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- fill in a separate form for each project or series of measurements.
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Introduction

Upon weathering, historical glass samples may turn brown-black due to the precipitation of bodies of highly oxidized Mn within the superficial leached-out glass. This type of alteration is treated by restorers with mildly Mn-reducing agents such as hydroxylamine (NH_2OH) (see Figure 1).

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) $\equiv Si\text{-}O\text{-}K + H_3O_+ \leftrightarrow \equiv Si\text{-}O\text{-}H + H_2O + K_{+(aq)}$
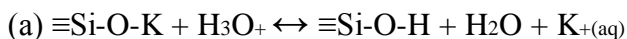
followed by diffusion of Mn-ions (present as Mn^{2+} and/or Mn^{3+} in the original glass [2; 3] towards the voids and formation of (b) brown-black precipitates, containing more oxidized Mn species, e.g.:

(b) $Mn_{2+} + \frac{1}{2}O_2 + H_2O \leftrightarrow MnO_2\downarrow + 2H_+$
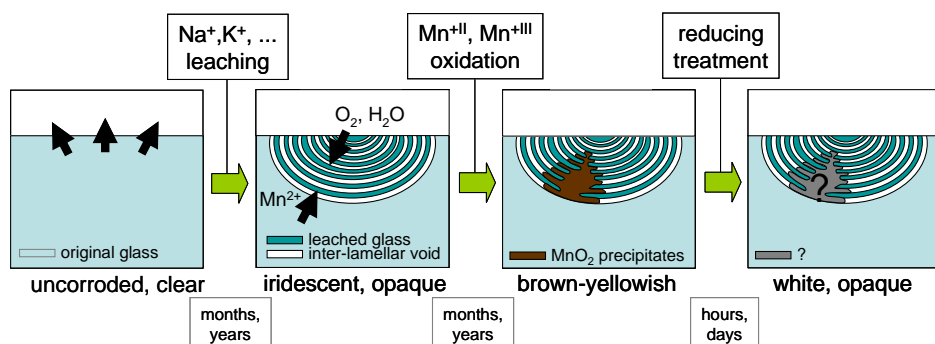

Fig. 1. Multi-step corrosion of historical glass, leading to discoloration; conservation treatment.

K-edge Mn-XANES has been performed on historical glass samples (see e.g. reference 2-3-4), principally with the aim of determining the oxidation state of the Mn, introduced by glassmakers as a colorant/decolorizer. Only one study has been performed attempting to use K-edge Mn-XANES on the Mn in the precipitation areas of historical glass artifacts [5].

Preparation

The historical (stained) glass samples that were examined originated from the Canterbury Cathedral (U.K.). These glass samples date to the 14th century and have suffered corrosion in wet environment (groundwater), for 3-4 centuries.

Cross sections of the corroded glass fragments were prepared and embedded in acrilic resin, on the cross-sections the XANES measurements were performed and the Mn-elemental maps were collected. The analyses were done before and after a 30 minutes treatment with hydroxilamine 5%.

The experiment

Photoreduction

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 6-7). Indeed photo-reduction of the more oxidized forms of Mn towards Mn(II) has been encountered, when using a focussed beam, as it is shown in Fig. 3, reporting the result of subsequent measurements on the same spot. To overcome this problem, a defocussed beam was selected for the collection of the XANES spectra, while for the maps the focussed beam (0.7x0.9 µm) was used, in order to maintain the highest detail as possible, considering that the collection time (200 ms) for each pixel was low enough to avoid reduction.
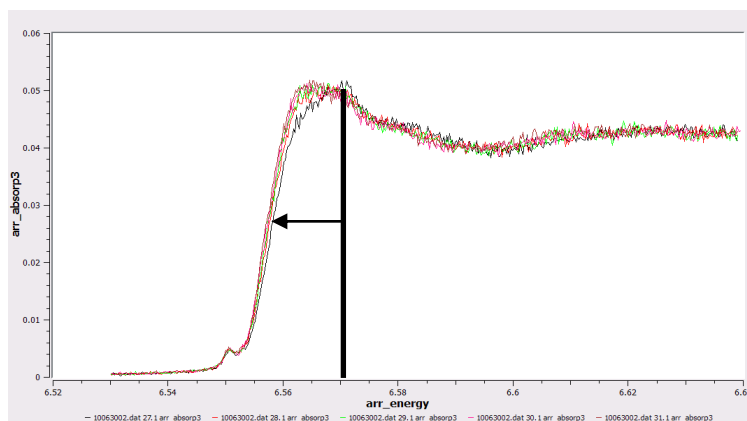

