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

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.

ESRF	**Experiment title:** Unraveling the skills of glass-makers from Byzantine Cyprus through XANES spectroscopy of lab-prepared glass.	**Experiment number**: HG 15
Beamline: BM26A	**Date of experiment**: from: 24/10/2013 to: 28/10/2013	**Date of report**: 22/01/2014
Shifts: 12	**Local contact(s)**: Dipanjan Banerjee	*Received at ESRF:*
Names and affiliations of applicants (* indicates experimentalists): Prof. Herman Terryn – Vrije Universiteit Brussel Dr. Simone Cagno – Norwegian University of Life Sciences/University of Antwerp * Prof. Koen Janssens – University of Antwerp Mr. Gert Nuyts – University of Antwerp* Mr. Andrea Ceglia – Vrije Universiteit Brussel*		

Report:

Introduction:

In the Roman and Byzantine period the glass production and distribution was well organised. Ancient glass makers did produce several hues ranging from yellow to green to blue. Besides the choice of raw materials, skilled glass-makers could also control the furnace redox conditions. Since glass colour is determined by colorant concentration and redox state, the redox control is a key parameter.

The aim of this experiment was therefor to provide relevant information on glass production technology in a detailed historical and geographical context. For this purpose 22 historical glass samples, excavated from several Cypriot basilicas dated between the 4th – 7th century A.D, were analysed. Additionally two series of lab-made glasses were succesfully analysed: one series with a fixed redox condition and varying Fe concentration (0.05 – 0.80 wt %) and one with a fixed Fe concentration of 0.50 wt%, but varying redox conditions.

$Fe^{3+}/\Sigma Fe$ was determined by pre-edge analysis of the acquired XANES spectra. This is made possible since the centroid of the Fe-K pre-edge (1s → 3d transitions) is correlated to the average oxidation state, while the intensity gives information concerning the geometry. The centroid is defined as the energy position at which half of the total area of the pre-edge is integrated. A set of Fe(II) and Fe(III) minerals was measured as standards in order to create a calibration line for all unknown glass samples. The following references were measured: $FeSO_4.4H_2O$ (chemical grade, +II), hercynite (mineral, +II), chromite (mineral, +II), magnetite (mineral, +II/+III), aegerine (mineral, +III), epidote (mineral, +III).

Quality of measurement/data:

A Si(111) double crystal monochromator was used, having an energy resolution of $\Delta E/E$ of about 10^{-4}. A transmission XANES spectrum of a metallic Fe foil was recorded to provide an accurate energy calibration for all the recorded spectra; the first inflection point of the Fe-K edge was set to 7112 eV [1]. All reference materials were measured in transmission and were mixed with PVC, with concentrations to obtain an edge jump of ~1.5-2. The thickness of all glass samples(historical and lab made) only allowed measurement in fluorescence with the sample oriented at 45° to the incoming beam and fluorescence yield was collected using a Vortex silicon drift detector at an angle of 45° with respect to the sample surface. Since bulk glass was measured an unfocused beam was used of which the size was only limited by using slits (horizontal:5 mm and vertical: 0.5mm). ROI fitting around the FeKa line (6113-6692 eV) was performed. XANES spectra were collected from ~270 eV below to ~460 eV above the Fe-K edge using different energy intervals; with a measuring time of 1-30 s/step resulting in a ~45 min measuring time per XANES spectrum.

Status and progress of evaluation:

XANES analysis: All acquired spectra, transmission and fluorescence, were normalised by means of the software package ATHENA. An edge-step normalisation was performed by a linear pre-edge subtraction and by regression of a (in general) third degree polynomial beyond the edge [2]. The pre-edge is extracted using an arctangent function to describe the background, although different models are used in literature [3]. However the same mathematical model is used throughout the entire data set, to ensure consistent conclusions. This procedure is illustrated in Figure 1.

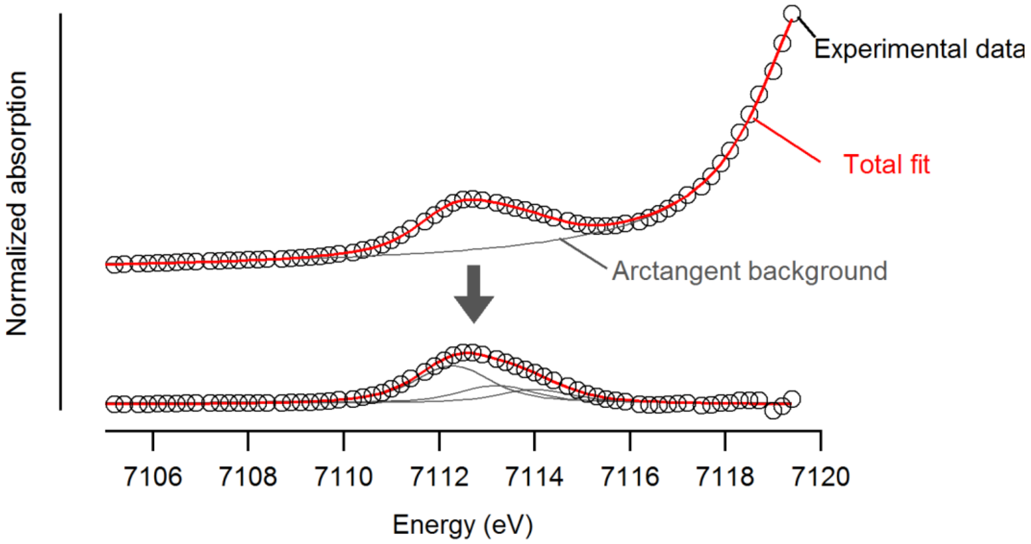

Figure 1 – Background subtraction and fitting of iron pre-edge for Hercynite mineral

Results:

Prior to the synchrotron experiment at DUBBLE, the glasses of the redox series were analysed by UV-vis-NIR transmission spectroscopy and XRF. Using the absorption of Fe^{2+} and the total iron concentration we calculated the $Fe^{3+}/\Sigma Fe$ (Table 1).

