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 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:** Combined SR-FTIR/µXRF "on-line" imaging applied to the study of the early stages of glass corrosion and the Mn-intrusion from the environment.	**Experiment number**: EC 873
Beamline: ID21 (SXM)	**Date of experiment**: from: 03/11/2011 to: 06/11/2011	**Date of report**: 14/03/2012
Shifts: 9	**Local contact(s)**: Giulia Veronesi	*Received at ESRF:*

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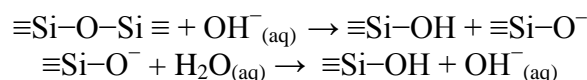
Report:

Introduction:

The weathering of silicate glasses is caused by a series of physico-chemical transformations in presence of water [1], the most important one being the leaching-out of mobile cations such as Na^+, K^+ and Ca^{2+}. This can result in the formation of lamellar structures in the glass making the glass opaque, but the glass can also change colour due to introduction of chromophoric metal ions from the environment or alteration of already present metal ions. First, molecular water penetrates into the glass weakening the silicate network by hydration and reverse hydrolysis reactions.

$$\equiv Si-O-Si\equiv \ + \ H_2O_{(aq)} \rightarrow \ 2\equiv Si-OH$$
$$2\equiv Si-OH \ \rightarrow \ \equiv Si-O-Si\equiv \ + \ H_2O_{(glass)}$$
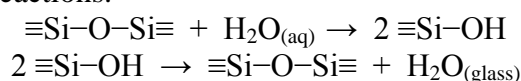
In a second step the most mobile cations from the glass will be leached out into the solution and are replaced by protons [2] from this solution. The mobility of the cations depends on charge, size and glass composition. As a result, some glass compositions (e.g. silica-rich glasses) are more resistant to leaching then others. The ions removed from the glass structure can also form weathering products (e.g. sulphates, chlorides, etc.) on the glass surface. [3]

$$\equiv Si-O^-M^+_{(glass)} \ + H^+_{(aq)} \rightarrow \ \equiv Si-O^-H^+_{(glass)} \ + M^+_{(aq)}$$
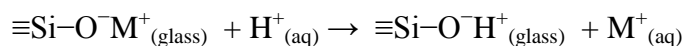
If the water that is in contact with the glass is not (regularly) replenished, the pH of the aqueous solution will increase, due to the cation/proton exchange, which results in a further degradation of the silicate network by hydroxyl ions.

$$\equiv Si-O-Si \equiv \ + OH^-_{(aq)} \rightarrow \ \equiv Si-OH + \equiv Si-O^-$$
$$\equiv Si-O^- + H_2O_{(aq)} \rightarrow \ \equiv Si-OH + OH^-_{(aq)}$$

These weathering processes cause the formation of a gellayer with a lower density than the original glass. The thickness of the gelllayer will gradually increase and the stress across the interface of the healthy and altered glass will cause thin layers of altered glass to crack off, exposing new surfaces of fresh glass to the weathering agents. Trace elements such as Mn, present in the natural environment (e.g. in the soil in which the glass was buried) can intrude in the leached layer and colour it. [4-5-6-7]

The aim of this experiment was to simulate natural weathering by artificially altering non-durable sensor glass (Fraunhofer sensor glass M1.0), which in a later stage can be used to evaluate treatment methods for naturally weathered historical glass. In order to simulate/accelerate the leaching of cations from the glass into the solution glass samples were placed in a HCl-solution (pH=0) during several hours. Secondly the glass fragments were placed in a 0.05M $MnCl_2$-solution, making Mn-intrusion from the solution into the leached

layer possible. In a last stap a 1% v/v hydrogen peroxide solution was used in an attempt to oxidize the Mn^{2+} to water insoluble MnO_2, mimicking the Mn inclusions that can be found inside leached layers of natural weathered historical glass. The glass fragments were characterized after each stage of the artifical weathering. High resolution µ-XRF maps were recorded to characterize and visualize the leaching/introduction of relevant elements (Si, Cl, K, Ca, Mn), while µ-XANES was used to determine the oxidation state (speciation) of the Mn present in the leached layer.
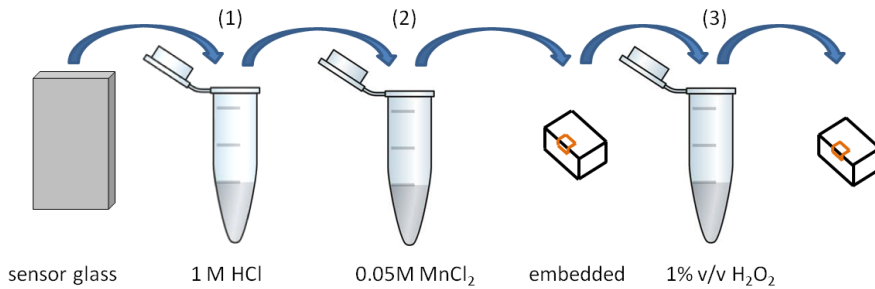

