



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 using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now 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:

An XAS study of lead speciation in chloride and disulphide solutions under hydrothermal conditions: deciphering the role of sulfur for base metal transport

Experiment number:
ES-451

Beamline: BM-30B	Date of experiment: from: 22 Feb 17 to: 28 Feb 17	Date of report: 06 March 17 <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Denis Testemale	

Names and affiliations of applicants (* indicates experimentalists):

Joel Brugger* and Barbara Etschmann*, Monash University

David Sherman*, University of Bristol

Report:
Aim

Recently thermodynamic modelling predicted that contrary to the established consensus, hydrosulfide complexes may be the predominant form of base metals in many natural fluids at high temperatures. This project aimed to test this hypothesis by determining the molecular structure, stability constants, and competition among Pb(II) chloro- and hydrosulfide-complexes at T up to 500C, 800 bar.

A secondary aim was to collect some data on the Pb-Cl and Pb-Br systems to complement the transmission only experiment conducted in Australia.

Experimental

Data were collected at the Pb L₃-edge (13035 eV) at the BM-30B (FAME) beamline, using the high T-P autoclave developed by the Institut Neel.

Sample*	Conditions**
PbO	Pellet
Diaboleite: Pb ₂ CuCl ₂ (OH) ₄	Pellet
Sol1: PbCl ₂ in 0.9 m NaCl +0.1 m HCl	30-500 °C, 800 bar
Sol2: PbCl ₂ in 0.1 m HCl	100-450 °C, 800 bar
Sol3: PbS in 1 m NaHS	100-400 °C, 800 bar
Sol4: PbCl ₂ in 10 m LiCl +0.05 m HCl	30-100 °C, 800 bar
Sol5: PbCl ₂ in 10 m LiCl +0.1 m HCl	30-500 °C, 800 bar
Sol6: PbBr ₂ in 1 m NaBr +0.1 m HBr	30-450 °C, 800 bar
Sol7: PbS in 1 m NaHS + S	300-450 °C, 800 bar
Sol8: PbCl ₂ in 0.1 m Na-Acetate	30-300 °C, 800 bar
Sol9: PbBr ₂ in 4 m NaBr +0.1 m HBr	30-500 °C, 800 bar
Sol10: PbCl ₂ in 1 m Na-Acetate + Acetic acid	30-250 °C, 800 bar
Sol11: PbCl ₂ in 0.1 m Na-Acetate + Acetic acid	30-250 °C, 800 bar
Sol12: PbBr ₂ in 0.1 m HBr	30-400 °C, 800 bar

*As this experiment was conducted immediately after the Y experiment (17038 eV), using the same glassy-C cell, it was determined that same water calibration could be used for this experiment.

** All the temperatures listed are thermocouple readings, they have not yet been corrected.

General observations/preliminary fits

- Sol3: PbS in 1 m NaHS – an intriguing “bump”/tiny step was observed at 300 °C, an actual step at 400 °C which decreased with time, indicating that the solubility of PbS could be higher than that previously expected. However given the noise in the spectra it was not out if the realm of possibility that the PbS solid that had been loaded into the cell was floating in the beam. The evidence while intriguing was not convincing.

- Sol7: PbS in 1 m NaHS + added S(s) – to decrease the pH of the solution, a piece of S was added. For this system a surprisingly large edge step was obtained. However, the spectrum varied suspiciously little with time or temperature. The last time we had such an unusual result it transpired that we must have been measuring the solid (and when we tried to repeat that experiment the results were radically different). Given the lack of variability of the spectra with temperature, the data are suspicious and not convincing.
- Preliminary fits** indicate that Pb(II) has a low coordination number in salty solutions ($< \sim 1$ m salt). EXAFS fitting struggles to decide between a total of 3 or 4 ligands total at low temperatures (eg 30-100 °C). Some quick ADF calculations suggest that the structure is happier with 3 ligands. NB for higher temperatures (~ 500 °C) the coordination number seems to decrease even more.
- Preliminary fits** indicate that Pb(II) has a higher coordination number in more “watery” solutions (ie 0.1 m HBr), that drops with increasing temperature. This higher coordination number is more noticeable (and higher) for Br-bearing solutions than for Cl.
- Preliminary fits** indicate that under the conditions measured, Pb(II) is never fully chlorinated, there is always some O present. And conversely, even under rather low Br concentrations (0.1 m HBr) (and Cl?), there is evidence of Br being coordinated at low temperatures.

