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Experiment Report Form

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Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
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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:** Effects of Mn-reducing treatments on the integrity of glass corrosion bodies	**Experiment number:** EC768
Beamline: ID21	**Date of experiment:** from: 27/6/2011 to: 1/7/2011	**Date of report:** 12/09/2011 *Received at ESRF:*
Shifts: 9	**Local contact(s):** Dr. Marine Cotte	

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Report:

Introduction

Upon weathering, historical glass samples may turn brown-black due to the precipitation of bodies of oxidized Mn within the superficial leached-out glass. Weathering of (historical) glass is a multi-step physico-chemical transformation involving (a) leaching of mobile cations from the glass (replacement by protons), leading to the formation of stacks of μm-thin lamellae of leached-out glass interspersed with voids [1].

(a) ≡Si-O-K + H3O+ ↔ ≡Si-O-H + H2O + K+ (aq)

followed by diffusion of Mn-ions (present as Mn^{2+} and/or Mn^{3+} in the original glass [2; 3]) towards the voids and formation of (b) brown-black precipitates, containing more oxidized Mn species, e.g.:

(b) Mn2+ + ½O2 + H2O ↔ MnO2↓ + 2H+

This type of alteration is treated by restorers with mildly Mn-reducing agents such as hydroxylamine (NH2OH). Such a treatment can be effectively monitored by means of absorption tomography and Mn-K edge XANES/XRF imaging (EC-602).

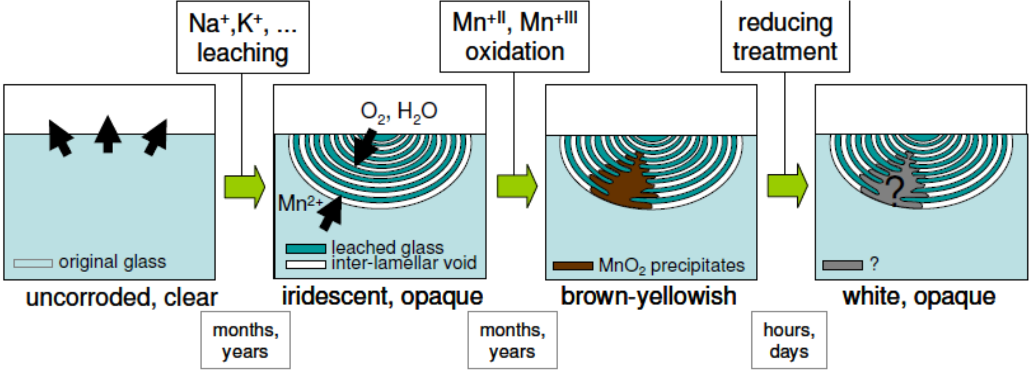


Figure 1 The different steps leading to the formation of Mn-browning and its restoration

However, also the gradual increase of the leaching damage inflicted by the NH2OH-solution to the healthy parts of the historical glass could be clearly visualized, highlighting the dangers associated with this method of restoration. The aim of the follow-up experiment is to compare the effect of other reducing solutions with that of hydroxylamine in order to optimize the balance between desired and unwanted effects.

In the previous experiment we had demonstrated how the Mn contained in the Mn bodies was in an oxidized form (see Report EC602 and ref. 4) and how the treatment with NH2OH 2% after an initial reduction of the oxidized Mn, was succesful in solvating the Mn following an exponential decay (Report EC602).

Preparation

In the current experiment, more treatments were tested than in EC602 (Table 1); the treatment was conducted in a discontinued way (Measurement/30 min treatment/measurement). The results of the treatment are also visible with an optical microscope with reflected light (Fig 2).

