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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 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.

ESRF	**Experiment title: Influence du taux de zirconium sur la structure de la couche altérée de grains de verre**	**Experiment number**: 02-01-86
	Date of experiment: from: 20-06-2001 to: 25-06-2001	DATE OF REPORT 15-10-2001
Shifts:	**Local contact(s)**: Françoise BLEY	*Received at ESRF:*

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Report:

Anomalous scattering at the K edge of zirconium atom has been performed on a series of altered glass grains containing different amounts of Zr. The glass composition was (SiO_2/B_2O_3/Na_2O/ZrO_2)=(70/15/15/0-10) and the grains size was in the range 30-50 microns. The alterations were driven as follow: a fixed amount of glass powder (300mg was put in a Teflon container with 50ml of pure water. The temperature of the experiment was 90°C and four different durations were chosen : 0.5-1-2-4 months in order to cover the whole dynamic of the alteration process. Finally, the 30 samples of 2mm thick were sealed in specific cells prior to the venue at the ERSF. Their thickness was 2mm yielding a typical transmission of 0.3 for 50% of solid volume fraction.

The 30 samples together with reference were examined at 6 energies ranging from 17717eV to 18000eV. The quantitative interpretation of an anomalous scattering experiment requires to work at the absolute scale of intensity. This has been done an all the required calibrations [PM0, PM1, Filters, CPS on the CCD]were done at each energy. The size of the beam at the sample position was 0.1*0.1mm2. The diagrams of scattering were accumulated for two sample-detector separations (465 and 2155mm) with the small beam-

stop yielding a Q range of 0.004-0.7Å^{-1}. A well known reference ie Lupolen was measured to ensure that the calibration was correct and the measured value of the intensity at the peak (6cm^{-1}) was in very good agreement with all the former measured on that polymer sheet.

The main important results that we have obtained are summarized in **Figure 2** and **3**. The effects of the Zr amount on the structure of the altered glass grains (after 4 months) are reported in **Figure2**. A large scattering due to a porous layer is clearly visible at large Q. Indeed, when the glass surface is left in contact with hot water for a very long time, the labile atoms, like B and Na, are leached out of the matrix, meanwhile Si is only partially solubilzed and Zr not at all. Therefore, a layer enriched in Si and Zr appears at the surface of the glass grains.

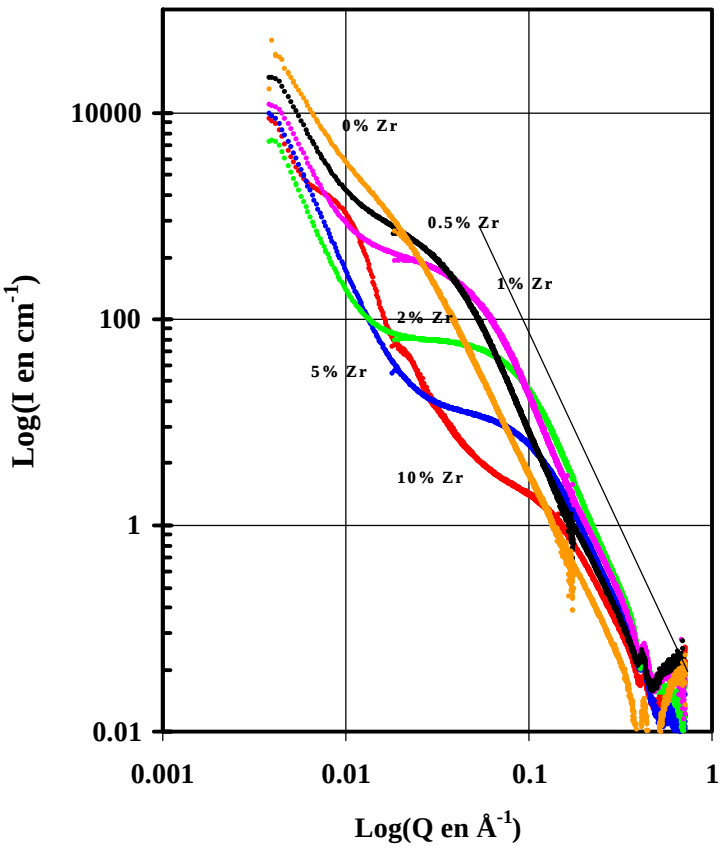

Figure 1

It is clear from **Figure 1** that : the higher the amount of Zr, the thinner the porosity. For every Zr amount, a porous specific surface can be defined as shown by the Porod regime observed at large. The full analysis of dependence of the porous specific surface on both the Zr initial content and time of alteration