Figure 2. Photoreduction in sample C12. Subsequent spectra acquired in focussed beam conditions. Black spectrum=first, red one=last
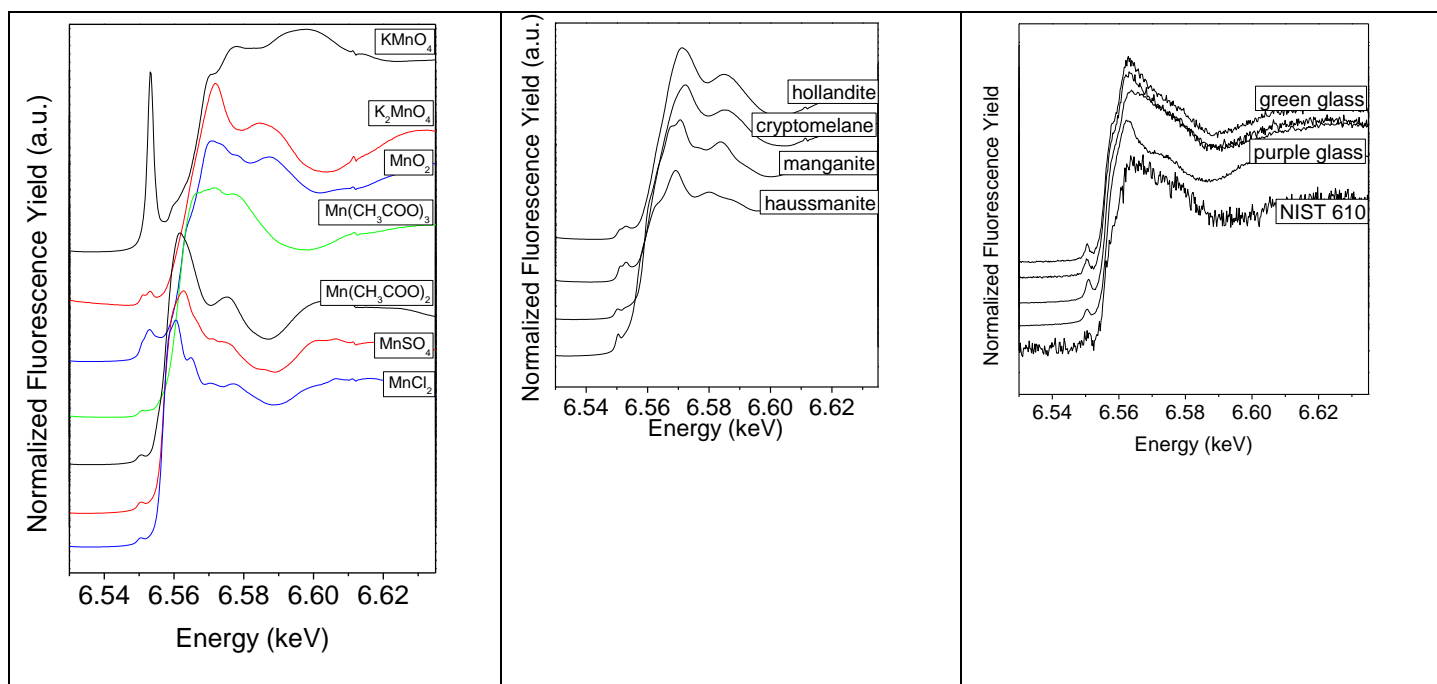

Figure 3. Mn K-edge XANES spectra of Mn salts, Mn-containing minerals and glasses

Collection of standards
XANES spectra of several Mn-containing materials were collected in transmission and fluorescence mode, comprising Mn-containing minerals, Mn salts and Mn-containing glasses. These spectra were then used as references for identifyng the Mn-species contained in the unknown samples. The spectra are shown in Fig. 3. We have sought to cover the full range of oxidation states of Mn with our references, as a salt or in a siliceous matrix (minerals/glasses).

