EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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.

	Experiment title:	**Experiment number**: HS-1937
Beamline: ID22	**Date of experiment**: from: 27/11/02 to: 2/12/02	**Date of report**:
Shifts: 15	**Local contact(s)**: Alexandre Simionovici	*Received at ESRF:*

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Report:

During the allocated beam time in ID22 (experiment HS-1937), *in situ* measurements of the solubility of strontianite ($SrCO_3$) in high pressure-high temperature (HP-HT) aqueous fluids (up to 11.60 GPa and 400…C) have been performed using externally heated diamond anvil cells (DAC) and Synchrotron X-ray fluorescence (SXRF).It was the continuation of an experiment performed on ID22 during November 2002 (report HS-1632), which probed the feasibility of *in situ* measurements of mineral dissolution rates at HP-HT conditons [1].

The cell was loaded with a single crystal of $SrCO_3$, together with a ruby chip (pressure jauge), in Rb-bearing aqueous solutions of known concentrations (0.01m or 0.1m). In some cases, 0.5m NaCl solutions were added in order to test the effect of chlorine in the dissolution of the mineral. The composition of the fluid surrounding the crystal was analysed *in situ* by monitoring the X-ray fluorescence of Sr^{2+} cations, as long as chemical equilibrium was reached. These analyses are possible thanks to the high resolution monochromatic beam (18 keV) provided by the KB focusing mirror, which ensured a focal spot of 2x5 μm^2 at the position of the cell and a flux of 5.10^{10} photons/s. X-ray fluorescence was collected in forward transmission geometry using a silicon solid stated detector set at 10 degrees from the incident beam.

The strategy for computing the molality of Sr^{2+} in the fluid in equilibrium with the crystal, was to use the known concentration of Rb^+ as internal standard for the dissolution process. For this reasons, the fluorescence yields of Rb and Sr were previously calibrated in this experimental configuration (i.e., loaded in the DAC), using solutions with known concentrations of these elements. The calibrations allowed to retrieved the experimental correction factor accounting for the optimisation of the fluorescence yield for Sr atoms when a 18 keV beam is used. Calibrations also showed that quantitative analyses of Sr-bearing solutions can be accomplished down to the 20 ppm level using forward transmission geometry.

Dissolution experiments of strontianite were then performed at different pressures (up to 11.60 GPa) along isothermal paths (25, 150, 200, 300 and 400 C). Figure 1 shows images of the experimental charge in the sample chamber during an isothermal compression-decompression path at 300 ¡C.
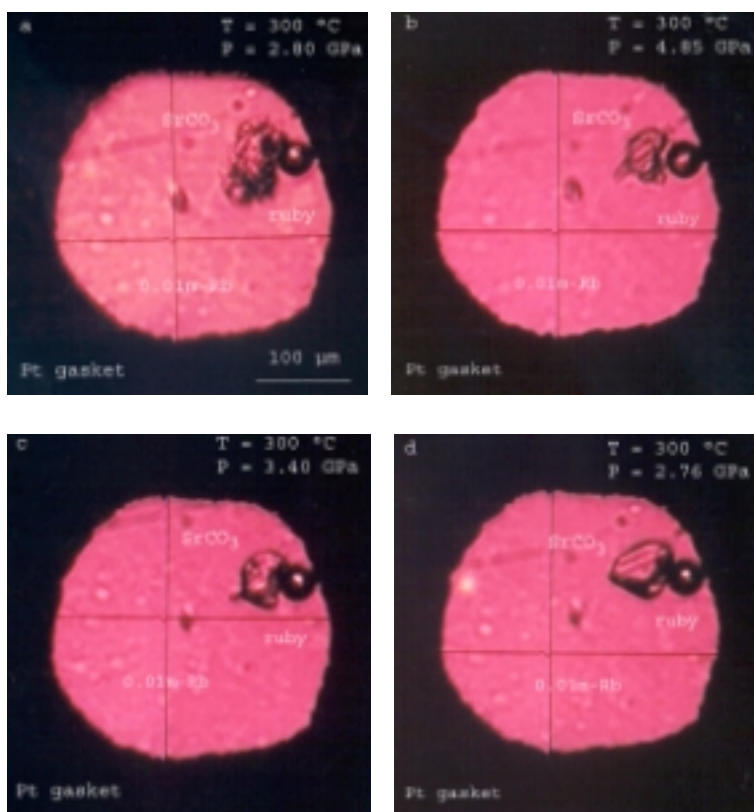

Fig.1. Experimental charge during HP-HT dissolution experiments

A shapeless $SrCO_3$ cristal is initially in equilibrium with the solution (P=2,8GPa, Fig.1.a). The dissolution is enhanced as pressure is increased at 300 C, the crystal reduces in size. (Fig.2.b). Then, during the decompression path, recrystallisation occurs (Fig.1.c) and the initial shapeless crystal developps well-defined faces when the starting contidions are reached again (Fig.1.d). This evidence of dissolution and reprecipitation during the experiment shows that equilibrium can be reach from both undersaturation and saturation side. Solubility at a given P-T point were obtained by analysing the fluid every 5 minutes as long as chemical equilibrium was reached. First analysis of the fluid (t = 0, Fig.2) was performed approximately half an hour after changing the P-T conditions. Kinetic data reveal that this time was enough for equilibrated the reaction at the highest temperatures investigated in this study (300 and 400 C).
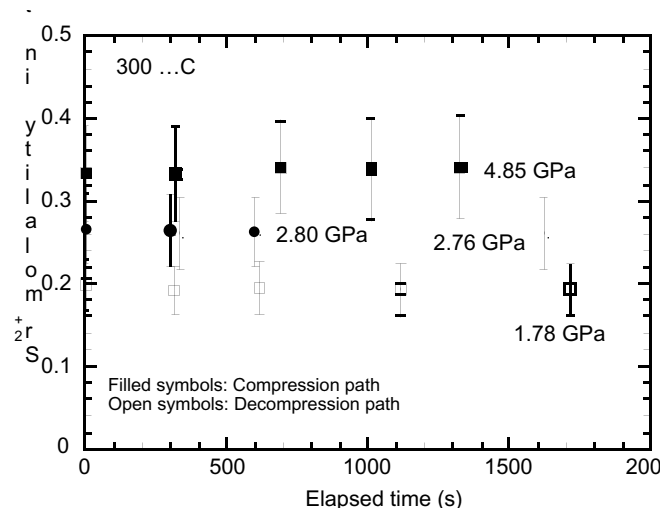
Figure 2 displays the evolution of Sr^{2+} concentration in the fluid as a function of time at the P-T conditions previously described in Fig.1.

