

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.

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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.

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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:

Combined SR-FTIR/ μ XRF “on-line” imaging applied to the study of the early stages of glass corrosion and the Mn-intrusion from the environment.

Experiment number:

EC1041

Beamline: ID21	Date of experiment: from: 06 sep 2012 to: 10 sep 2012	Date of report: 01/03/2013
Shifts: 18	Local contact(s): Giulia Veronesi	<i>Received at ESRF:</i>

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Report:
Introduction

Historical glass, especially medieval glass, can undergo weathering under the influence of time and environmental conditions. Previous experiments (EC873) at beamline ID21 [1], were already performed to better understand the processes involved in this natural degradation process. And in addition to study artificially altered glass samples prepared for the use of evaluation of conservation methods. In that experiment non-durable glass sensors produced by the Fraunhofer Institute (type M1.0) were used in a first step as a starting material for artificial alteration. These were immersed in acidic (pH = 0, 2, 4) and neutral solutions (1 h - 8 h). In a second stage the glass samples were immersed in a 0.5 M MnCl_2 solution (24 h, 48 h and 72 h), allowing intrusion of Mn from the solution into the gel layer. The samples were characterised at different stages with reflectance FTIR spectroscopy, μ XRF mapping and μ XANES. μ XRF maps were recorded at different stages of the experiment at energies around the Mn-K edge (6.539 keV) and with a step size of 2 by 2 μm . These confirmed the leaching of K^+ and Ca^{+2} from the glass and the intrusion of Mn from the solution. Mn was found throughout the entire leached layer, but with a concentration gradient peaking at the surface XANES point measurements were recorded at various points where Mn was present. No spatial variation was found, but linear combination fitting of the spectra with various Mn reference compounds indicated that $\text{Mn}^{2+}\text{Mn}^{3+}_2\text{O}_4$ is the main Mn compound in the gel layer, as was hypothesised by Watkinson et al. [2]. Since all glass

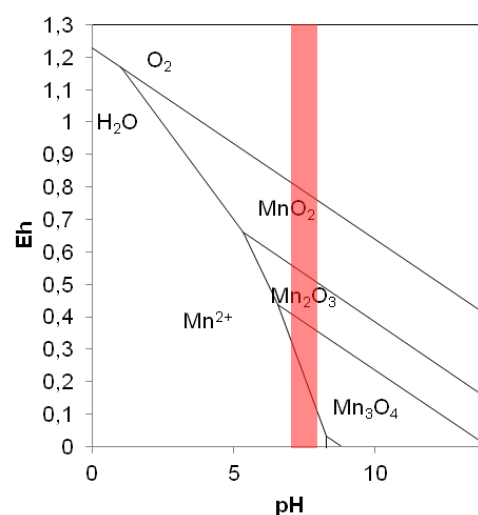


Figure 1: Figure shows the Pourbaix diagram of the Mn-O-H system (aq.) at 1 bar and assuming a dissolved species activity of 0.01. The pH area of the treatment with 0.5 M MnCl_2 is shown by the red bar.

fragments were immersed into a MnCl_2 solution it is highly probable that the manganese entered the glass as Mn^{2+} ions. In historically weathered glass Mn is often found in a highly oxidised state (e.g. MnO_2) resulting in the existence of conservation treatments that are based on reduction of highly oxidised Mn to the more mobile Mn^{2+} . The standard corroded glass samples studied could be used for the evaluation of conservation treatments. Secondly these findings had proven that Mn^{2+} could be oxidised solely by the presence of dissolved oxygen.

The pourbaix diagram (Figure 1) of a Mn-O-H system [3-5] also pointed out that in the conditions employed, MnO_2 was expected to be more stable than Mn_3O_4 . This means that the formation of Mn_3O_4 is likely to be kinetically favoured over the formation of MnO_2 and further oxidation of Mn_3O_4 , being a solid state reaction, is most likely to be very slow. It can also be concluded that a pH 4 could be used to create MnO_2 instead of Mn_3O_4 . In this experiment self-made Mn containing glass was placed in a pH 4 buffer solution in order to examine if a leached layer is formed and if Mn at these pH value will be oxidised to insoluble MnO_2 . The latter can be expected since at this pH Mn_3O_4 is thermodynamically expected to be unstable. This self-made glass was created by using oven conditions (pre-heating: 1h at 800°C, 15 °C/min; melting: 1 h at 1250°C, 5 °C/min; annealing: 5 h at 500 °C, 5°C/min). and ratio of raw materials (24.3 g of untreated Dessel sand, 14.9 g K_2CO_3 and 10.8 g CaCO_3) proven to generate rather homogeneous glass, but with adding +/- 1 g of MnCl_2 to the batch. In this manner visually homogeneous purple glass was obtained. In a second part of this experiment a first test was performed to test the influence of different reducing treatment solutions, e.g. 1 wt % of citric acid ($\text{C}_6\text{H}_8\text{O}_7$) and hydroxylamine (NH_2OH), using the artificially corroded glass fragments.