Validation of the treatment and quantitative information
XANES spectra of the original glass, leached layer and Mn-bodies have been collected of three untreated sample (C2, C10 and C12). In Figure 4 the areas where the XANES spectra were collected are shown on a photograph of sample C12: the collection followed a line crossing first the Mn-precipitation area, then the leached layer, and finally the healthy glass.
When observing Figure 4, it is clear that the Mn is *in-situ* reduced by the hydroxylamine: it is the first time that the effect of this treatment is proven by μ-XANES. The next step has been that of extracting quantitative information from the XANES spectra. To do so, all the reference and unknown spectra have been normalized and calibrated (Mn foil) using the Athena IFEFFIT software package. For quantitatively estimating the average valence state of Mn, a linear combination fit has been used.
In figure 4, XANES spectra of the Mn-precipitation areas, altered and healthy glass for sample C12 before/after treatment are shown. The effect of the treatment is clear and the resulting product is Mn(II), while the oxidation state of the original material appears to be a mixture of Mn(II) (IV) and (VI), the weights of each component are shown in the figure. The presence of Mn(VI) in the precipitation bodies is also a novelty, being only Mn(IV) reported in literature [5,8,9]. It is evident that, in any case of μ-XANES experiments on Mn-deposition in glass, measures have to be taken (such as the use of a defocussed beam, in this case) in order to avoid the possibility of local photo-reduction. The presence of water-soluble manganates could also explain the ease of removal by means of a low concentrated reducing solution, such as that used in our experiment.