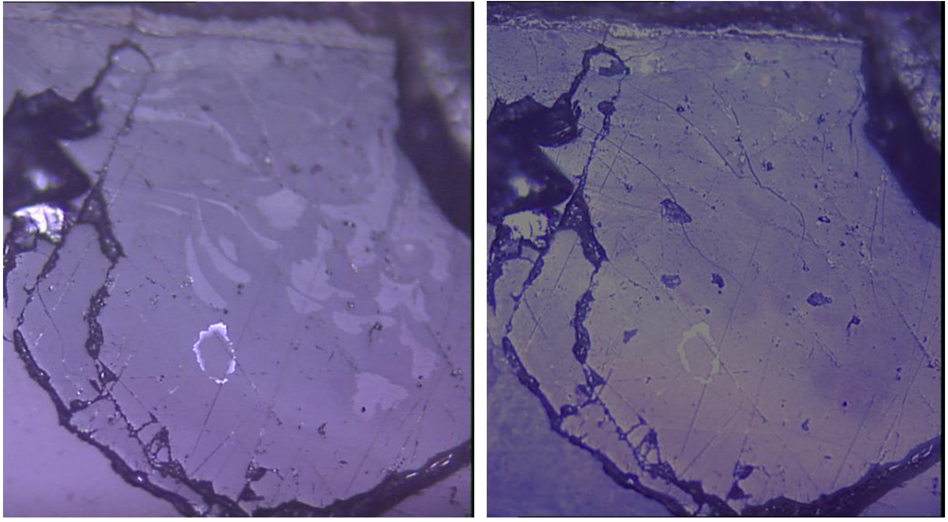
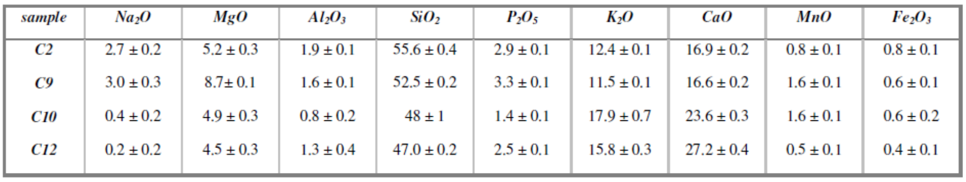


Fig 2 optical microscope images of sample C9 before/after treatment with 5% NH2OH. The superficial Mn-bodies have disappeared.

The historical (stained) glass samples that were examined originated from the excavations done in Sidney Sussex College, Cambridge (U.K.). These glass samples date to the 14th century and have suffered corrosion in wet environment (groundwater), for at least 3-4 centuries.

Prior to the experiments at ID21, samples of the same type (prepared in pillar-like shapes suitable for tomography) have been scanned by means of table-top absorption tomography (Skyscan, 3.4 µm resolution) and at ESRF, ID19 to establish the general shape and position of the corrosion bodies. An in-depth study (SEI, BEI, elemental maps, calculation of Mn-concentrations) of the polished surfaces has been performed with SEM/EDX on the same samples. The chemical composition of the fragments is that of a non-durable medieval potash-lime glass (Table 1).

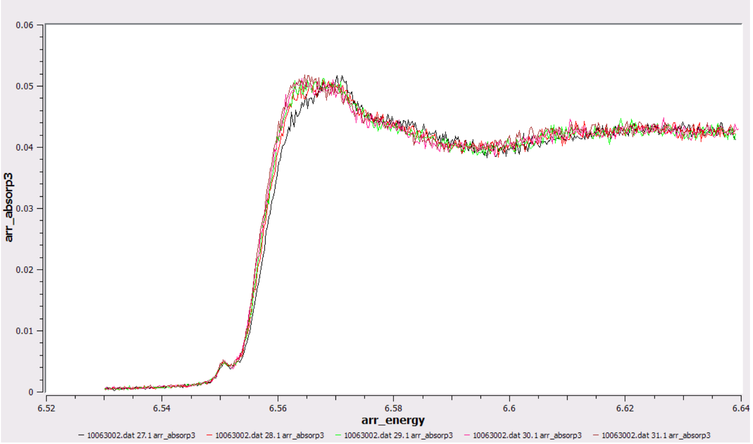


sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO	Fe_2O_3
C2	2.7 ± 0.2	5.2 ± 0.3	1.9 ± 0.1	55.6 ± 0.4	2.9 ± 0.1	12.4 ± 0.1	16.9 ± 0.2	0.8 ± 0.1	0.8 ± 0.1
C9	3.0 ± 0.3	8.7± 0.1	1.6 ± 0.1	52.5 ± 0.2	3.3 ± 0.1	11.5 ± 0.1	16.6 ± 0.2	1.6 ± 0.1	0.6 ± 0.1
C10	0.4 ± 0.2	4.9 ± 0.3	0.8 ± 0.2	48 ± 1	1.4 ± 0.1	17.9 ± 0.7	23.6 ± 0.3	1.6 ± 0.1	0.6 ± 0.2
C12	0.2 ± 0.2	4.5 ± 0.3	1.3 ± 0.4	47.0 ± 0.2	2.5 ± 0.1	15.8 ± 0.3	27.2 ± 0.4	0.5 ± 0.1	0.4 ± 0.1

