EUROPEAN SYNCHROTRON RADIATION FACILITY

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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 via the User Portal:

https://wwws.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.

ESRF	**Experiment title:** Solubility of metal carbonate minerals in subduction environments: the deep Earth carbon cycle	**Experiment number**: ES-743
Beamline: ID27	**Date of experiment**: from: 11/05/2018 to: 16/05/2018	**Date of report**: 14/07/2021 *Received at ESRF:*
Shifts: 12	**Local contact(s)**: Mohamed Mezouar (email: mezouar@esrf.fr)	

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Report:

Summary:

High-pressure/temperature rhodochrosite ($MnCO_3$) solubility experiments in pure water and saline solution [1 m NaCl(aq)] were carried out at the ID27 beamline. Rhodochrosite crystals of known volume (~40 x 40 x 40 μm) were loaded in the sample chamber 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 to monitor the solubility of rhodochrosite, which increased with increasing pressure/temperature conditions. In addition, XRF spectra of $MnCl_2 \cdot 4H_2O$(aq) reference solutions loaded in the DAC were collected at ambient temperature. We also attempted to measure the solubility of siderite ($FeCO_3$) in aqueous fluids and the solubility of rhodochrosite in 4.5 m NaCl(aq), but observed precipitation on the diamond culets in contact with the sample chamber and terminated the experiment.

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 250 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:

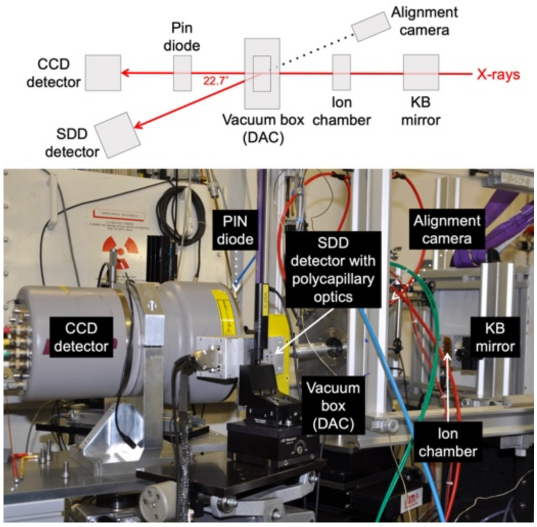
The DAC was heated resistively using an external heating device, in which the DAC and its heater were enclosed in a vacuum chamber equipped with Mylar windows that permit transmission of X-rays. A high vacuum of up to 10^{-6} bars ensured a homogenous heating during the long duration of the experiments 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 was 20 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= 20 keV (λ=0.6199 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 ID27

Conclusion:

Thanks to the exceptional experimental setup at ID27, solubility data could be collected up to 6.8 GPa and 415 °C. The detailed experimental results can be found in the following publication:

Stefan Farsang, Marion Louvel, Chaoshuai Zhao, Mohamed Mezouar, Angelika D. Rosa, Remo N. Widmer, Xiaolei Feng, Jin Liu, and Simon A. T. Redfern (2021): Deep carbon cycle constrained by carbonate solubility. *Nature Communications, 12,* 4311. https://doi.org/10.1038/s41467-021-24533-7

References:

Dewaele, A., Svitlyk, V., Bottin, F., Bouchet, J., and Jacobs, J. (2018) Iron under conditions close to the $\alpha - \gamma - \epsilon$ 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.