Maps
At ESRF ID21, Mn K-edge chemical state maps of selected areas of the samples have been recorded at two different energies: 6.5630 keV and 6.5714 keV, that are, respectively, the energy most efficiently exciting Mn(II) and the one most efficiently exciting Mn(IV).
Subsequently, the glass samples were treated for two times 30 minutes with hydroxylamine 2% in de-onised water, rinsed with ethanol and then let dry out. Maps were collected after the first and the second treatment.
The maps of sample C12 at the three stages of treatment (0-30-60 minutes) are shown in Figure 5. It is clear from these images that the more oxidized Mn-species, shown in red (orange due to the co-existing Mn^{2+} shown in green) tend to disappear with the increasing treatment time. Mn(II) is abundant in the altered layer, and in a lesser measure in the deposition areas. It can be seen that in place of (most of the) Mn(IV), Mn(II) is found in certain deposition areas. Thus, the 5% hydroxylamine treatment proves to be effective in two steps:
- reduction of the oxidized Mn-species to Mn(II)
- leaching of Mn(II) from the superficial areas of the sample
In addition to that, we can see that after 60 minutes there is still some Mn present in the leached glass layer. The presence of residual Mn could lead to the unwanted re-oxidation and re-precipitation of the dark Mn-bodies.
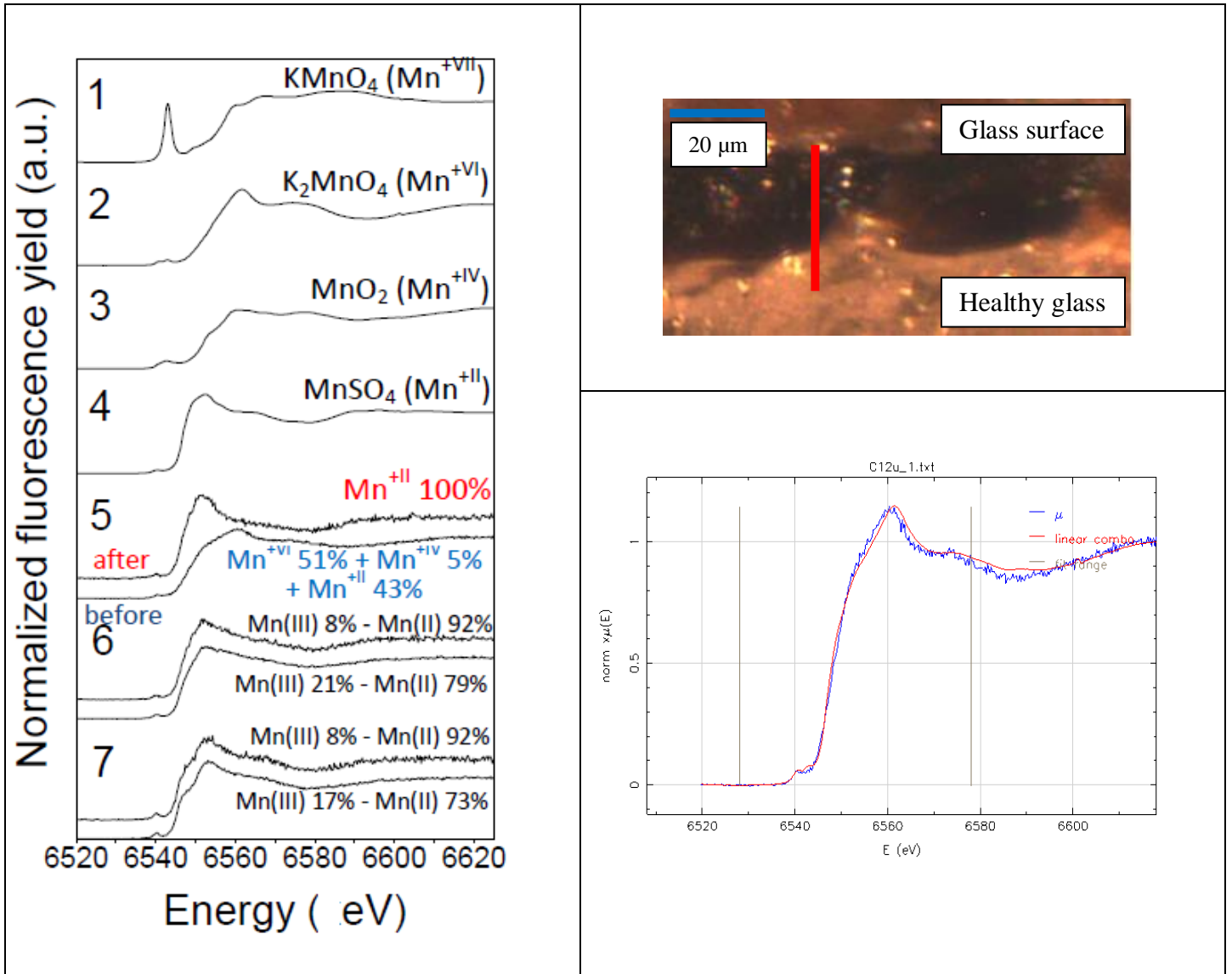
Fig.4-left. Mn K-edge XANES spectra of the following sample areas: (5) Mn-precipitation area; (6) leached layer; (7) healthy glass, compared with references (1-4). The spectra of the treated samples (30 min/hydroxylamine 5%) are shown above those of the untreated ones.

Fig.4-top. Photograph of the sample area where the spectra were collected, on the evidenced line, before and after treatment.

Fig.4-bottom. Mn K-edge XANES spectrum of Mn-precipitation area (blue curve) and best fitting function (red curve) corresponding to 51% Mn^{6+} + 5% Mn^{4+} + 43% Mn^{2+}
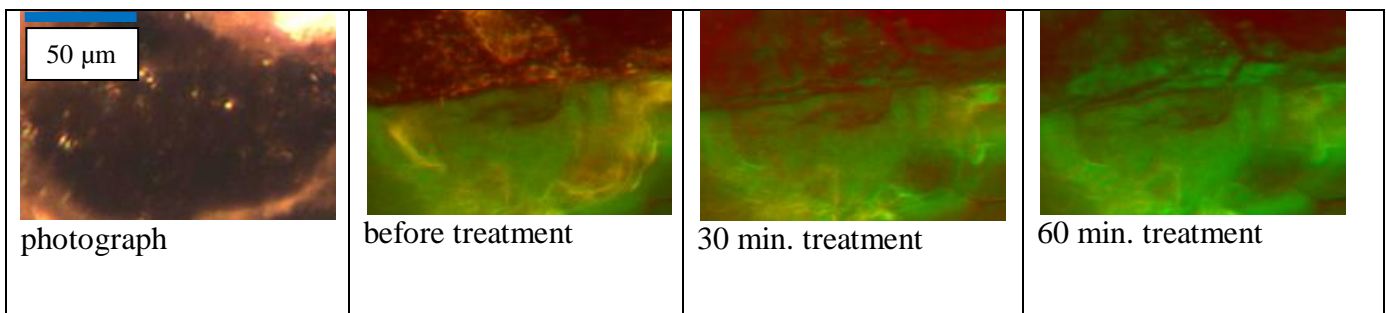