allows us to propose a model for the alteration of that kind of borosilicated glass, which will be compared to recent simulations (of another group) by means of Monte-Carlo. Nevertheless, the reason which motivated the anomalous part of the experiment was to check whether the Zr atoms formed a separated phase (like ZrO_2) in the altered layer or if they remain homogeneously dispersed in the residual skeleton. **Figure 2** proposes an unambiguous answer to the question. Indeed, taking the glass containing 10% Zr and altered 4 months, the diagram obtained at 17717eV is shown in this figure together with the one obtained at 18000eV. It can be seen that the scattering is solely divided by a factor which is constant in the full Q range. The factor is in good agreement with the calculation base on the composition of the altered layer (deduced from chemical titrations of the leaching solution).

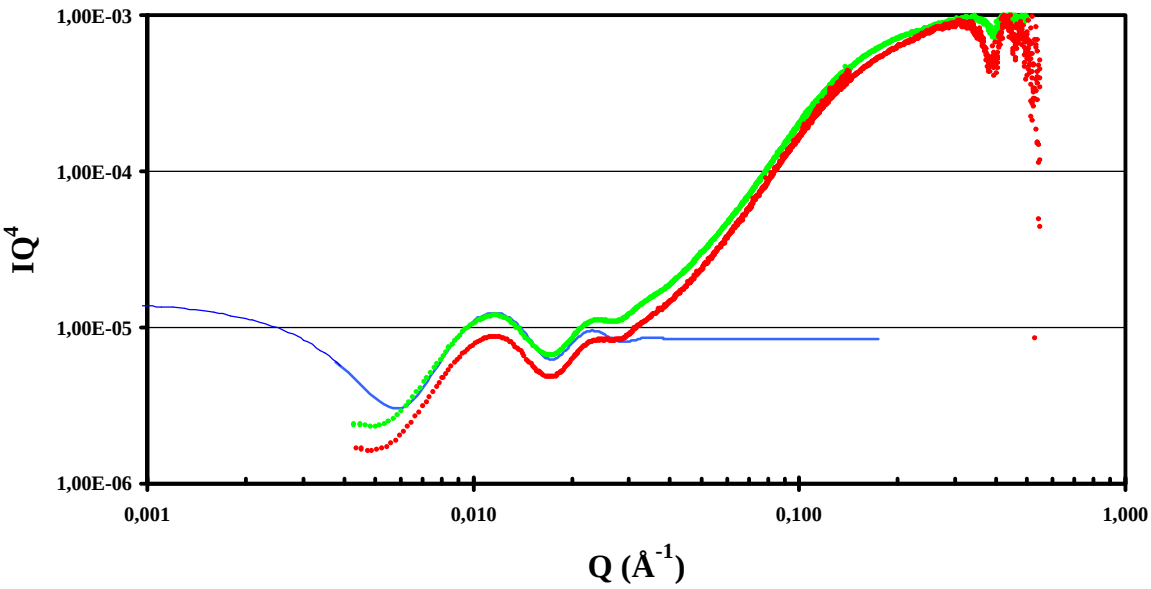

Figure2

The scattering curve is not deformed when the energy approaches the edge of absorption, showing that the variation in electron density is the same everywhere in the skeleton. A similar result was obtained for every amount of Zr and every time of alteration. This is an important (although a bit disappointing when compared to the amount of efforts!) conclusion which makes the interpretation of the data much easier at a fixed energy. Finally, data were fully interpreted on this basis and important conclusions were drawn from the experiment : in a static mode (no renewal of water), the alteration proceeds through a constant amount of porous surface, which is controlled by the solubility of the Si, itself depending on the initial addition of Zr in the composition.