

## 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://www.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.



	<b>Experiment title:</b> In situ study of the local structure in hydrous silicate melts by x-ray Raman scattering	<b>Experiment number:</b> EC765
<b>Beamline:</b> ID 16	<b>Date of experiment:</b> from: 22.06.2011 to: 28.06.2011	<b>Date of report:</b>
<b>Shifts:</b> 18	<b>Local contact(s):</b> Dr. Marco Moretti-Sala	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> K. Mende*, C. Sternemann*, A. Nyrow*, Ch. J. Sahle* Fakultät Physik / DELTA, TU Dortmund, 44221 Dortmund, Germany  M. Wilke*, C. Schmidt* Geoforschungszentrum Potsdam, 14473 Potsdam, Germany		

**Report:** Silicate melts take part in many processes of geological relevance like magmatism, volcanic eruptions, melting and mineralisation mechanisms. Melts can take up substantial amounts of H<sub>2</sub>O, particularly at high pressure, which has strong influences on physical and transport properties (e.g. Mysen & Richet 2005 [1]) and thus affects geological processes. This makes the water incorporation of silicate melts a topic of great scientific interest which has been subject to controversial discussions.

X-ray Raman scattering (XRS) is sensitive to changes in the local chemical surrounding of the probed atoms. It yields similar information as soft x-ray absorption or electron energy loss spectroscopy. Due to the high energy of the incident as well as the scattered photons, XRS can give access to low energy absorption edges using highly absorbing sample environments such as diamond anvil cells. The measurements were performed at beamline ID16 at ESRF using the multi analyser spectrometer in Rowland geometry with 9 Si(660) analyser crystals at a fixed analyser energy of 9.69 keV. The spectrometer covered a solid angle of 117° to 143°.

There still is an ongoing debate, whether glasses quenched from melts really lock up the melt's structure at a certain temperature and hence can be used to investigate melts. To probe the sensitivity of XRS spectra with respect to changes in local structure induced by water dissolution on the network former Al and the network modifier Na, quenched melts were measured together with the crystalline reference samples. The experiment first concentrated on the influence of the incorporation of H<sub>2</sub>O on the network former Al. Therefore measurements of the Al L<sub>2/3</sub>-edge of brazilian crystalline albite [NaAlSi<sub>3</sub>O<sub>8</sub>] and glassy albite with and without incorporated H<sub>2</sub>O were performed. The acquired spectra (not shown) reveal only subtle changes between dry and water containing albite glasses, thus indicating no substantial effect of water on the structure around the Al atoms.

We then performed measurements at the K-edge of the network modifier Na. Materials with differently coordinated Na were studied to prove the sensitivity of the spectral shape of the absorption edge to structural changes in the local surrounding of Na atoms. The investigated materials were crystalline sodium carbonate [Na<sub>2</sub>CO<sub>3</sub>] with 6-6-9 coordinated sodium [2], crystalline albite (7-fold coordinated sodium [3]) as well as albite glass (fully polymerized) and NS3 glass (partly polymerized).

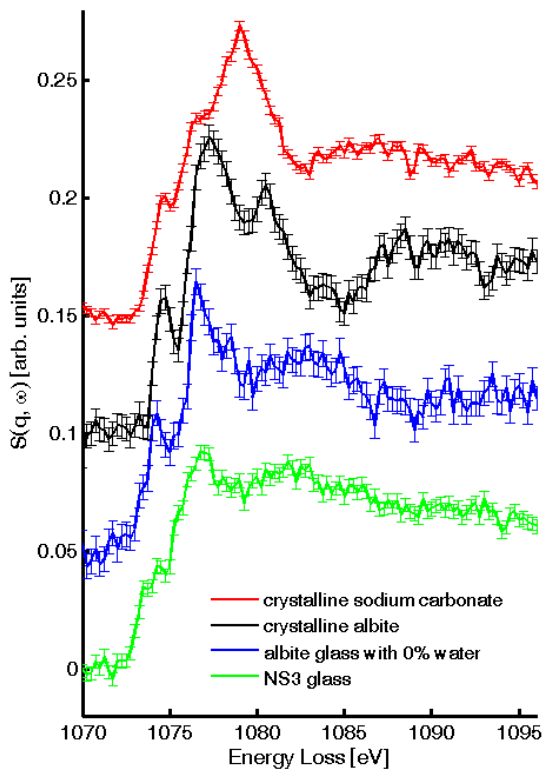


figure 1: Na K-edge of different materials.

