



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: High pressure-High temperature reactivity of aqueous fluids with mantle minerals: an in situ study of mineral dissolution using X-ray fluorescence

Experiment number:
HS1632

Beamline:
ID 22

Date of experiment:
from: 07/11/2001 to: 12/11/2001

Date of report:
28/02/2002

Shifts:
15

Local contact(s):
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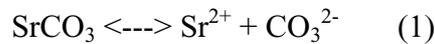
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Report:

Diamond anvil cells, equipped with internal heater, were installed for the first time on ID 22. They were used to measure the synchrotron-induced X-ray fluorescence of Rb and Sr solutions *in situ* at simultaneously high pressures and high temperatures. An incident X-ray beam of 18 keV was used and fluorescent X-rays of 13.4 (Rb) and 14.2 keV (Sr) were detected at the rear side of the high pressure cell, in a 165° geometry. Despite the strong Compton scattering in this geometry, concentrations as low as 1000 ppm of Rb and Sr could be detected and analyzed in the fluid. In further experiments, it should be possible to modify the collection angle and thus to lower the detection limit by an order of magnitude. Temperature was measured with a thermocouple whereas, pressure in the sample chamber was measured using ruby fluorescence. For this purpose, a pressure measurement optical system from the ESRF high-pressure laboratory was installed on the beamline. Solutions with known proportions and concentrations of Rb and Sr were loaded into capillary cells and diamond-cell to calibrate Rb and Sr fluorescence yields in this experimental configuration. The diamond anvil cell was then loaded with Rb-containing solutions, ruby and single crystal of strontianite (SrCO₃) in a drilled rhenium gasket. The composition of the fluid was analysed during heating at high pressure (up to 250°C and 4.15 GPa), the Sr/Rb ratio being followed away from the crystal as a function of time. This experiment gives the first data on the dissolution rate and solubility of strontium carbonate at conditions relevant to deep mantle subduction in the Earth.

Results

The following calibration solutions of rubidium and strontium nitrates have been measured in both capillary cells and diamond anvil cell at both ambient and high pressure (up to 1GPa): Rb0.08M-Sr0.02M, Rb0.05M-Sr0.05M, Rb0.02M-Sr0.08M, Rb0.0005M-Sr0.0005M. Dissolution experiments of strontianite single crystals in Rb0.01M solutions were then performed along isothermal paths at the following pressures (GPa), temperatures (°C) respectively : 0.4, 0.7, 0.9, 1, 1.3, 1.8, 2.4, 3.1, 3.6, 4.1 GPa and 25, 100, 250°C. Typical spectra obtained at high pressure and high temperature (1GPa, 100°C), in the diamond-cell are shown in the figure together with a reference spectra of the solution at ambient conditions for comparison (0.4 GPa, 25°C). The strontium carbonate solubility is dramatically enhanced as pressure is increased; For example, the Rb/Sr ratio measured at 3.6 GPa and 250°C is 0.05, in a solution initially Rb0.01M and containing no Sr, which means that strontianite is 100 time more soluble at these conditions than at ambient conditions. It was carefully checked (by loading an empty cell with a strontianite single crystal) that no pollution by X-rays of Sr coming from the single crystal came at significant levels in the area of the fluid probed by the X-ray beam. We checked that thermodynamic modelling of the reaction:



using low-pressure type of data is globally consistent with those experimental results. The obvious reason for the solubility increase of strontium carbonate with increasing pressure at constant temperature is the large negative reaction volume ($\Delta V = -58.9 \text{ cm}^3/\text{mol}$). Such a solubility increase had been observed at lower pressures but no available thermodynamic data base on aqueous species in solution allowed to extrapolate qualitatively and quantitatively to pressures such as those investigated in the present study. Our experimental results have thus important consequences for modelling quantitatively the behaviour of strontium in subduction zones, and more generally for better constraining thermodynamic modelling of aqueous species at extreme pressures and temperatures.

Those data were obtained by fixing the X-ray beam at one point in the fluid, away from the single crystal, and by waiting long enough (typically 30 minutes) for having a constant value. The increase in the strontium concentration obtained by analyzing the fluid at a fixed point every 10 minutes allowed to get first data about dissolution rates of strontianite at high pressure and high temperature. This experiment is indeed quite unique in providing the possibility of collecting kinetic data in-situ which are very difficult to obtain on quenched samples. More experiments should be performed for better constraining the thermodynamic model of dissolution at high pressures and high temperatures and for obtaining rate laws of strontianite dissolution at different pressures and temperatures.

Between november 2001 and now (february 2002), the data have been processed, ie the X-ray fluorescence spectra have been analyzed and converted to concentrations. During spring 2002, we expect to prepare one manuscript about technological aspects of the experiment and one about the geochemistry of strontium solubility at high pressures and temperatures.

