

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.



	Experiment title: Nature and significance of aqueous Zn(II) hydrosulphide complexes in hydrothermal fluids	Experiment number: ES-17
Beamline:	Date of experiment: from: 24 to: 31/July/2013	Date of report: 20/8/2014
Shifts: 18	Local contact(s): Denis Testemale	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Prof Joël Brugger Mr Yuan Tian *MS Yuan Mei *Dr. Denis Testemale *Dr. Barbara Etschmann *Dr Weihua Liu		

Report:

The experiment suffered from issues with sample stability, which were eventually traced down to contamination in the provided glassy carbon tubes. ~9 shifts were spent 'debugging' these issues and calibrating the temperature in the autoclave.

The experiment scope had to be reduced accordingly. We had two aims for this experiment.

- (1) Confirm experimentally some features of Zn(II) complexing in the chloride solutions predicted from *ab initio* (i.e. *first principle*) molecular dynamics simulations.** We measured 4 solutions at different Zn:Cl ratios from room-T to 500°C at 1000 bar and were able to (i) confirm the persistence of high order Cl complexes (ZnCl_3^- and ZnCl_4^{2-}) up to high temperature (500°C, 1000 bar) and (ii) provide evidence that with increasing temperature, ZnCl_3^- becomes increasingly present as a trigonal planar $[\text{ZnCl}_3]^-$ form rather than the tetrahedral $[\text{ZnCl}_3(\text{H}_2\text{O})]^-$ form predominant at lower temperature, via a careful analysis of the XANES data.

These results have been submitted for publication to *Geochimica Cosmochimica Acta*. As of today (August 20th), we're working on addressing 'major revisions' that result from reviewers' concerns with the MD method used to obtain quantitative thermodynamic information on Zn-Cl complexing, and the development of a thermodynamic model valid over a wide range of P,T. We're confident that we can address the issues. The

good news is that no reviewer attacked our interpretation of the XANES and EXAFS data.

Abstract of the submitted manuscript: The solubility of zinc minerals in hydrothermal fluids is enhanced by chloride complexation of Zn^{2+} . Thermodynamic models of these complexation reactions are central to models of Zn transport and ore formation. However, existing thermodynamic models, derived from solubility measurements, are inconsistent with spectroscopic measurements of Zn speciation.

Here, we use *ab initio* molecular dynamics simulations to predict the speciation of Zn-Cl complexes from 25-600 °C. Qualitatively, the simulations reproduced the main features derived from *in situ* XANES and EXAFS measurements: octahedral to tetrahedral transition with increasing temperature and salinity, stability of ZnCl_4^{2-} at high chloride concentration up to ≥ 500 °C, and increasing stability of the trigonal planar $[\text{ZnCl}_3^-]$ complex at high temperature. This excellent qualitative agreement serves to ground proof the MD model and enticed us to attempt a fully quantitative *ab initio* study via the thermodynamic integration method. Remarkably, the stability constants for the Zn-Cl complexes derived from the *ab initio* simulations accurately predict the experimentally observed changes in $\text{ZnO}_{(s)}$ and $\text{ZnCO}_{3(s)}$ solubility as a function of chloride concentration from 200/ P_{sat} to 600 °C/2 kbar. We find large changes in Zn-Cl complexation with temperature. We confirm that the $[\text{ZnCl}_4]^{2-}$ complex dominates in salty fluids even at $T > 400$ °C and provide a thermodynamic model that is consistent with MD, XAS data and existing solubility studies up to 600 °C. This study shows that quantitative molecular dynamic techniques can alleviate uncertainties in the interpretation of solubility data, and are especially useful at high temperature due to the faster kinetics of the ligand exchange reactions.

(2) Provide the first in-situ spectroscopic information on the nature and stability of Zn(II) bisulfide complexes. We originally planned to perform a series of measurements for solutions with different concentrations of bisulphide. However, the $\text{ZnS}_{(s)}$ solubility was about one order of magnitude lower than expected. Because of this and with regard to the time lost for commissioning, we had to change the focus of the experiment, and instead focussed on getting good quality XANES and EXAFS out of a single 2 m NaHS solution. The results, however, are key to confirm the predictions from *ab initio* MD that contrary to chloride, the bisulfide ligand does not form tetrahedral complexes with Zn(II); rather, a trigonal planar $\text{Zn}(\text{HS})_3^-$ complex is formed. We have finished the *ab initio* MD simulations for this system, and plan to submit a paper on the role of hydrogen bonding in determining the transport of metals in hydrothermal systems, using the contrast between Zn bisulfide and Zn chloride complexes as a case study.