EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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 via the User Portal:
https://wwws.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 form 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

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th 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.

ESRF	**Experiment title:** Solubility of metal carbonate minerals in subduction environments: the deep Earth carbon cycle	**Experiment number**: ES-791
Beamline: BM23	**Date of experiment**: from: 21/11/2018 to: 27/11/2018	**Date of report**: 13/05/2021
Shifts: 18	**Local contact(s)**: Angelika Rosa (email: arosa@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Summary:

High-pressure/temperature smithsonite ($ZnCO_3$) solubility experiments in pure water and saline solutions [1 m NaCl(aq) and in 4.5 m NaCl(aq)] were carried out at the X-ray absorption beamline BM23. Smithsonite crystals of known volume (~20 x 20 x 20 µm) were loaded in the sample chamber of the diamond anvil cell (DAC) together with the aqueous fluid. The DAC was then pressurised and heated. X-ray fluorescence (XRF) spectra of the fluid were collected at different pressure/temperature steps in order to monitor the solubility of smithsonite, which increased with increasing pressure-temperature conditions. In addition, XRF spectra of $ZnCl_2$(aq) reference solutions loaded in the DAC were collected at ambient temperature. A high-pressure high-temperature experiment investigating potential Re dissolution in the fluid was also run. The concentration of Re in the fluid remained constant at different pressure-temperature conditions.

DAC:

Two membrane-type DACs (Letoullec et al. 1988) from ID27, equipped with type Ia single crystal diamond anvils with culet diameters of 500 µm were used. A partially perforated diamond anvil with a remaining thickness of ~150 um facing the XRF detector was employed to minimize the absorption of the fluorescence signal from the diamond. Rhenium gaskets were employed, pre-indented from an initial thickness of 200 µm to ~80 µm, then laser drilled with a 200 µm diameter hole, and lined with a 25 µm gold layer to prevent Re dissolution in the high *P*-*T* fluid.

Heating and temperature determination:

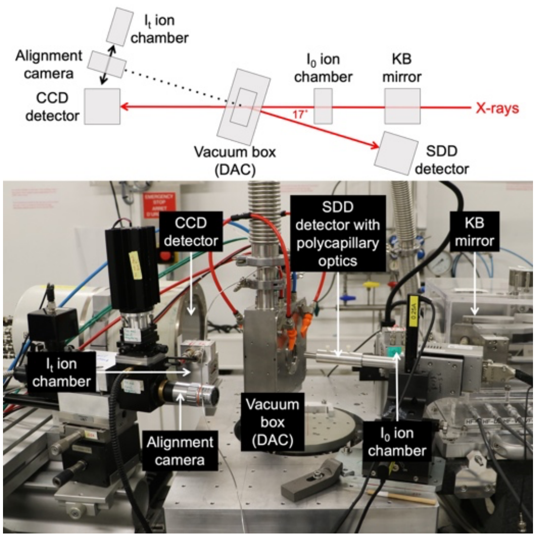
The DAC was heated resistively using an external heating device, in which the DAC and its heater were enclosed in a vacuum chamber equipped with Mylar windows that permit transmission of X-rays. A high vacuum of up to 10^{-6} bars ensured a homogenous heating during the long duration of the experiments and prevents the oxidation of the diamonds and heater. The setup further allows for a fine and remote control of the pressure and temperature (Dewaele et al. 2018). For the latter, a K-type thermocouple is positioned close to the heater. A second thermocouple was placed in contact with one of the diamonds to monitor the sample temperature.

Pressure determination:

Pressure was monitored based on the diffraction signal of gold and the thermal equation of state reported by Fei et al. (2007). The incident X-ray beam energy for X-ray diffraction (XRD) was 15 keV. Diffraction data were recorded using a 165 mm diameter MarCCD XRD detector positioned on the downstream side of the DAC. A CeO_2 standard was used to calibrate the distance, detector tilt, and rotation parameter.

XRF:

The incident X-ray beam energy for XRF was E_0= 11.0 keV (λ=1.1271 Å). The XRF signal was collected using a HITACHI Vortex Si drift diode detector with a 40 mm^2 active area and a sensitive layer thickness of 1 mm equipped with XOS polycapillary focusing optics, which allows the extraction of emitted fluorescence signal from a small sample area of 50×50 (h×w) μm^2.



The experimental setup at BM23

Conclusion:

Thanks to the exceptional experimental setup at BM23, solubility data could be collected up to 6 GPa and 400 °C. The solubility of smithsonite was found to increase with salinity, pressure, and temperature in the studied pressure range. The detailed experimental results can be found in the following publication:

Stefan Farsang, Marion Louvel, Angelika D. Rosa, Monica Amboage, Simone Anzellini, Remo N. Widmer, and Simon A. T. Redfern (2021): Effect of salinity, pressure and temperature on the solubility of smithsonite ($ZnCO_3$) and Zn complexation in crustal and upper mantle hydrothermal fluids. *Chemical Geology, 578,* 120320. https://doi.org/10.1016/j.chemgeo.2021.120320

References:

Dewaele, A., Svitlyk, V., Bottin, F., Bouchet, J., and Jacobs, J. (2018) Iron under conditions close to the α − γ − ϵ triple point. Applied Physics Letters, 112, 1–5.

Fei, Y., Ricolleau, A., Frank, M., Mibe, K., Shen, G., and Prakapenka, V. (2007) Toward an internally consistent pressure scale. Proceedings of the National Academy of Sciences, 104, 9182–9186.

Letoullec, R., Pinceaux, J.P., and Loubeyre, P. (1988) The membrane diamond anvil cell: A new device for generating continuous pressure and temperature variations. High Pressure Research, 1, 77–90.