



## 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>

### Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

#### Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

### Deadlines for submitting a report supporting a new proposal

- 1<sup>st</sup> March Proposal Round - **5<sup>th</sup> March**
- 10<sup>th</sup> September Proposal Round - **13<sup>th</sup> September**

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.

### Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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.

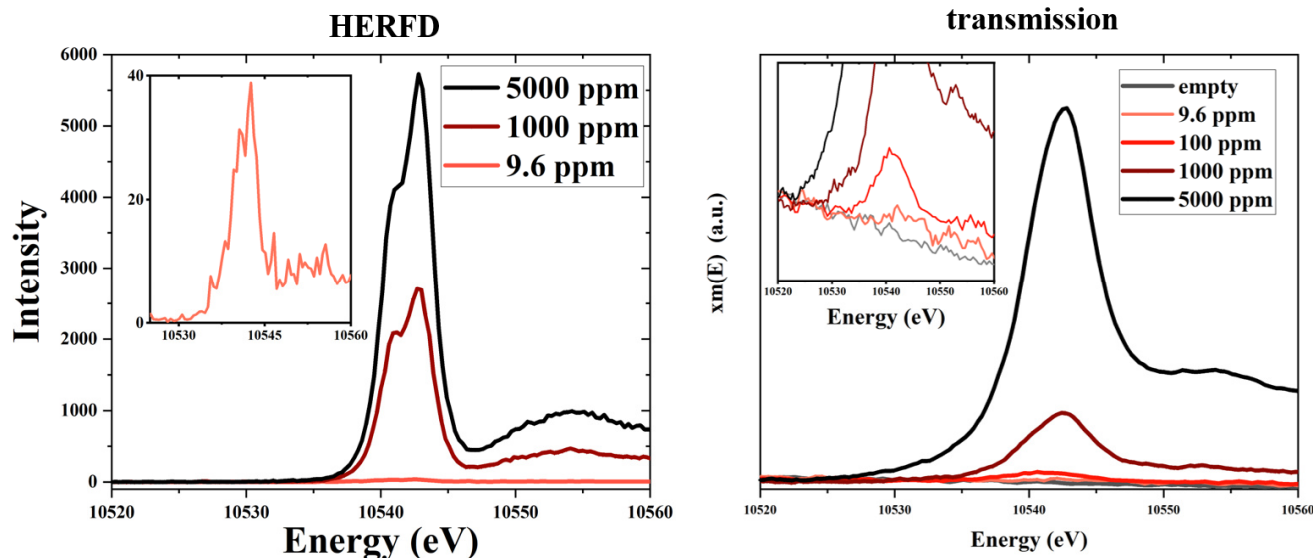


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|---|---|--|
|   | <b>Experiment title:</b><br><b>Mobilization of rhenium in magmatic fluids with implications for its exploration</b> | <b>Experiment number:</b><br>ES 976    |
| <b>Beamline:</b><br>FAME-UHD<br>BM23  | <b>Date of experiment:</b><br>from: 21.4.2021 to: 26.4.2021<br>from: 30.4.2021 to: 3.5.2021                         | <b>Date of report:</b><br>13/09/2022   |
| <b>Shifts:</b>  | <b>Local contact(s):</b><br>Elena Bazarkina<br>Denis Testemale  | <i>Received at ESRF:</i><br>13/09/2022 |
| <b>Names and affiliations of applicants</b> (* indicates experimentalists):<br>Angelika D. Rosa* ESRF, Grenoble, France<br>Joao Elias Figueiredo Soares Rodrigues* ESRF, Grenoble, France<br>Harald Mueller |   |  |

## Report:

We studied systematically the solubility and speciation of Re in fluids as a function of pressure, temperature ( $P/T$ ), and fluid composition (sulfur, chlorine,  $fO_2$ ) using X-ray fluorescence spectroscopy and High- Energy Resolution Fluorescence Detection (HERFD). Such information can only be obtained through *in-situ* synchrotron radiation experiments at high  $P/T$  conditions. We covered the range of  $P/T$  conditions that correspond to Re mobilization during hydrothermal and magmatic processes (0.08-0.5 GPa, and 300 – 400 °C) using optimized devices such as the hydrothermal autoclave and the resistively heated diamond anvil cell. We have conducted two key experimental sessions at FAME-UHD and BM23.

