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ESRF

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.

ESRF	**Experiment title:** The Hydrothermal Geochemistry of Tantalum	**Experiment number:** A16-1-811
Beamline: BM-16	**Date of experiment:** from: 22 Feb 22 to: 01 March 22	**Date of report:** 31 Aug 22
Shifts: 18	**Local contact(s):** Denis Testemale	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Joel Brugger* and Barbara Etschmann, Monash University

Weihua Liu, CSIRO

Aim

Tantalum (Ta) is recognized as one of the so-called '*critical minerals*', with wide applications in the electronics and green energy industry but limited supply chain. An understanding of the speciation and solubility of Ta in hydrothermal solutions is key in helping both Ta exploration and mineral processing. High-resolution X-ray absorption spectroscopy (XAS) can reveal fine features of the XANES spectra, thus help identifying important Ta aqueous complexes (with O, F and Cl) that are hard to identify using conventional XAS detection techniques.

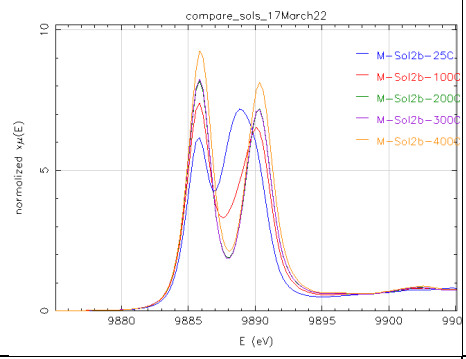
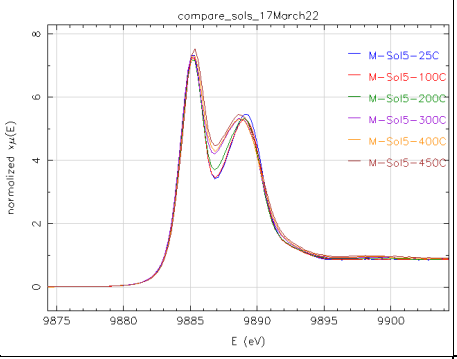
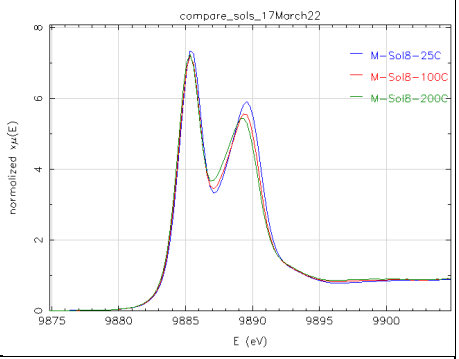
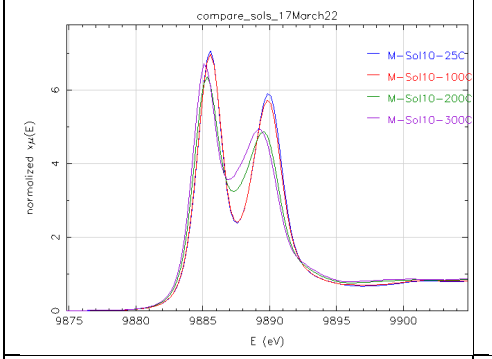
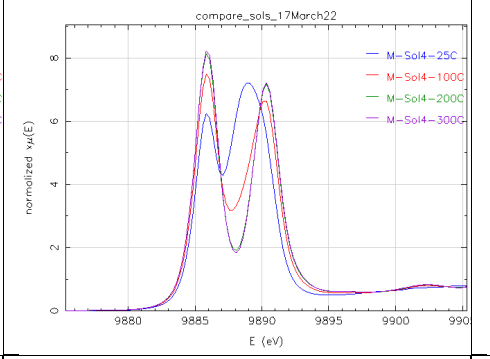
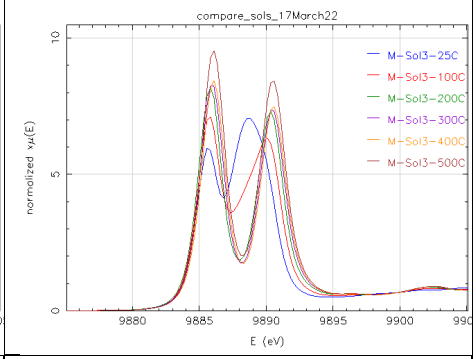
Experimental

Data were collected at the Ta L_3-edge (9881 eV) at the BM-16 (FAME-UHD) beamline, using the high T-P autoclave developed by the Institut Neel.