	UV-vis	XANES
AGCred1	0.81	0.779
AGCred2	0.80	0.792
AGCred3	0.58	0.564
AGCred4	0.457	0.631
AGCred5	0.24	0.235

Table 1 – Comparison between $Fe^{3+}/\Sigma Fe$ computed by optical spectroscopy and XANES for glass redox series.

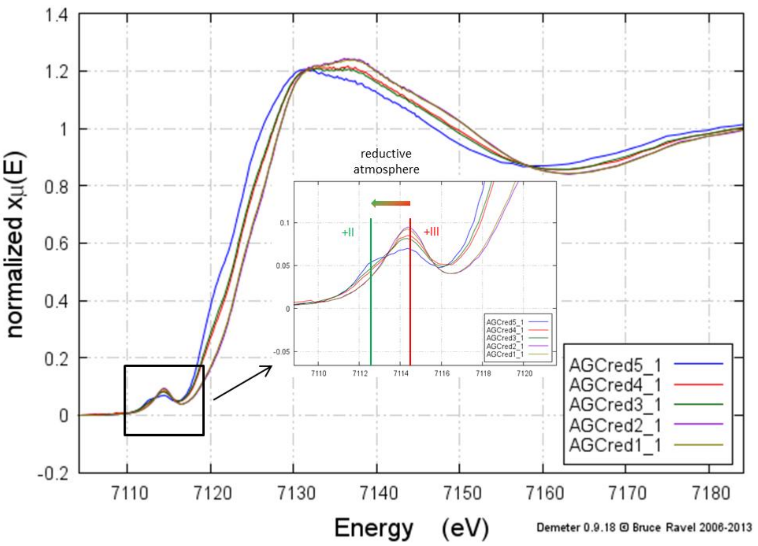

Figure 2 – XANES spectra of lab-made glass series of varying redox conditions (with [Fe] = 0.5 wt%)

The influence of the redox conditions on the XANES spectra of the reference glasses is shown in Figure 2. The centroid of the Fe-K pre-edge (1s → 3d transitions) is correlated to the average oxidation state of iron. Therefore using the centroid positions of reference compounds we were able to set a calibration line (Figure 3). Magnetite is excluded for the calibration line because it is known that in its Fe pre-edge there are also other transitions not linked to the oxidation state [4]. We applied this calibration values to compute the Fe^{3+}/ΣFe of the redox glass series (Table 1). There is a very good correlation between the points, except for AGCred4. The reason of this deviant behavior is under investigation. We suspect it might be linked to the homogeneity of the glass plate.

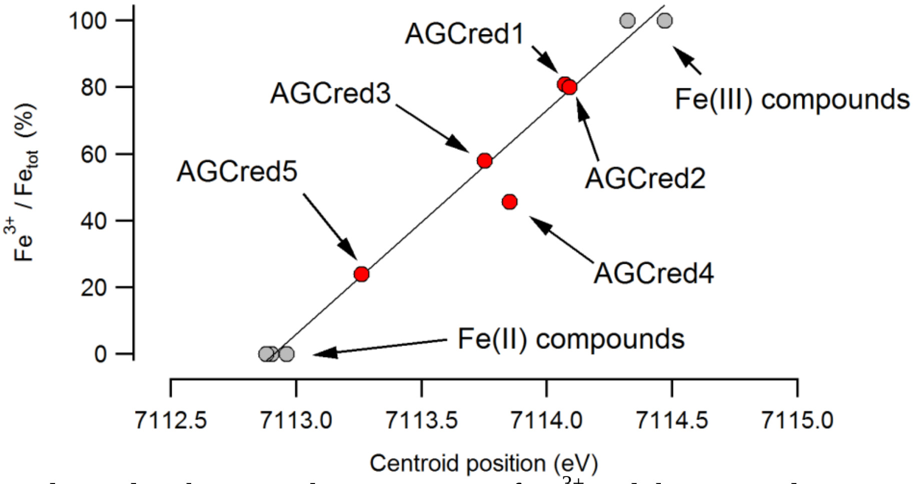

Figure 3 – Correlation line between the percentage of Fe^{3+} and the centroid position for reference compounds. Also the glass redox series is plotted using the Fe^{3+}/ΣFe obtained by transmission spectroscopy

Conclusions

We calculated the Fe^{3+}/ΣFe in 28 historical samples excavated in two different archaeological contexts. There are at least two groups of glasses: one melted under reducing condition (Fe^{3+}/ΣFe = 0.4-0.6) and one group made under oxidizing conditions (Fe^{3+}/ΣFe > 0.9). In antiquity, glass industry was structured in a centralized model. Large primary factories, located near the raw materials produced glass which was then exported to secondary workshops. There, final objects were made. Although this is still under study, from the results of this experiment, we can conclude that a specific glass type corresponds to a peculiar redox value of iron. EXAFS analysis of the spectra is still in progress.

References

[1] McMaster, W.H., Kerr Del Grande, N., Mallett, J. H. and Hubbell J. H., , Report National Bureau of Standards, (1969). [2] Ravel, B.and Newville, M., Journal of synchrotron radiation, 12(2005), 537–41.[3] Farges, F., Lefrère, Y., Rossano, S., Berthereau, A., Calas, G. and Brown Jr., G. E., Journal of Non-Crystalline Solids, 344(2004), 176–188. [4] Wilke, M., Farges, F. and Petit, P. E., American Mineralogist, 86(2001), 714–730