Figure 1: *Different stages in the artificial weathtering of the Fraunhofer M1.0 sensor glass. (1) accelerated leaching in HCl-solution (pH=0) (2) Mn-intrusion in 0.05M $MnCl_2$ solution (3) oxidation of Mn^{2+} by a 1% v/v H_2O_2 solution.*

Quality of measurement/data:

A flux of 10^9 ph/s using Fresnel zone plate focussing optics was available. Previous experiments [8-9] showed photo-reduction of Mn-inclusions after an irradiation time of 120 s (with a similar set-up), the zone plate was slightly defocussed during the XANES point measurements resulting in a 5 by 5 microns spot-size to avoid this effect. A 2 micron step size and a 500 ms dwell time were used for the X-ray maps as a good balance between the necessary resolution needed to visualize the formed leached layer (and Mn-intrusion) and the time needed to record the X-ray maps. Since the measuring time for each individual pixel was only 500 ms, photo-reduction was avoided during the acquisition time of the maps. A Silicon Drift Detector was used for the µ-XANES point measurements and the µ-XRF mapping. Several Mn-reference spectra were recorded with 100 µm beam and photodiode detector.

Status and progress of evaluation:

For both the XRF mapping and the XANES measurements the PyMCA software package was used for the fittting of the XRF spectra , as is visualised in figure 2.
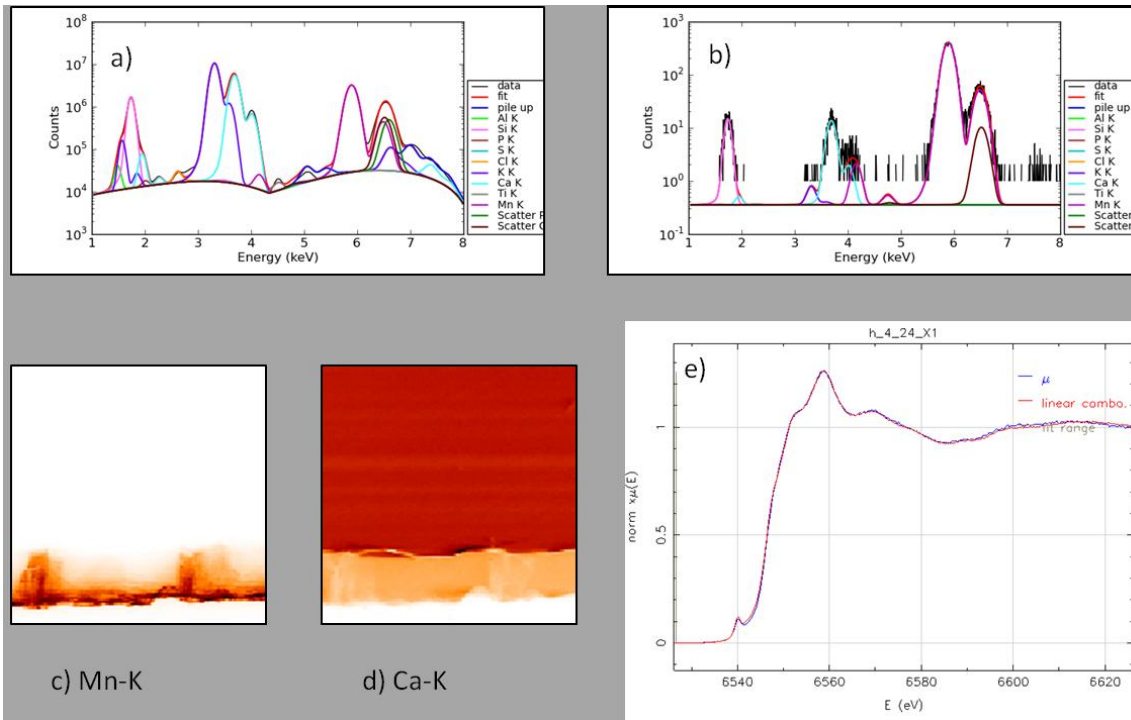

Figure 2: *After scanning the surface of the resins with the focused x-ray beam, the X-ray fluorescence spectra of the Si drift diode array (a) are fitted with PyMCA and the resulting elemental maps can be calculated from the fitted intensity (c: Mn-K and d: Ca-K). For the XANES measurement a point of interest is scanned with a X-ray beam varying in energy and for each energy a XRF spectrum (b: spectrum with excitation energy +/- 6.56 eV) is recorded. After fitting these spectra the intensities of the Mn-K lines are given as a function of the excitation energy resulting in a XANES spectrum (e).*

Several points were measured on each sample, distributed over the entire leached layer. The XANES spectra were then fitted with measured reference compounds, by means of linear combination fitting using the ATHENA software package. The reference compounds included several Mn-oxides and minerals.