Experimental:

A flux of 10^9 ph/s using Fresnel zone plate focussing optics was available. Previous experiments [1] showed photo-reduction of Mn inclusions after an irradiation time of 120 s (with a similar set-up). However radiation damaged was checked in our self-made Mn containing glass and was proven to be absent. A 1 micron step size and a 100 ms dwell time were used for the X-ray maps as a good balance between the necessary resolution needed to visualise the formed leached layer and the time needed to record the X-ray maps. Since the measuring time for each individual pixel was only 100 ms, photo-reduction was surely avoided during the acquisition time of the maps. A Silicon Drift Detector was used for the μXANES point measurements and the μXRF mapping. Several Mn-reference spectra were recorded with 100 μm beam and photodiode detector.

For each described treatment a glass fragment was immersed in the respective solution and after treatment it was embedded in acylic resin. In this manner the sample could be cut using a diamond saw, revealing a cross-section perpendicular to the treated glass surface. XRF mapping could then be performed to evaluate the leaching process and to localise manganese for XANES point measurements. For both XRF mapping and XANES measurements the PyMCA software package was used for fitting of XRF spectra and ATHENA, a software package widely used for XAFS data analysis, was used for the normalisation of the XANES spectra [6]. A Mn reference foil provided the energy calibration for all the XANES spectra (first inflection point of the Mn K-edge set at 6539 eV [7]).

FTIR measurements were carried out to characterise the change of the silica network during alteration. For this purpose glass samples were measured in reflection mode (800 cm^{-1} 4000 cm^{-1} , 300 spectra per point) using the Thermo Scientific scanning FTIR microscope with an energy resolution of 8 cm^{-1} .

Results:

In the previous experiment (EC873), as was mentioned in the introduction, Fraunhofer Institute type M1.0 glass was also treated in a solution with pH 4 for 4 h and an altered Si layer of +/- 15 μm was observed [1]. The self-made glass having a composition, with the exception of Mn, similar to the M1.0 glass was treated

with a pH 4 solution for 4 and 24 h. In Figure 2b a FTIR spectrum of the original glass surface is given, clearly showing that the glass surface is (partially) altered, with the typical relative decrease of the Si-O⁻ peak and the relative increase of the Si-O-Si bands at around 1250 cm⁻¹ [8]. However no clear leached layer is observed in the elemental distribution maps (Figure 2a), meaning no leaching of K or Mn. A series of XANES spectra (Figure 2c) are taken at varying depth in the glass and also here no alteration of the Mn speciation is observed. Preliminary XAS analysis indicates that Mn in the self-made glass is mainly present as Mn(II).

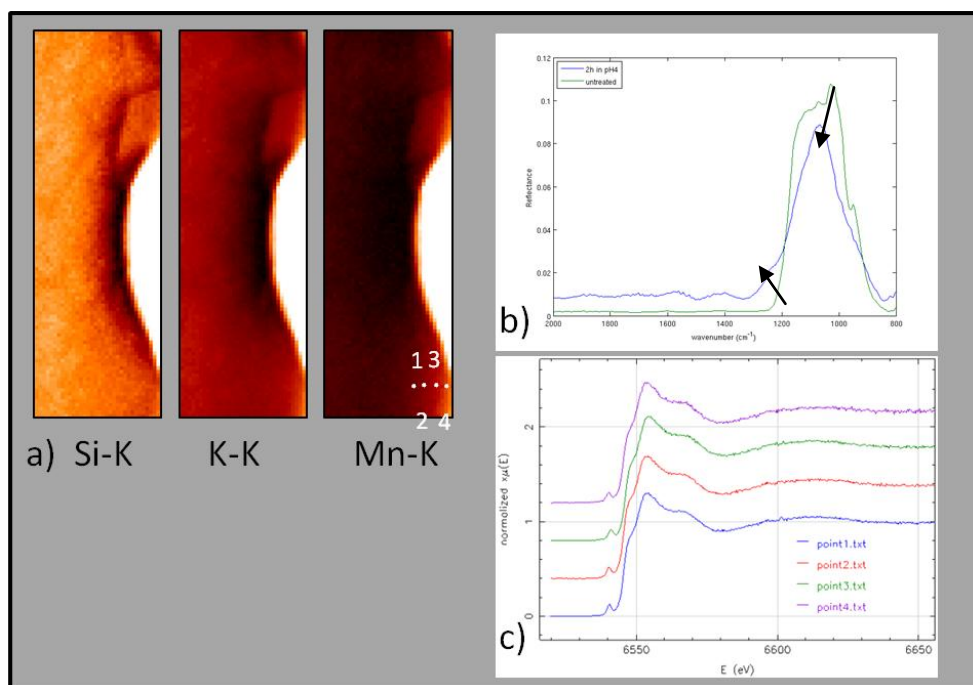


Figure 2: (a) shows the elemental distribution maps of a cross-section of self made Mn containing glass after 2 h in pH 4 buffer solution; (b) shows the FTIR spectrum of the glass surface and in (green = an untreated glass surface, blue = treated glass surface) (c) the XANES spectra of the points marked on the Mn distribution map are given.

