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

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 $CaCO_3$ minerals at (P, T) subduction zones conditions"**	**Experiment number**: ES-30
Beamline: ID27	**Date of experiment**: from: 06/10/2013 to: 09/10/2013	**Date of report**: 27/02/2014
Shifts: 9	**Local contact(s)**: *Mohamed Mezouar*	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Sébastien Facq[1], *Isabelle Daniel*[1], *Sylvain Petitgirard*[2] *and Hervé Cardon*[1].

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Report:

Parameters of the ID 27 beamline:

- *E_0= 20 keV (λ=0.6199 Å) M_0 K-edge*
- *Vortex detector coupled to a polycapillary (50 mm focal distance)*
- *Horizontal focalization: 3.7 µm*
- *Vertical focalization : 4 µm*
- *Sample-detector distance : 498.0960 mm*
- *Direct beam coordinates : x=1081.671 et y=971.5441*
- *Tilting plane rotation angle: 37.33696°*
- *Tilt in plane detector angle: -0.366689*

Diamond anvil cells used:

- Two diamond anvil cells LeToullec HT from ID27 with high temperature seats and high resistivity graphite furnaces (700 µm high) equipped with conical *perforated diamonds* (0.70+1.30+25°, 500 µm culet).

Methodology:

- Internal heating using high resistivity graphite furnaces (700 µm high) in a vacuum cell (α 10^{-6} mbars)
- K-type thermocouple in direct contact with the back-side of the diamond.
- Pressure and temperature measurement using XRD crossed determination of an hot-pressed pellet of Au-hBN.

- Rhenium lined with platinum (compression chamber of 92 µm high and 200 µm diameter).
- The average value of I_0 is directly collected during the scan.

The first day has been dedicated to the decrease of the beam energy down to 20 keV, the alignment of the VorteX detector and the measurement of standard $CaCl_2$ aqueous solutions.

Second day: Dissolution of calcite in pure water at 310°C

During this experiment, it appears that potassium K and sulfur S are present in the X-Ray fluorescence signal (Fig.1). After several tests to determine the origin of this unexpected pollution, it turns that the presence of these two elements comes from the cleaning procedure of the diamonds with sulfuric acid H_2SO_4 and potassium nitrate KNO_3 at high temperature after the drilling process. Despite several rinsing of diamonds after the cleaning, a thin film or maybe some particles were stuck inside the perforated diamond. The presence of the K lines of K is particularly annoying due to the overlap of the Kβ line of K with the Kα line of Ca (Fig.1).

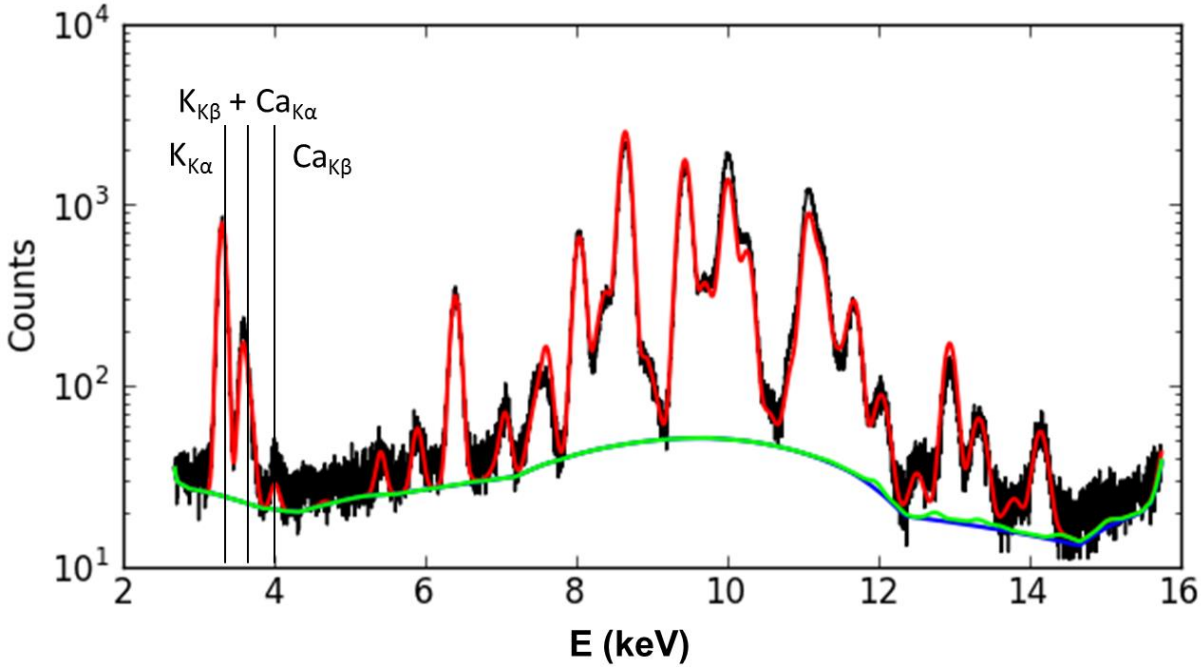

Fig.1: X-ray fluorescence signal collected in the fluid during the dissolution of calcite in pure water at 310°C.

Despite this problem, the intensities of the K lines of Ca was high enough to be collected at 310°C up to 5 GPa allowing for the calculation of the concentration of Ca released in the fluid during the dissolution of calcite in pure water and subsequently the estimation of the solubility of calcite under these conditions. This clearly demonstrates the feasibility of the project conducted at ID27 to perform X-Ray fluorescence measurements of the amount of Ca at low energy.

Third day: Dissolution of calcite in pure water at 700°C

During this experiment, the furnaces surrounding the diamonds were not able to maintain a constant high temperature value avoiding the solubility measurements.

Conclusion:

- **The origin of the presence of the K lines of K and S has been isolated and its source localized. This problem of contamination is already solved for future experiments by using nitric acid rather than KNO_3 in conjunction with sulfuric acid to clean the diamond anvils.**

- **The ability of the furnace to maintain constant high temperature (>600°C) has also been improved since by a using a new configuration of the furnaces inside the newly developed fluoX diamond anvil cell (test successfully performed in October 2013).**

Finally, thanks to the exceptional potential of the high-pressure dedicated ID27 beamline to perform solubility measurements particularly difficult to achieve at low energy, solubility data have been obtained at 310°C up to 5GPa during the dissolution of calcite in pure water for the first time in a DAC. However, other isotherms at higher temperature (600-700°C) are particularly crucial to obtain new high-pressure thermodynamic properties of speciation and complexation from the solubility of calcite that will be implemented in the SUPCRT92 thermodynamic databases (http://www.predcent.org/), in collaboration with Pr. Sverjensky (John Hopkins University, Baltimore, USA).