The spectra are presented in figure 1. It is clearly visible, that the Na K-edge is very sensitive to changes in the chemical surrounding of the scattering atoms. The differences in crystalline structures such as albite and sodium carbonate result in a considerable variation of the shape of the Na K-edge. The spectra of crystalline albite, albite glass and NS3 glass are discussed in reference [4]. In contrast to the Al L-edge, spectra of glassy and crystalline albite show huge alterations in its features, such as the broadening of the pre-edge and the white line as well as the structure in an energy loss region of 1078 eV to 1087 eV. Moreover, the Na K-edge is also found to be a sensitive tool to study polymerization due to strong spectral changes between different glasses.

To investigate the effect of H<sub>2</sub>O on the polymerization of melts, the Na K-edge of glassy albite with 5 wt% H<sub>2</sub>O has been measured. The results are presented in figure 2. In comparison to the crystalline albite, the water containing albite glass shows the same features as the dry albite glass. However, one can clearly see the influence of H<sub>2</sub>O in the broadening of the peaks which might indicate changes in polymerization of the glass due to water dissolution. To further understand the effects of varying chemical surroundings and the inclusion of water in melts calculations are currently performed. To be able to calculate XRS spectra of melts, molecular dynamics simulations are used to produce accurate possible melt structures.

After measuring the crystalline and glass samples, we were able to measure the Na K-edge of NS3 melt at 600°C inside a hydrothermal diamond anvil cell (HDAC), see figure 3. The spectrum was obtained using only one scan and summing up results of 4 analysers. However, due to heater endurance problems (which have meanwhile been fixed), we were not able to obtain in situ spectra of melts with better signal to noise ratio. Nevertheless, we showed the feasibility of in situ studies of the melts, which opens exciting perspectives for future studies providing significant new information related to the local structure of melts at conditions of the inner Earth.

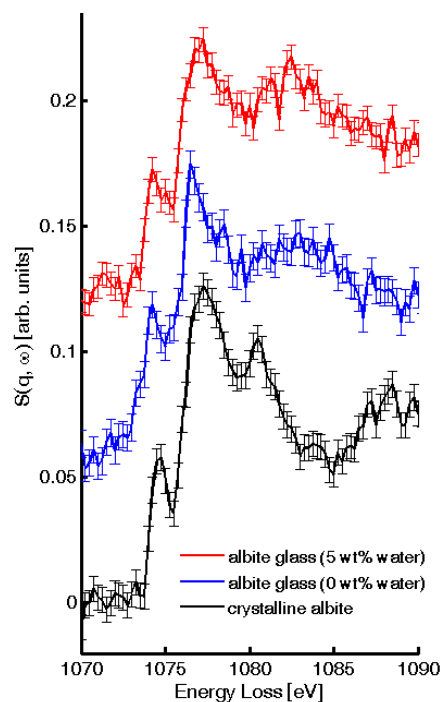


figure 2: Na K-edge of different albite samples.

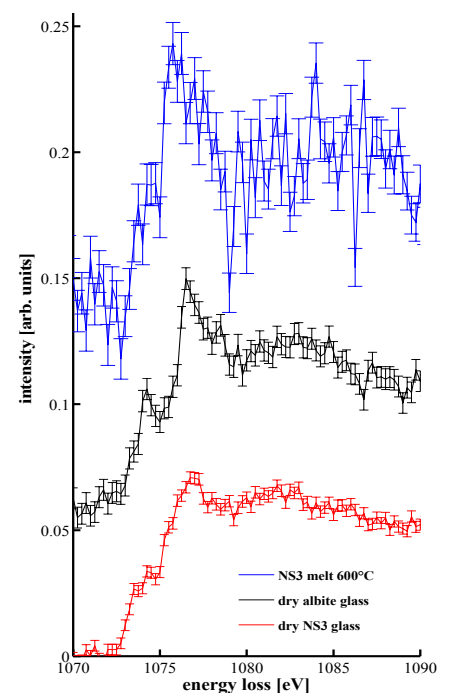


figure 3: Na K-edge of NS3 melt in situ at 600°C in comparison to glassy samples.

[1] B. Mysen & P. Richet, *Silicate Glasses and Melts: Properties and Structure*. Elsevier (2005)

[2] N. V. Zubkova, *N.Jb.Mineral.Mh.* p.85–96 (2002)

[3] H. Maekawa *et al.* *Phys Chem Minerals* 24: 53–65 (1997)

[4] C. Sternemann, Ch. J. Sahle, K. Mende, C. Schmidt, A Nyrow, L. Simonelli, M. Moretti Sala, M. Tolan, and M. Wilke. accepted by *J. Phys.: Conf. Ser.* (2012)