Table 1 composition Sidney College glass samples [4]

Results

The first test performed at ESRF ID21 was the evaluation of the effect of the incident synchrotron beam on the samples, since beam-induced reduction/oxidation of different chemical species are often reported in literature (see e.g. references 5-6). Photo-reduction of the more oxidized forms of Mn in the Mn-bodies towards Mn(II) has been encountered (Fig 3), when using a focussed beam (0.3x0.8 µm), already after 30s of irradiation on the same spot (Fig. 3). To overcome this problem, a defocussed beam (20x20 µm) was selected for the collection of the XANES spectra, while for the maps the focussed beam was used, in order to maintain the higher detail, considering that the collection time (200 ms) for each pixel was low enough to avoid *in situ* reduction.



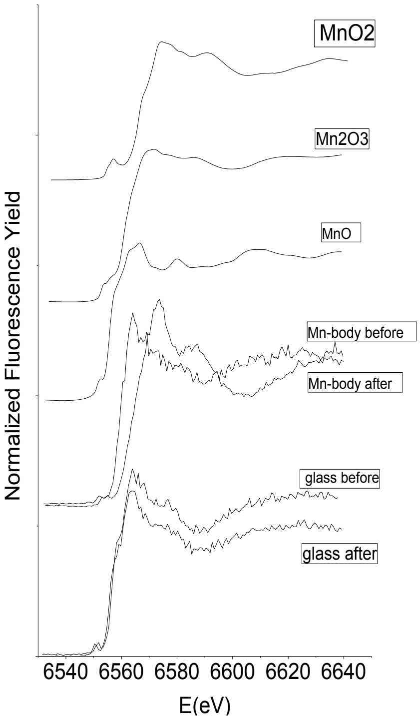


Fig 3 Photo-reduction: 4 Mn K-edge XANES spectra of a Mn-body collected in the interval of 120 s. It is visible how the white line moves to lower energy.
Fig 4 (right) Mn K-edge XANES spectra before/after treatment of historical glass (no change) and Mn-body (reduction), plus spectra of Mn references

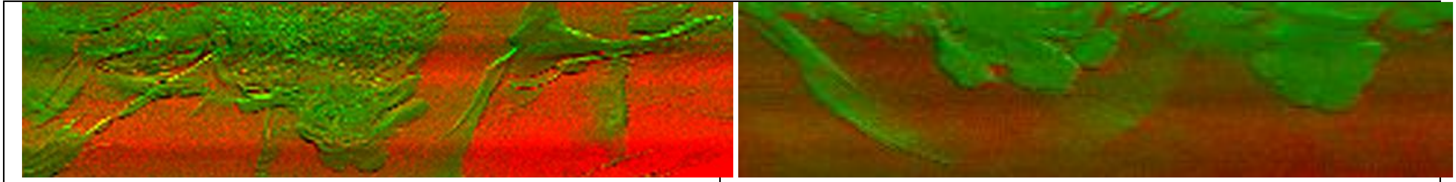
μ-XANES
XANES spectra of several Mn-containing materials were collected in transmission and fluorescence mode, comprising Mn-containing minerals, Mn salts and Mn-containing glasses. We have sought to cover the full range of oxidation states of Mn with our references. These spectra were then used as references for identification of the Mn-species contained in the unknown samples. Some spectra are shown in Fig. 3 for comparison.

XANES spectra of the original glass, leached layer and Mn-bodies have been collected of three polished cross sections of untreated samples (C9L, C9R and C10) and on one unpolished section of a sample (C10): the collection followed a line crossing first the Mn-precipitation area, then the leached layer, and finally the healthy glass.