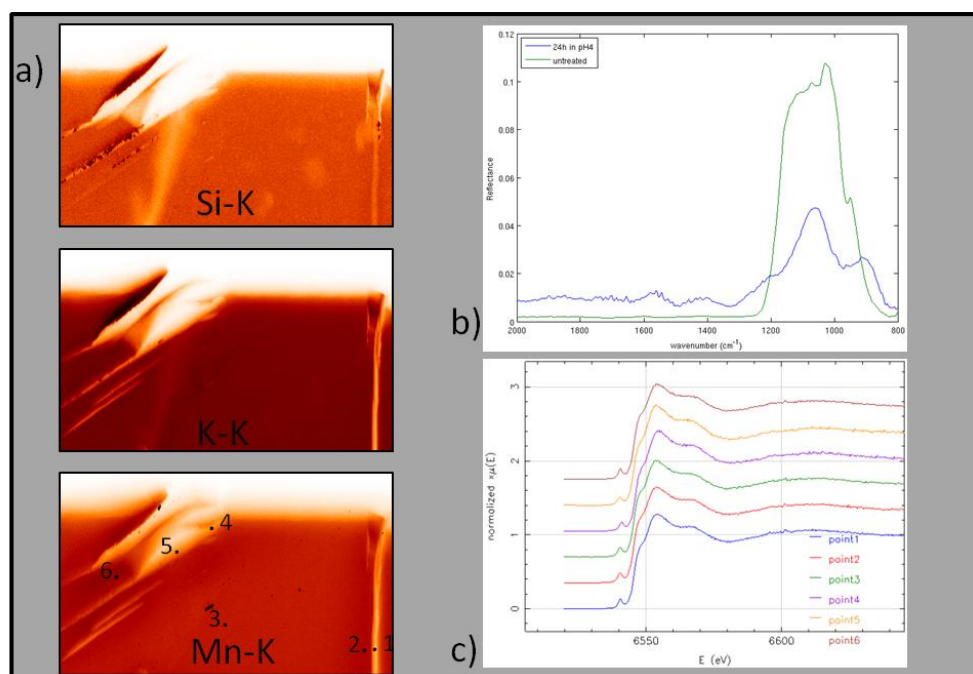


Figure 3: (a) shows the elemental distribution maps of a cross-section of self made Mn containing glass after 24 h in pH 4 buffer solution; (b) shows the FTIR spectrum of the glass surface (green = an untreated glass surface, blue = treated glass surface) and in (c) the XANES spectra of the points marked on the Mn distribution map are given.

After 24 h in a pH4 solution the glass surface is altered further, which can be observed in the FTIR spectrum (Figure 3b) as a relative increase of the Si-O-Si bands around 1100 cm⁻¹ and 1250 cm⁻¹ in comparison to the Si-O⁻ stretching around 900 cm⁻¹ [8]. In the elemental distribution maps (Figure 3a) a leached layer can be observed of +/- 6 μ m. First XAS analysis (Figure 3c) does not show any significant variation of the Mn speciation among the points measured, including point 4 inside the apparent leached layer.

A first evaluation of reducing treatment methods for Mn browning, using artificially corroded glass, was performed in a second part of this experiment. Two glass fragments were artificially corroded in the same manner as during the EC873 experiment: Firstly they were immersed in a pH0 solution for 6h, thus inducing the creation of a leached layer and consecutively they were immersed in a 0.5M MnCl_2 solution for 24 h. After drying in ambient air the glass fragments were immersed for 30 min in two reducing solutions. One was treated with a 1wt% hydroxylamine solution and the other with a 1wt% citric acid solution

