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:** Density of H_2O-CO_2-NaCl fluids at crustal conditions and controls on the formation of ore deposits	**Experiment number**: 30-02-1136
Beamline: BM30B	**Date of experiment**: from: 5/03/2018 to: 14/03/2018	**Date of report**: 27/02/2020
Shifts: 21	**Local contact(s)**: Jean-Louis Hazemann	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Carmen Sanchez-Valle*, Institute for Mineralogy, University of Münster, Germany

Marion Louvel*, Institute for Mineralogy, University of Münster, Germany

Christina Springklee*, Institute for Mineralogy, University of Münster, Germany

Report:

The goal of experiment 30-02-1136 was to determine the density of H_2O-CO_2-NaCl fluids at crustal conditions by the X-ray absorption technique in the FAME autoclave (*Fig.1A*). Fluids in this ternary sytem are a good approximation for most fluids encountered in a broad range of geological settings, including geothermal wells, hydrothermal venting systems in the seafloor and a variety of hydrothermal ore deposits. Despite their relevance, their density and PVTx properties remain poorly constrained at pressures above 0.1 kbar.

During the allocated beamtime, we determined the density of binary H_2O-NaCl and H_2O-CO_2 fluids up to to 1 kbar and 500 °C, thus extending by one order the magnitude in pressure the available density data set in H_2O-CO_2 fluids. A total of 18 runs were conducted in binary fluids with salinities of 1 to 4 mol/kg H_2O and molar fractions of CO_2, XCO_2, from 0.04 to 0.14. The experiments were conducted using glassy carbon X-ray tranparent inner cells. The saline fluids were freshly prepared from high purity NaCl powder and distilled H_2O. H_2O-CO_2 fluids with different XCO_2 were prepared by thermal decomposition of oxalic acid dihydrate, $H_2C_2O_4.2H_2O$, in excess H_2O in the inner cell of the autoclave (*Fig.1B*).

The density of the fluids was obtained from the measured X-ray absorption signals using the by the Beer-Lambert law:

$$\ln\left(\frac{I_0}{I_1}\right) = \frac{\mu}{\rho}\cdot x$$

where I_0 and I_1, are respectively the intensity of the incident and transmitted X-ray beam through the sample. *Fig.1C* displays the absorbance measured in the sample enclosed in the autoclave (*Fig.1B*) and the contributions from the different parts of the assembly (e.g. inner cell or He pressure medium). The mass absorption coefficient of the material (μ/ρ) is an additive function of composition, but independent of pressure and temperature, thus the density at high P-T, ρ_{PT}, is obtained as: $\mu_0/\rho_0=\mu_{PT}/\rho_{PT}$, where the ratio ($\mu_0/\rho_0$) at a reference P-T is calculated from density models (e.g. *Driesner*, 2007; *Duan et al.*, 2008) and compilations of atomic parameters available in the literature.

The technique was validated by experiments conducted in H_2O-NaCl fluids, where densities over a broad range of P-T conditions are available. The results for different P-T and salinities are reported in Figure 2A. The agreement with the model of *Driesner* (2007) is excellent for most of the conditions, with the exception of the highest temperature data points which likely reflect the onset of phase separation in the system.

The results from measurments in the H_2O-CO_2 system up to 400 °C and 0.8 kbar are reported in *Fig.2B* together with literature data. Our densities are systematically lower than densities from vibrating tube densitometry (*Seitz and Blencoe*, 1999), although the deviation decreases upon increasing pressure, being smaller than 4% at 0.8 kbar. The origin of this discrepancy might be the formation of CO in the fluid due to the incomplete loss of H_2 from the high pressure cell as confirmed on complementary Raman studies in the autoclave at run conditions conducted in the laboratory after the synchrotron experiments. We have thus conducted exploratory experiments in the autoclave using silver oxalate, $Ag_2C_2O_4$,

as CO_2 source and the absence of CO in the resulting fluid was confirmed by Raman spectroscopy. This observation holds promise for successful density measurements in the H_2O-CO_2 and H_2O-CO_2-NaCl systems in future synchrotron campaigns.