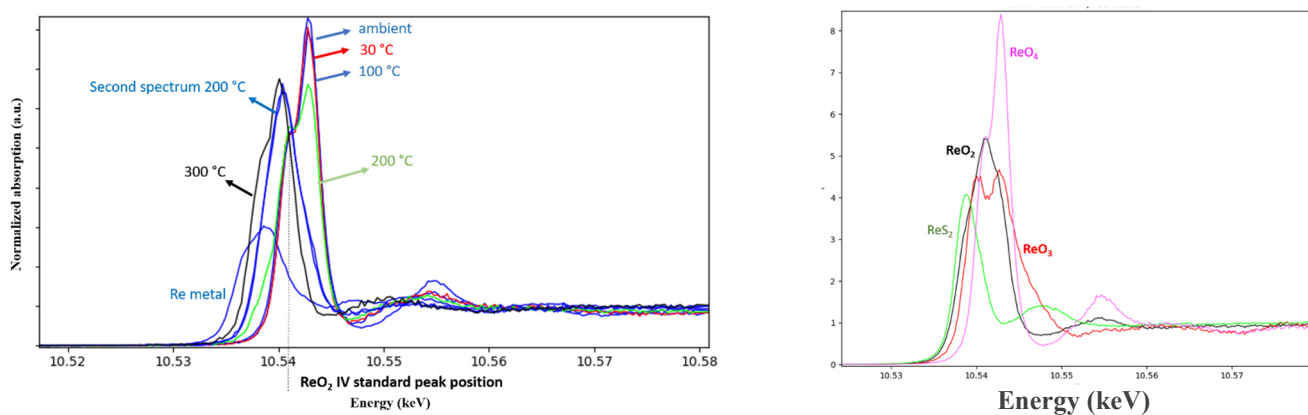
At FAME-UHD 12 high  $P/T$  runs were conducted in the autoclave up to 400°C and 800 bars and in HERFD-XAS mode and on the Re L3 edge (10.535 keV – emission at 8.6525 keV). The X-ray emission spectrometer was equipped with six silicon (642) crystal analyzers and energy resolved Ketek fluorescence detector. Tungsten L3 edge spectra (10.207 keV) were acquired throughout the experiment in transmission mode to verify the monochromator angle to energy calibration. We tested first the signal quality using Re standard solution obtained from the dissolution of  $NaReO_4$  in distilled water, Re concentrations ranging from 9.6 to 5000 ppm. These solutions were prepared by Harald Mueller (ESRF Chemistry Laboratory). Best signal quality and no precipitation in the beam were observed for the solutions with intermediate concentrations ranging from 2500 – 3333 ppm of Re. With the current beamline and detection settings 9.6 ppm of Re could still be well resolved both with HERFD and transmission XAS (**Figure 1**). The HERFD data suggest that potentially even lower concentrations are detectable. Subsequently Re speciation experiments were conducted using pure water, HCl solutions with concentrations of 0.1, 1.7, and 5 M, a 1.7 M NaCl solution, a 0.135 mol/L  $Na_2S$  solution, and a mixture consisting of a 0.135 mol/L  $Na_2S$  and + 0.144 mol/L NaOH solution (**Figure 2a**). We used the Re standard solutions to calibrate the XRF counts to concentrations for the solubility experiments and performed one solubility experiment of  $ReS_2$  in 2.66 mol/L  $Na_2S$  2.66 mol/L NaOH.



**Figure 1.** XANES spectra acquired in HERFD (left panel) and transmission XAS detection mode (right panel) on Re standard solutions.

