

## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> Mobility of molybdenum in chloride and hydrosulphide bearing hydrothermal vapour and liquid: an XAS study	<b>Experiment number:</b> ES-708
<b>Beamline:</b>	<b>Date of experiment:</b> from: 11.07.2018 to: 17.07.2018	<b>Date of report:</b>
<b>Shifts:</b>	<b>Local contact(s):</b> Denis Testemale	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): *Weihua Liu, CSIRO Mineral Resources, Australia *Joel Brugger, Monash University, Australia *Barbara Etschmann, Monash University, Australia		

## Report

*Update: The results of this experiment has been published:*

*Liu et al., The role of sulfur in molybdenum transport in hydrothermal fluids: Insight from in situ synchrotron XAS experiments and molecular dynamics simulations, 2020, Geochimica et Cosmochimica Acta 290, 162-179. <https://doi.org/10.1016/j.gca.2020.08.003>*

The experiment was conducted on 11-17 July 2018 (18 shifts). The beamline and in situ apparatus have behaved nicely with no technical issues during the experiments, except that there was ~4 hour beam loss due to the storage ring shutdown.

The aim of this study was, using the in situ XAS techniques, to measure the coordination structure and solubility of molybdenum in hydrothermal chloride and hydrosulphide-bearing hydrothermal vapour and liquid at up to 600 °C and 100-1000 bar, so as to better understand the transport and deposition properties of Mo ore systems.

The objectives of the study have been largely achieved: we have measured EXAS and XANES spectra of total 18 solutions at temperature up to 450°C and 800 bar. In general the data collected from the solution phase are of good quality at temperature up to 400°C, but at higher temperatures and in the low density fluids the Mo oxides started to precipitates therefore we were not be able to measure the solubility/speciation of Mo in the vapour phase.

The XAS data of two series of sample solutions have been successfully collected:

1. Mo speciation in sodium hydrosulphide solutions: We have for the first time identified a Mo-S species (likely species between  $\text{MoO}_4^{2-}$  and  $\text{MoS}_4^{2-}$ ) predominate in the NaHS solutions with NaHS concentration ranging from 0.07-2 mol/kg. The spectra changes as a function of NaHS concentration are shown in Figure 1.
2. Mo speciation in HCl-NaCl chloride solutions: We found that Mo-Cl-O speciation predominate in the NaCl-free acidic HCl solution, and possibly polynuclear species in the acidic HCl-NaCl solutions. With increasing temperature, molybdate species (e.g.,  $\text{HMoO}_4^-$  or  $\text{H}_2\text{MoO}_4(\text{aq})$ ) become important in both solutions (Figure 2).

We are now conducting detailed data fittings, and plan to use ab initio molecular dynamics simulations to aid data interpretation, aiming a better understanding of Mo speciation in Cl and S-bearing hydrothermal fluids.