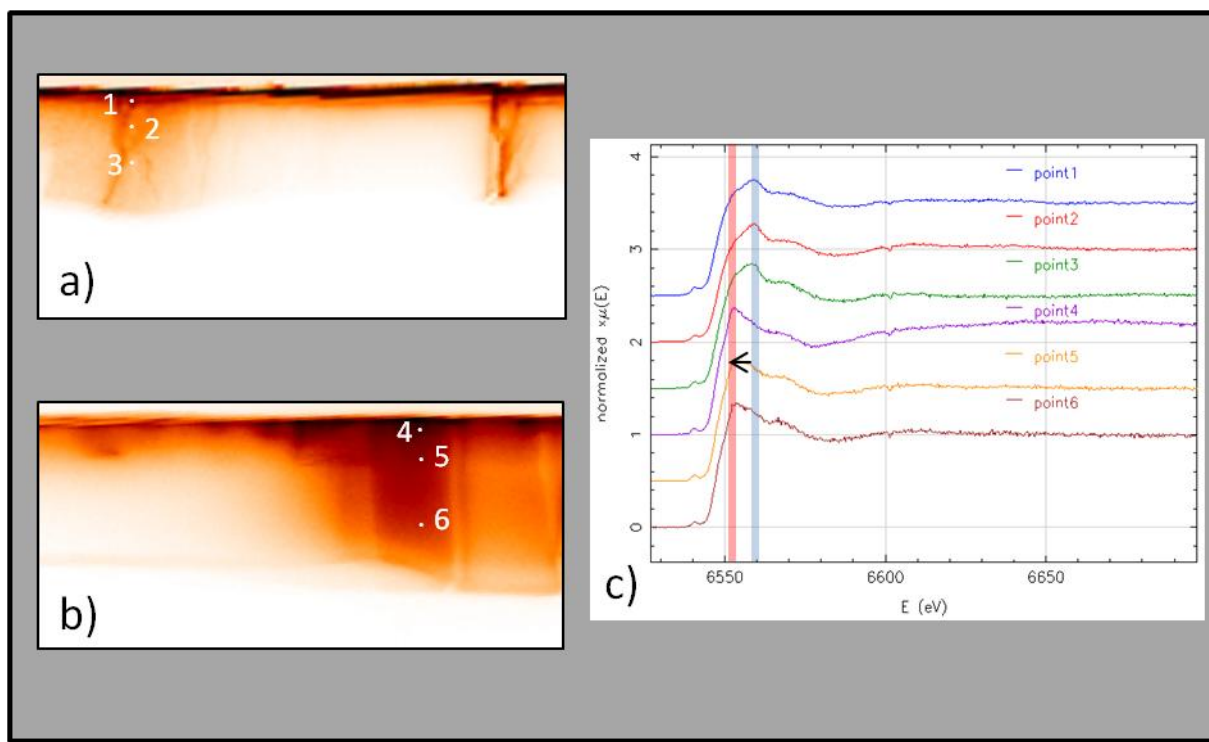


Figure 4: Mn elemental distribution maps of artificially altered glass fragments after reducing treatments with 1 wt % hydroxylamine (a) and 1 wt % of citric acid (b) for a treatment time of 30 min. (c) shows the XANES spectra of the points marked on the elemental distribution maps.

The results of this experiment are summarised in Figure 4. If the results of the treatment with hydroxylamine are compared to the results of EC873 of a glass fragment after the artificial alteration, the treatment appears to have little or no effect. All measured points still resemble the spectrum of Mn_3O_4 (points 1, 2 and 3 in Figure 4c), which is formed by the artificial alteration [1]. In addition the Mn distribution map (Figure 4a) quite clearly shows the highest Mn concentration inside cracks. However after a treatment of 30 min with 1 wt % of citric acid the Mn distribution (Figure 4b) appears to be more diffuse, suggesting that Mn is indeed being removed from the leached layer. Also the XANES spectra taken at varying depth inside the leached layer indicate that Mn is no longer only (at least solely) present as Mn_3O_4 . However these spectra could not be fitted with the available reference compounds, including MnCl_2 .

Conclusion and future

In this experiments the possibility of artificially altered glass fragments to evaluate different treatment methods for manganese browning was proven for the first time. Preliminary experiments indicate that citric acid is more effective in removing Mn_3O_4 in comparison with hydroxylamine. However in the future it is needed to create altered glass samples that are altered in a less aggressive manner (more neutral pH values in the first step). Additionally it is needed to create MnO_2 inclusions inside the leached layer instead of Mn_3O_4 thus resembling more the real situation in historically altered glass. A first attempt to alter Mn(II) containing glass at pH4, a pH where only MnO_2 is thermodynamically stable, did show leaching after a treatment of 24

h, but no oxidised Mn was found inside the leached layer. In future experiments the leaching process on self-made glasses will be further explored. For that purpose glasses will be produced with a varying Mn content and speciation.

References

[1] Procedia Chemistry. (accepted); [2] Archaeometry (2005) 47, 69-82; [3] *Handbook of inorganic chemicals* (2003); [4] National Bureau of Standards (U.S.) technical note. (1968), 270-273; [5] U.S. Geology Survey Bulletin technical note (1978); [6] Journal of Synchrotron Radiation (2005) 12, 537-541; [7] *Compilation of X-ray cross sections* (1969); [8] Comptes Rendus Physique. (2009) 10, 590-600