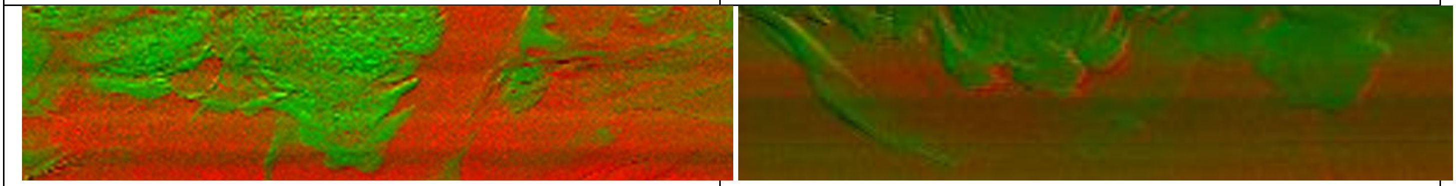
In Fig 4 the XANES spectra of the Mn bodies and the glass before/after treatment with NH_2OH are shown. Observing Figure 4, it is clear that the Mn is reduced by the hydroxylamine in the Mn-bodies. Quantitative information over the Mn-species present in the analyzed samples have not yet been extracted, but from the preliminary observation of the spectra we can say that, as observed in the previous experiment, Mn(IV) is present in the Mn-bodies [4,8,9,10] and a reduction from the 4+ to the 2+ state takes place in the Mn-body. It is not clear if the measured area after the treatment contains Mn(II) as a salt or if it is the contribution from the altered glass itself. In the sample treated with 5% citric acid no reduction was observed.

μ-XRF
At ESRF ID21, Mn K-edge chemical state maps of selected areas of the samples have been recorded at three different energies: 6.563 keV, 6.570 keV and 6.6 keV, that are, respectively, the energy most efficiently exciting Mn(II) and the one most efficiently exciting Mn(IV), and an energy far above the edge (exciting all Mn). These energies were selected on the basis of maxima of the XANES spectra collected previously. Subsequently, the glass samples were treated for 30 minutes with NH_2OH 5% in deionised water, rinsed with ethanol and then let dry out and mapped. The maps of sample C9l and C9r (treated-untreated) are shown in Figure 5. It is clear from these images that in the Mn-bodies, only (or in great majority) Mn(IV), shown in green, is present. Mn(II), shown in red, is contained, instead, in the altered glass surrounding the Mn-bodies and in the healthy glass beneath. This result agrees with the outcome of the XANES measurements. After 30 minutes of NH_2OH reducing treatment we can observe how part of the Mn-bodies has indeed disappeared, while most of them are still present. Probably the removed Mn was that immediately on and underneath the treated surface. On the other hand, a solution of 5% citric acid in deionized water appears to have none (or little) effect on the Mn-bodies in the same time (pictures on the right). Since MnO_2 is insoluble in water, the 5% hydroxylamine treatment proves to be effective in two steps:
- reduction of the oxidized Mn-species to soluble Mn(II) salts
- leaching of Mn(II) from the superficial areas of the sample

Obviously, in order to obtain a successful treatment (full removal of Mn-bodies) the treatment time has to be increased (see Report EC768 ID19) or measures have to be taken to allow more penetration of the treating solution. An attempt has been made in this direction, by treating sample C10 from the top with a wet compress, but imaging done on a cross section of that sample did not provide appreciable results, probably because of the thickness of the sample or problems in polishing/sample preparation.



C9l before treatment **C9r before treatment**



C9l after treatment 5% NH_2OH (30 min)+KCl,NaCl **C9r after treatment 5% $C_6H_8O_7$ (30 min)**

Fig 5. Mn-oxidation state specific maps (Mn2+ red, Mn4+ green) of sample C9l and C9r

Conclusion and future

The combined μ-XANES/μ-XRF experiment has provided useful results, on the one hand confirming what first discovered in experiment EC602, on the other hand expanding the investigation with the test of another product used in restoration (citric acid). We have proved that the Mn-bodies are almost entirely made of Mn(IV) and that the treatment works in two steps: reduction of Mn(IV) first and solvation of Mn(II) after. In 30 minutes only a small amount of Mn is removed from the Mn-bodies, thus the treatment has to last much longer (e.g. 24 hours). Moreover, the treatment done on a cross-sectioned surface does not effectively mimic the real treatment, in which the treating solution must enter the glass from the top. Quantitative evaluation of the XANES spectra will be performed in the next future. We consider the results obtained at ID21 to be exhaustive for our research and thus we do not ask for additional beamtime at this beamline, on the other hand, some research questions (e.g minimum treatment time, minimum required concentration, reduction of the leaching damage) are still open for what concerns the ID19 part of this experiment (see report EC768 ID19). With the aim of answering those questions, proposal p28872 has been submitted, as a continuation of experiment EC768.

References

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