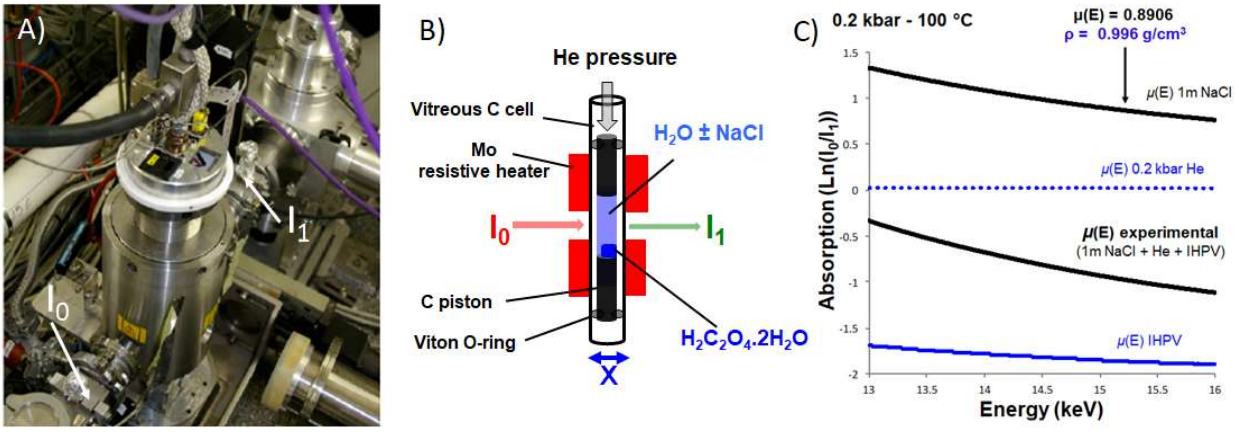

Fig.1. A) Autoclave installed at FAME beamline (ESRF, Grenoble) for X-ray absorption measurements. The intensity of the incident I_0 and transmitted I_1 X-ray beam is measured with ionization chambers. B) Details of the inner part of the autoclave showing the vitreous carbon cell loading for density measurements on H_2O-NaCl(±CO_2) fluids. C) X-ray absorption as a function of the incident X-ray energy through the sample assembly (experimental) and correction for the absorption in the He pressure medium and the autoclave (IHPV) to retrieve the density of a the 1m H_2O-NaCl fluid.

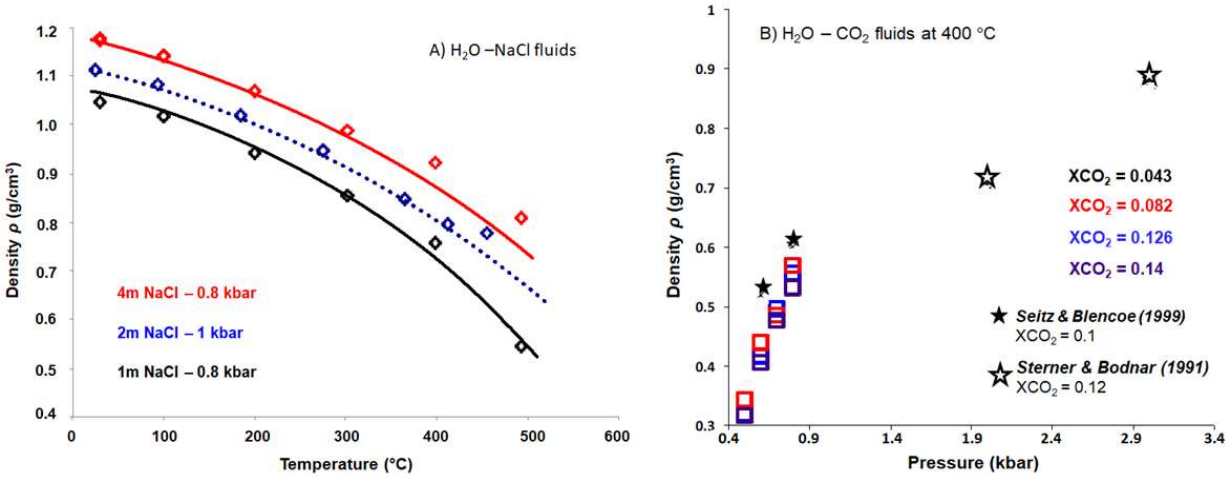

Fig.2. A) Density of H_2O-NaCl fluids as a function of temperature from X-ray absorption measurements (symbols) and comparison with predictions (lines) from the density model of *Driesner* (2007). B) Density of H_2O-CO_2 fluids as a function of pressure from these experiments (squares) and comparison with experimental data from vibrating tube densitometry (full stars) and fluid inclusion studies (open stars).

The present experiments demonstrate that the X-ray absorption technique combined with the FAME auclave is well suited to derive the density of hydrothermal fluids at P-T up to 2 kbar and 500 °C, covering the pressure gap between other techniques such an the vibrating tube densimetry (< 0.5 kbar) and the hydrothermal diamond anvil cell (> 5 kbar). The preliminary results have been presented as an oral communication at the Fall AGU 2018 meeting in Washington D.C. (USA). A technical paper describing and validating the experimental approach is currently in preparation and will be submitted in Spring 2020.

After identifying and solving the technical drawbacks that limited the success of the previous experiments, we plan to apply for additional beamtime to complete the studies in the H_2O-CO_2 and H_2O-CO_2-NaCl system. The expected results will provide the first PVTx model for binary and ternary CO_2-bearing fluids that are ubiquitous in the Earth's crust.

References:

Driesner, T. (2007) The system H_2O-NaCl. Part II: Correlations for molar volume, enthalpy, and isobaric heat capacity from 0 to 1000 degrees C, 1 to 5000 bar, and 0 to 1 X_{NaCl}. *Geochim. Cosmochim. Acta* 71(20), 4902-4919.

Duan, Z., Hu, J., Li, D., and Mao, S. (2008) Densities of the CO2-H2O and CO2-H2O-NaCl systems up to 647 K and 100 MPa. Energy and Fuels 22, 166-1674.

Seitz JC, Blencoe JG (1999) The CO_2–H_2O system. Experimental determination of volumetric properties at 400 °C, 10-100 MPa. *Geochim. Cosmochim. Acta* 63, 1559–1569.