Results:

The different weathering conditions that have been analyzed, are summarized in table 1.

sample	pH 0 HCl (h)	0.5M $MnCl_2$ (h)	1% v/v H_2O_2
1	2	24	
2	2	24	1
3	4	24	
4	6	24	
5	8	48	
6	8	48	1
7	8	72	

Table 1: *Summary of the time of exposure of the different steps of artificial weathering.*
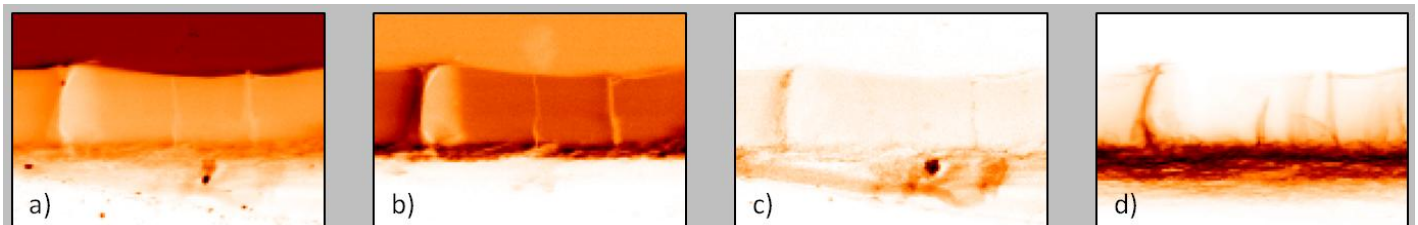

Figure 3: *Elemental maps of sample 5 (8h HCl solution and 24h MnCl$_2$-solution) (a) Ca-K map, (b) Si-K map, (c) Cl-K-map and (d) Mn-K map.*

The elemental distribution maps (figure 3) could be used to determine the leaching depth (figure 4) of each cation since it is possible to look at the intensity profile of elements alongside a line perpendicular to the surface (figure 4). The experiment pointed out that the leaching depth is +/- equal for K and Ca, but that K is leached out completely while Ca remains partially in the leached layer, this in good agreement with the mobility difference between K^+ and Ca^{2+}. The thickness of the leached layer reaches a maximum of +/- 58 μm after 6 h in 1M HCl (red line figure 4 (f)). Furthermore the line profiles proof that Mn has indeed penetrated the leached layer, since Mn is found together with Si. μ-XANES could then be used to determine the speciation of Mn on different locations inside and on top of the leached layer. In every sample measured the most dominant speciation was proven to be the mineral hausmannite ($Mn^{2+}Mn^{3+}_2O_4$) (figure 2 (e)), even before emerging the sample in H_2O_2-solution.
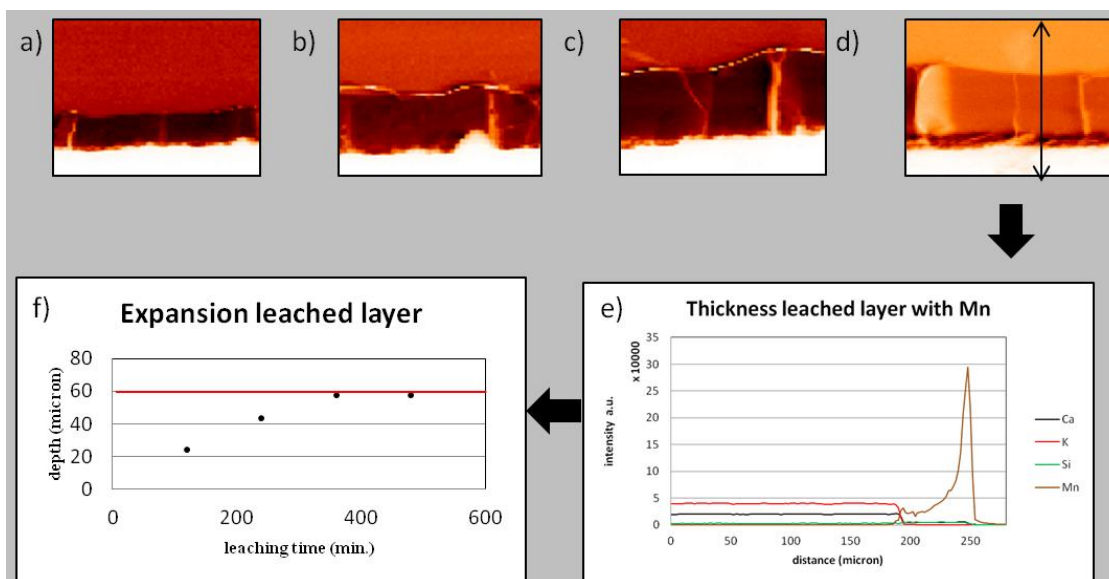