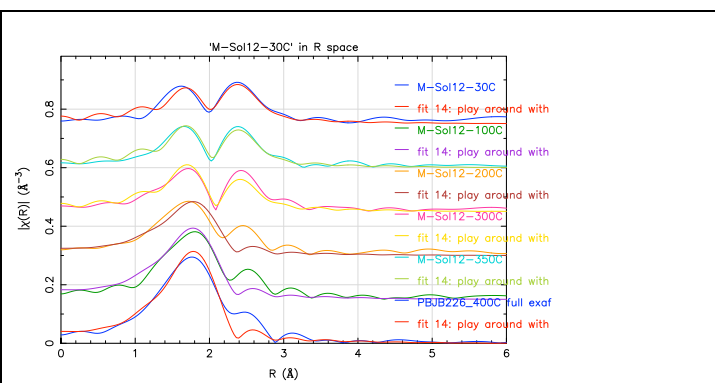
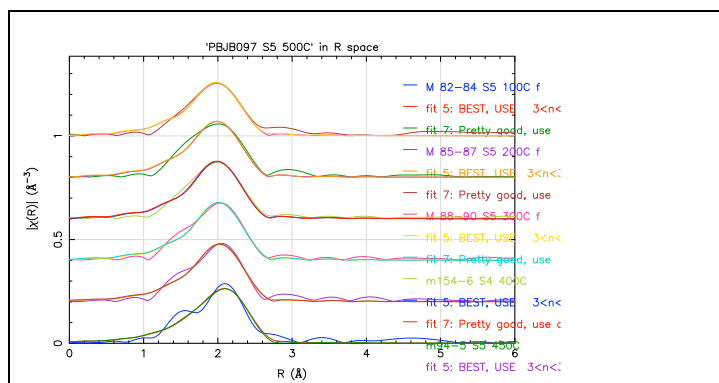


Fig. 1 Sol5=10 m LiCl+0.1m HCl, fitting with the total number of ligands constrained to be 3 (fit 5) and 4 (fit 7).

Fig. 2 Sol12 = PbBr₂ in 0.1 m HBr. Appears to be some Br coordinated even at 30 °C, as the peak at ~ 2.5 Å is larger than just that due to the Fourier termination error of the O path.

Some preliminary fit results

	T (°C)	nO	R(O) Å	nCl	R(Cl) Å	σ^2	χ^2_{red}	
Sol5	100	1.3(2)	2.48(8)	3(1)	2.75(3)	0.019(6)	101	
10m LiCl+ 0.1mHCl	200	1.3(4)	2.41(3)	1.7(2)	2.71(2)	0.010(1)		
Fit5	300	1.0(3)	2.40(3)	2.0(3)	2.68(2)	0.012(1)		
Total number of ligands	400	1.0(3)	2.38(3)	2.0(3)	2.66(2)	0.012(1)		
Constrained to be 3	450	0.9(4)	2.37(4)	2.1(4)	2.65(2)	0.013(2)		
	500	1.0(6)	2.39(7)	2.0(5)	2.65(3)	0.014(3)		
	T (°C)	nO	R(O) Å	σ^2	nCl	R(Cl) Å	σ^2	χ^2_{red}
Sol5	100	1.4(7)	2.45(5)	0.020(9)	2.6(7)	2.75(2)	0.015(4)	114
10m LiCl+ 0.1mHCl	200	1.6(6)	2.46(4)	0.018(13)	2.4(6)	2.70(2)	0.014(5)	
Fit7	300	1.4(6)	2.46(3)	0.018(18)	2.6(6)	2.67(2)	0.015(5)	
Total number of ligands	400	1.2(6)	2.44(3)	0.014(22)	2.8(6)	2.64(2)	0.017(7)	
Constrained to be 4	450	1.2(9)	2.44(5)	0.018(34)	2.8(9)	2.64(2)	0.017(8)	
	500	1(1)	2.43(8)	0.009(29)	3(1)	2.64(4)	0.021(13)	

Though think perhaps there should be a change in total ligand number with T

Impact and publication

- From this we conclude that bisulfide may be an important complex, but not at $T < \sim 400$ °C.
- The rest of the data nicely complement our other data, so in theory a publication should be written shortly (though in practice it might take a little longer than desired given other commitments/time constraints).
- MD simulations/ADF results provide extra evidence/constraints for the EXAFS results.