It must be noted the agreement between Sr^{2+} molalities measured at 2.80 GPa (~0.26m) during the compression and decompression paths. This proves the attainment of equilibrium solutility from both unsaturation and saturation contitions.

Fig.2. Time-dependence of the Sr^{2+} concentrations at 300 …C and different pressure conditions.

Figure 3 illustrates typical X-ray fluorescence spectra recorded in 0.1mRb-chlorine free (3.a) and 0.1mRb-0.5m NaCl (3.b) fluids in equilibrium with $SrCO_3$, during isothermal compressions at 400 C. It can be observed that $SrCO_3$ solubility strongly increases between 1.57 and 5.60 GPa in chlorine-free solutions (Fig.3.a) whereas $SrCO_3$ solubility in 0.5m NaCl is almost constant in the studied P-range (Fig.3.b). This result is in contradiction with previous low pressure solubility and partitioning studies in quenched samples which show that saline fluids (NaCl) are good solvents at crustal conditions due to the complexing of cations with chlorine [2,3]. In dense fluids, ion-pairing must be inhibited by the elevated value of the dielectric

constant of the fluid, decreasing the solvent power of saline fluids . However, more experiments should be performed at different temperatures to better constraint the effect of chlorine-rich fluid on the dissolution of minerals at HP-HT conditions.
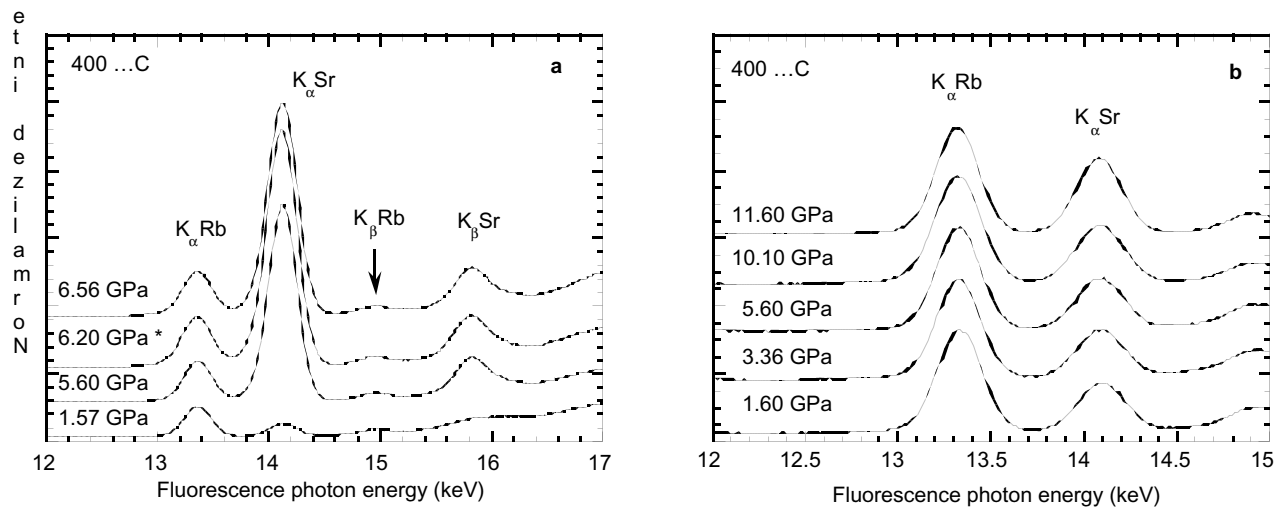

Fig.3. SXRF spectra collected in Cl⁻-free (3.a) and 0.5 NaCl aqueous fluids (3.b) in equilibrium with solid $SrCO_3$ at the P-T conditions indicated. Typical exposure time was 300s.

This experiment gives the first data on the dissolution rate and solubility of strontium carbonate at conditions relevant to cold subduction zones.

At the present, data have been proceseed and the measured Sr^{2+} concentrations are being used to determine the solubility constant (K_s) of $SrCO_3$ at HP-HT conditions, allowing further thermodynamic modelling of carbonate dissolution. These results will be presented in 2 international meetings and we expect to prepare a manuscript about the geochemistry of carbonate solubility in HP-HT fluids.

References

[1] Sanchez-Valle et al. (2003) Dissolution of strontianite at high P-T conditions: an *in situ* Synchrotron X-ray fluorescence study. In press, American Mineralogist.
[2] Keppler H., 1996. Constraints from partitioning experiments on the composition of subduction-zone fluids. Nature, 380, 237-240.
[[3] Ayers J. C. and Eggler D. H., 1995. Partitioning elements between silicate melt and H_2O-NaCl fluids at 1.5 and 2.0 GPa pressure: Implications for mantle metasomatism. *Geochim. Cosmochim. Acta*, 59, 4237-4246.