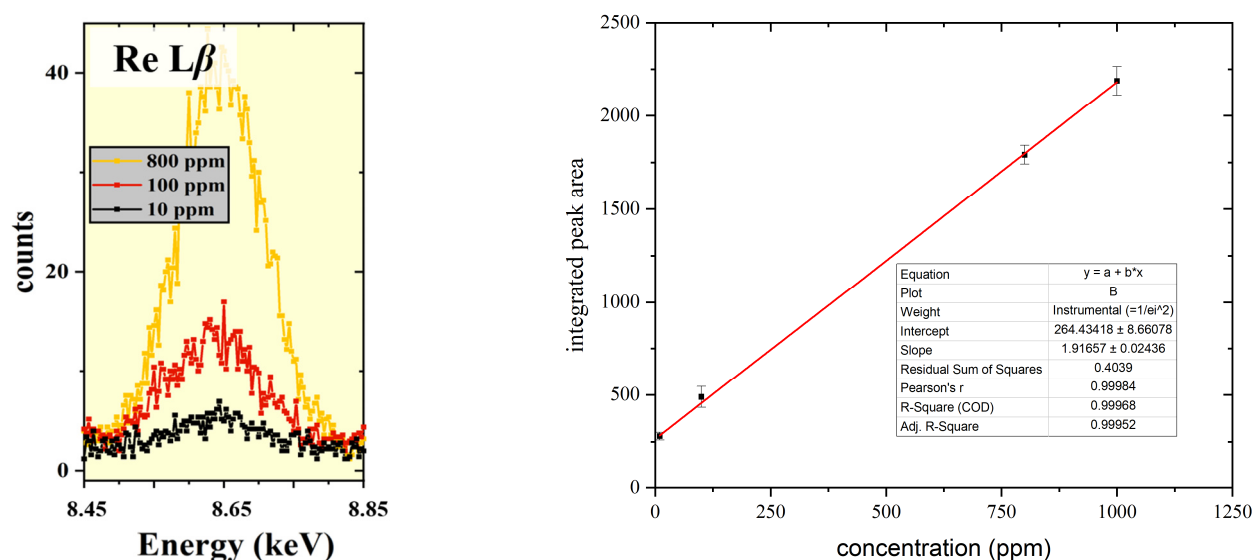
The first analysis of the data reveals high thermal stability of the  $[\text{Re}^{\text{VII}}\text{O}]_4^-$  complex in neutral solutions including water, 1.7 M NaCl, low concentrated HCl solutions (0.1 M), and oxygen-rich solutions such as 0.135 mol/L  $\text{Na}_2\text{S}$  and + 0.144 mol/L NaOH. At higher chlorine concentrations and acid solutions ( $>1.7$  M HCl) the thermal stability of  $[\text{ReO}]_4^-$  complexes reduces to 100 °C (**Figure 2a**). Beyond 100 °C the white line of the HERFD-XANES spectra shifts to lower energy and changes the shape, indicating changes in the oxidation state of Re and dominant complex composition. We expect that at these conditions either oxo-chloro complexes of Re form similar to observations on molybdenum in acid solutions [Borg et al., 2012] or pure chlorine complexes form as proposed by Xiong & Wood [2002]. Careful analysis of both HERFD-XANES and EXAFS observations is currently in progress to resolve the speciation of Re above 200°C. The HERFD-XANES spectrum of Re in 0.135 mol/L  $\text{Na}_2\text{S}$  solution also shows strong changes if compared with  $[\text{Re}^{\text{VII}}\text{O}]_4^-$  complex. Under these conditions, Re complexes with S are expected to predominate. The reference compounds analyzed include Re metal,  $\text{Re}^{\text{VII}}\text{O}_2$ ,  $\text{Re}^{\text{VII}}\text{O}_3$ ,  $\text{NaRe}^{\text{VII}}\text{O}_4$ , and  $\text{Re}^{\text{VII}}\text{S}_2$  (**Figure 2b**).

The dissolution experiment on  $\text{ReS}_2$  in sulfur-bearing solution revealed an unexpectedly high solubility of Re at 400 °C and 800 bars. Further solubility experiments of Re,  $\text{ReO}_2$ , and  $\text{ReS}_2$  are required to constrain its transport and enrichment in natural ore-forming fluids. These additional experiments are required to complement our pioneer measurements at FAME-UHD. We, therefore, plan to submit another proposal to finalize this dataset.



**Figure 1. Left panel:** Evolution of Re L3 edge HERFD-XANES spectra in 1.7M HCl – 3333 ppm  $\text{NaReO}_4$  –  $\text{H}_2\text{O}$  solution with temperature at 800 bars. The shift of the XANES spectra to lower energies with increasing T indicating an change of oxidation state and dominant Re complex. **Right panel:** Re L3-edge HERFD-XANES spectra of reference compounds, Re metal compound is displayed in the left panel.

At BM23 we tested first the detection limits of Re in the diamond anvil cell using a SDD Vortex detector for X-ray fluorescence detection combined with a polycapillary optics similar to our previous works (Farsang et al., 2021). For this purpose, several standard solutions prepared by dissolving NaReO<sub>4</sub> in distilled water were loaded in steel gaskets and sealed under very low pressure <0.1 GPa. The calibration results, shown in **Figure 3**, are very promising and reveal that concentration down to the ppm level can be detected inside the diamond anvil cell and polycapillary optics at BM23 after the EBS. Subsequently, we tested the solubility of pure Re metal in 0.1 M HCl solution loaded in a Re gasket lined with platinum. We did not detect any dissolution of Re up to 400 °C (steps of 50 °C) and 1 GPa suggesting a very low solubility of Re (below 10 ppm) at these conditions even after 1 day of heating. In the available beamtime the beamline alignment, calibration, and this first dissolution experiment could be performed, which provide very promising results to further study of Re solubility. We, therefore, plan to submit also an additional proposal to BM23 to detect Re solubility at higher P/T conditions not easily achievable using the autoclave system. According to our observations at BM16, the Re solubility in S-bearing solutions would be important to verify under T-P which can be reached with a diamond anvil cell.



**Figure 3. Left panel:** Re L3 edge fluorescence spectra acquired on standard Re solutions with different concentrations. **Right panel:** Detector counts to Re concentration curve acquired with this setup demonstrating the feasibility to resolve 9 ppm of Re.

## References

Y. Xiong & S. A. Wood (2002). Experimental determination of the hydrothermal solubility of ReS<sub>2</sub> and the Re–ReO<sub>2</sub> buffer assemblage and transport of rhenium under supercritical conditions. *Geochem. Trans.*, 3(1) 1-10

Borg, S., et al., (2012). An XAS study of molybdenum speciation in hydrothermal chloride solutions from 25–385 °C and 600 bar. *Geochimica et Cosmochimica Acta* 92 292–307.

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