Sample	Conditions	Sample	Conditions
Ta_2O_5	Pellet		
Sol2: $TaCl_5$ + 1 m HF	30-500 ºC, 800 bar	Sol8: TaF_5 + 6 m HCl	25-400 ºC, 800 bar
Sol3: TaF_5 + 2.87 m HF	25-500 ºC, 800 bar	Sol9: Ta_2O_5 + 1 m NaOH	200-500 ºC, 800 bar
Sol4: TaF_5 + 1 m HF	25-400 ºC, 800 bar	Sol10: TaF_5 + 0.1 m HF	25-500 ºC, 800 bar
Sol5: $TaCl_5$ + 6 m HCl	25-500 ºC, 800 bar	Sol13: Ta_2O_5 solubility	25-400 ºC, 400 bar

General observations

1. XANES indicate that Ta-salts in HCl have a structure that does not change much with temperature. Preliminary fits suggest that Sol5 and Sol8 can be fitted with 6xO at all T, T-O~1.82 to 1.85 Å (Sol5) & Ta-O ~ 1.86 Å (Sol8).
2. Ta-salt in HF: The XANES spectra have a distinct change that occurs around 100-200 ºC, depending on the HF concentration), however fits indicate ~8xF from 25 to 400 ºC. This is consistent with the room temperature study of Wilson et al. (2015, DOI: 10.1002/ejic.201600981) that noted 7-8 fluorine coordinated to Ta in solutions containing 1-27 M HF; suggesting that the change in XANES could be related to the change from 7 to 8 fluorine ligands.

Effect of Ta salt in acid (HF, HCl)		
		
Sol2: $TaCl_5$ + 1 m HF	Sol5: $TaCl_5$ + 6 m HCl	Sol8: TaF_5 + 6 m HCl
Effect of increasing HF concentration		
		
Sol10: TaF_5 + 0.1 m HF	Sol4: TaF_5 + 1 m HF	Sol3: TaF_5 + 2.87 m HF

Impact

These measurements at the Ta edge complement previous efforts by M. Louvel (Experimental reports 30-02-1089 and 30-02-1096 – Louvel et al., 2015*), Brugger and Etschmann (Experimental report 30-02 1088, Liu et al. 2017*) and Louvel, Brugger and Etschmann (Experimental report 30-03 1102, ES-550) investigating hydrothermal speciation of other critical metals.

The results were presented at XAFS2022. We aim to publish this work, possibly in conjunction with Nb data (aim to submit an application in the September 2022 round), as Nb and Ta are geochemical twins.

Previous work on critical metals, with data collected at ESRF.

*Louvel, M., Etschmann, B., Guan, Q., Testemale, D. and Brugger, J. (2022) Carbonate complexation enhances hydrothermal transport of rare earth elements in alkaline fluids. Nature Communications 13, 1-11.

* Guan, Q.S., Mei, Y., Etschmann, B., Testemale, D., Louvel, M. and Brugger, J. (2020) Yttrium complexation and hydration in chloride-rich hydrothermal fluids: A combined ab initio molecular dynamics and in situ X-ray absorption spectroscopy study. *Geochimica Et Cosmochimica Acta* 281, 168-189.

*Guan, Q., Mei, Y., Etschmann, B., Louvel, M., Testemale, D., Bastrakov, E. and Brugger, J. (2022) Yttrium speciation in sulfate-rich hydrothermal ore-forming fluids. *Geochimica et Cosmochimica Acta* 325, 278-295

*Guan, Q., Mei, Y., Etschmann, B., Louvel, M., Testemale, D., Spezia, R. and Brugger, J. (2022b) Speciation and thermodynamic properties of La (III)-Cl complexes in hydrothermal fluids: a combined molecular dynamics and in situ X-ray absorption spectroscopy study. *Geochimica et Cosmochimica Acta*, 330, 27-46.

*Louvel & Mavrogenes, 2015, 'Hydrothermal controls on the genesis of REE deposits: Insights from an in situ XAS study of Yb solubility and speciation in high temperature fluids (T<400C)'. *Chemical Geology*, 417, pp. 228-237

*Liu, Etschmann, Hazemann, Testemale, Migdisov and Brugger, 2017. Revisiting the hydrothermal geochemistry of europium(II/III) in light of new in-situ XAS spectroscopy results. *Chemical Geology*, 459, 61–74.