Figure 4: Determination of the leaching depth in 1M HCl-solution in function of the treatment time ((a) 2h, (b) 4h, (c) 6h and (d) 8h), (e) shows the intensity (a.u.) of K-K, Ca-K, Mn-K and Si-K line in function of the depth, the thickness of the Si-enriched layer is used as a reference for the leaching depth in (f).
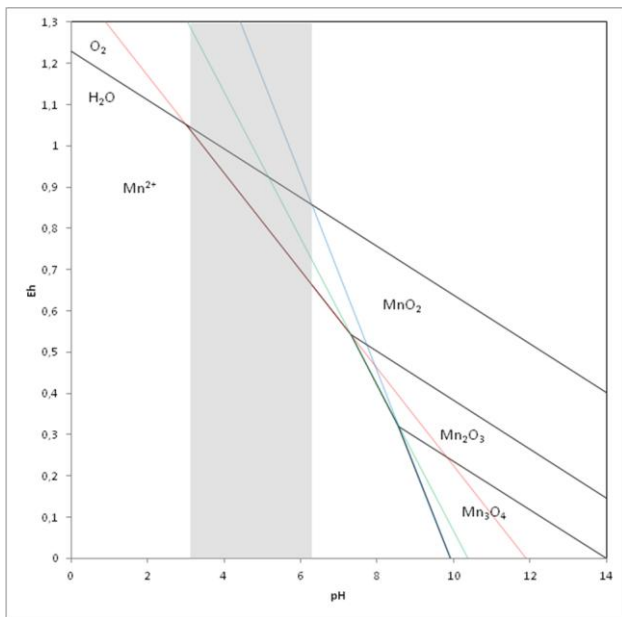
Conclusion and future

Figure 5: A Mn-O-H system (aq.) at 25ºC and 1 bar; dissolved species activity 10^{-3}. The grey area represents the pH range where MnO_2 (s) is thermodynamically stable, while hausmannite can not be formed. red line: standard reduction potential MnO_2/Mn^{2+}, green line: standard reduction potential Mn_2O_3/Mn^{2+} and blue line: standard reduction potential Mn_3O_4/Mn^{2+}[10].

This experiment was a first attempt to create artificially weathered glass in order to use it in a later stage as reference weathered glass to evaluate glass treatment methods. The intrusion of Mn from the $MnCl_2$-solution was proven, however hausmannite precipitated at neutral ph ($MnCl_2$-solution), while naturally weathered historical glass often shows MnO_2 inclusions giving it a typical black colour. Thermodynamical analysis of a Mn-O-H system (figure 5) points out that at aplied conditions MnO_2 should be more stable than hausmannite. Meaning that hausmannite formation is kinetically favoured and further oxidation to MnO_2, being a solid state reaction, is most likely to be very slow. In order to avoid this problem for future experiments glass fragments will be emerged in a $MnCl_2$ solution buffered at pH +/- 4, in this pH region MnO_2 still is the most stable Mn-compound while haussmanite should not be formed (figure 5).

References

[1] J. Am. Ceram. Soc. (2008) 91:728–35; [2] Earth Planet. Sci. Lett. (1998) 163:43–51; [3] Anal. Bioanal. Chem. (2004) 379:628-39; [4] J. Non-Cryst. Solids (2006) 352:368-79; [5] Microchim. Acta (2000) 135:121-30; [6] J. Anal. At. Spectrom. (2011) 26, 2442-2451 [7] Archaeometry (2011) 53, 103:122; [8] ESRF experimental report EC602; [9] ESRF experimental report EC768; [10] U.S. Geol. Surv. Bull. (1978) 1452