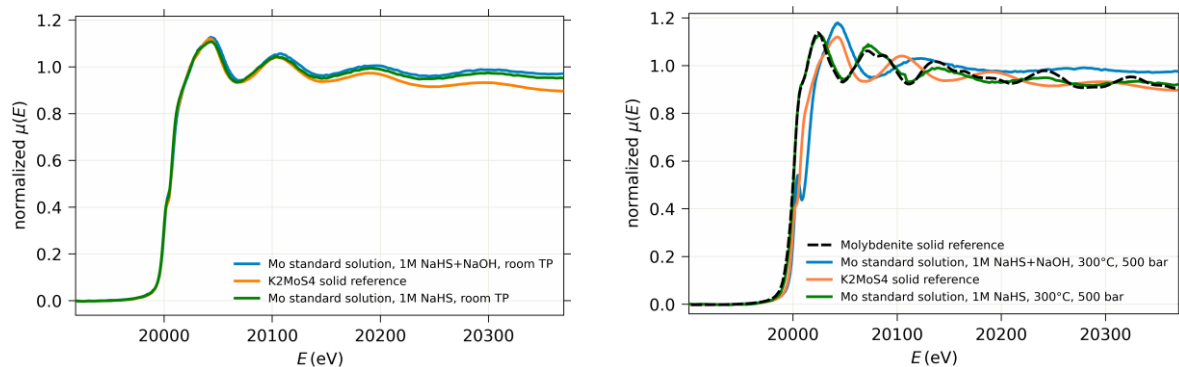


Fig. 1. XAS spectra of Mo-bearing S-rich standard solutions in 1M NaHS (+/- NaOH) matrix at ambient conditions (left) and at high TP (right).

Solubility experiments in sulfur-bearing systems provided consistent results with our previous measurements (Table 1). Our results revealed discrepancies with values calculated using published so far thermodynamic properties of thiomolybdate species, especially, MoS_4^{2-} (Liu et al., 2020). Under alkaline conditions in thiosulfate solution, our data are one order of magnitude lower compared to the calculated values. This observation could point to slow kinetics of sodium thiosulfate decomposition (Kokh et al., 2020). At the same time, values obtained under acidic pH are one-two orders of magnitude higher compared to the calculated values for the MoS_4^{2-} complex. This could point to formation of an aqueous Mo-species with the S_3^- ion, which becomes abundant at acidic conditions.

Table 1. Molybdenite solubilities measured in different S-bearing solutions *in situ* at 300°C, 500 bar.

| Exp. №, beamtime | Composition | pH _T | Mo, ppm | Mo, ppm, calc. |
|------------------|---|-----------------|---------|----------------|
| 1, ES-1278 | 1 M NaHS | 6.8 | 2.8 | 5.2 |
| 3, ES-1050 | 1 M NaHS | 6.8 | 2.8 | 5.2 |
| 2, ES-1278 | 1 m $\text{Na}_2\text{S}_2\text{O}_3$ + 0.3 m NaOH | 6.8 | 2.0 | 34.6 |
| 5, ES-1050 | 1 m $\text{Na}_2\text{S}_2\text{O}_3$ + 0.3 m NaOH | 6.8 | 3.8 | 34.6 |
| 3, ES-1278 | 0.8 m $\text{Na}_2\text{S}_2\text{O}_3$ | 5.3 | 0.3 | 0.49 |
| 5, ES-1278 | 1 m S, 0.4 m NaOH | 5.0 | 4.2 | 0.22 |
| 4, ES-1050 | 0.9 m $\text{Na}_2\text{S}_2\text{O}_3$ + 0.3 m HCl | 4.4 | 3.1 | 0.01 |

Finally, a standard solution with 150 ppm Mo in H_2O was heated together with NS3 glass which completely dissolved at TP . This run revealed no difference in the spectra compared to those measured at basic conditions in equivalent silica-free solutions. This similarity evidences the absence of any complexation of Mo with Si through e.g. an oligomeric species, i.e. there's no evidence for a change in symmetry nor for the presence of a second coordination shell where Si could be located (Fig. 2). Solubility experiments in a S-free system with quartz (exp 6), however, revealed efficient Mo dissolution (1162 ppm), i.e. higher than predicted in the absence of quartz. Work is in progress to provide a thermodynamic interpretation of these results.

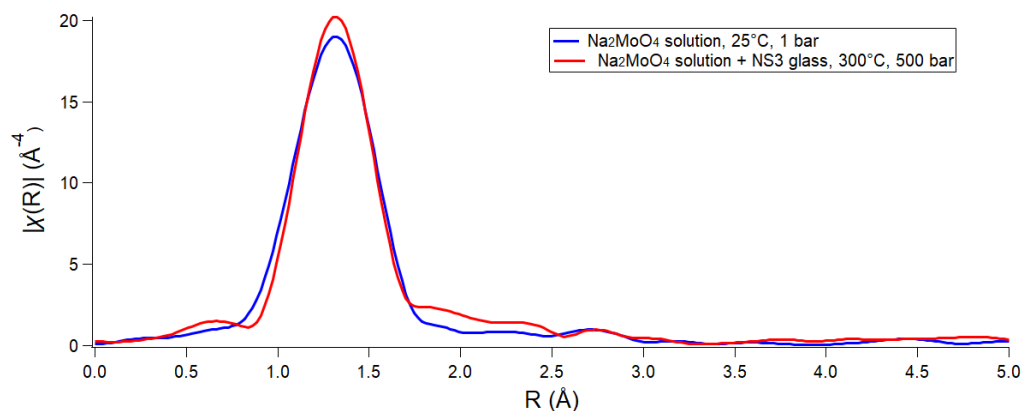


Fig. 2. Fourier transform of EXAFS measured on 150 ppm Mo standard solution with NS3 glass.