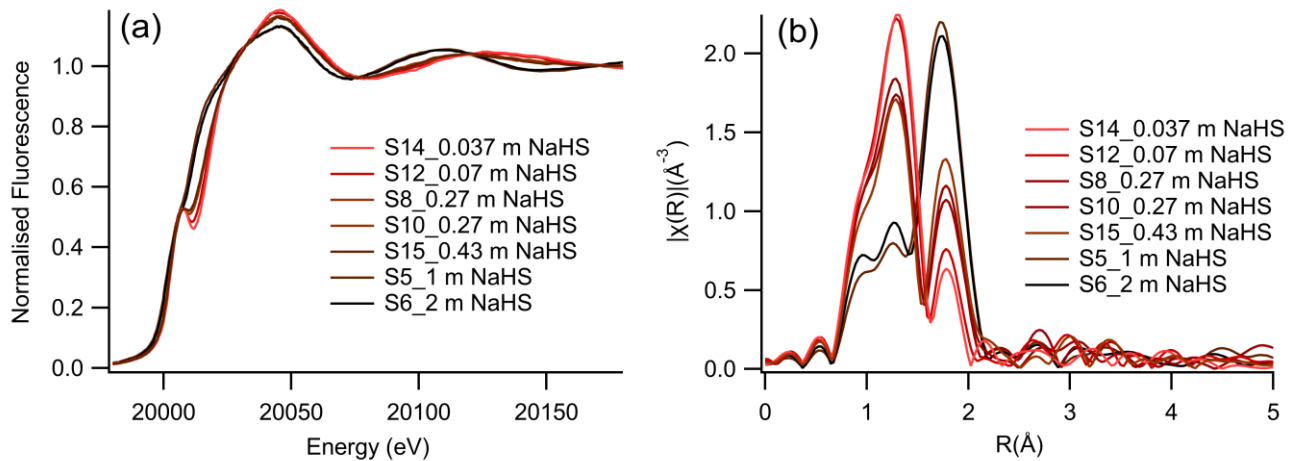


Figure 1. (a) XANES spectra and (b) Fourier transforms of EXAFS spectra of Mo in NaHS solutions at 103°C and 800 bar, with NaSH concentration ranging from 0.07 to 2 mol/kg.

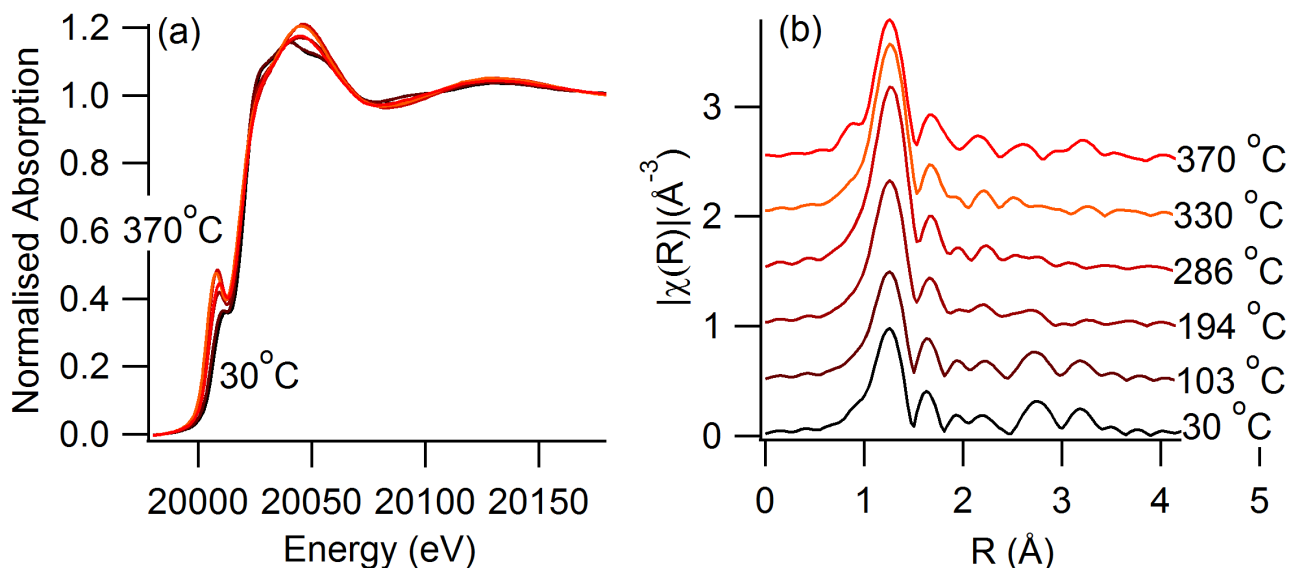


Figure 2. (a) XANES spectra and (b) Fourier transforms of EXAFS spectra of Mo in 0.25 m HCl and 5 m NaCl solution at 30-370°C and 800 bar.