Figure 5. Sample C12, Mn elemental maps at different treatment stages. The green represent Mn(II), the red represents Mn(IV).

Conclusion and future

The results of this experiment have proven the effectiveness of the treatment used. In the untreated sample, a mixture of Mn(VI), (IV) and (II) could be identified in the precipitation areas, while a combination of Mn(II)

and (III) is present in the leached and healthy glass. After the treatment the oxidation state of the glass does not change, while the in the precipitation area only Mn(II) could be found.

From the Mn-elemental maps collected at different energies it can be visually observed how the treatment first reduced the Mn to the 2+ state and then removes it in acqueous solution. It is important to note that after the tested time not all the available Mn in the altered glass layer has been removed.

This experiment has provided only a limited view of the phenomenon (1 reagent/1 concentration): in order to have a full perspective more reducing and complexing agents (citric acid, EDTA, acetylacetone) should be tested on corroded glass samples, in order to evaluate the effectiveness and formulate responsible guidelines for glass restoration.

On the other hand, also the glass composition (e.g. soda glass, potash glass, etc.) represents an important factor that must be evaluated. With this aim, experimentally produced/aged glass chips, with different compositions, should be the subject of a further step of this study, in order to substitute the unique historical glass samples with a more viable and reproducible test-material.

With the aim of testing more products with different concentrations, and different glass compositions, proposal p26444 has been submitted on 01/09/2010, as a continuation of experiment EC602.

References
[1] Newton, R.G., The weathering of medieval window glass, J. Glass Studies, 17 (1975) 161-168; Melcher, M.; Schreiner, M., J. Non-Cryst. Solids 352 (2006) 368-379. [2] Chalmin E., Farges F., Brown GE, A pre-edge analysis of Mn K-edge XANES spectra to help determine the speciation of manganese in minerals and glasses, Contrib. Mineral. Petrol., 157 (2009) 111-126. [3] Quartieri S. et al., Fe/Mn XANES study of Ancient Roman Glasses, Eur. J. Mineral., 14 (2002) 749-756. [4] Quartieri S. et al., J. Non Cryst. Solids, 351 (2005) 3013-3022. [5] Schalm, O. et al., Manganese staining of archaeological glass: the characterization of Mn-rich inclusions in leached layers and a hypothesis of its formation, Archaeometry (2010) accepted. [6] Yi, J et al., Synchrotron X-ray-Induced Photoreduction of Ferric Myoglobin Nitrite Crystals Gives the Ferrous Derivative with Retention of the O-Bonded Nitrite Ligand, Biochemistry, 49 (2010) 5969-5971. [7] James-Smith, J. et al., Arsenic speciation in fluid inclusions using micro-beam X-ray absorption spectroscopy ; American Mineralogist, 95 (2010), 921-932. [8] Doménech-Carbó, A., Doménech-Carbó, M. T., and Osete-Cortina, L., Identification of manganese(IV) centers in archaeological glass using microsample coatings attached to polymer film electrodes, Electroanalysis, 13 (2001), 927–35. [9] Doménech-Carbó, M. T., Doménech, A., Osete, L., , A study on corrosion processes of archaeological glass from the Valencian region (Spain) and its consolidation treatment, Microchimica Acta, 154 (2006), 123-142.