DUBBLE – EXPERIMENT REPORT

We kindly request you to answer the questions (max 2 pages) and return the **DUBBLE – Experiment Report form** within 2 months of the completion of the experiment to dubble@nwo.nl. Also include a hard copy of this report in the documents you send out for claiming your costs of travel ./ subsistence from FWO-Vlaanderen via Prof. Bart Goderis. Do **not** send any **DUBBLE - claim form for costs of travel/subsistence** by e-mail to dubble@nwo.nl.

For information please contact Bart Goderis, tel.: +32-16-327806, e-mail: bart.goderis@chem.kuleuven.be

Beam time number: 26-01-1148		
Beamline: **BM26A - DUBBLE**	**Date(s) of experiment:** **13/04/2018-17/04/2018**	**Date of report:** **14/06/2018**
Number of Shifts: **12**	**Local contact(s):** **Dipanjan Banerjee**	

1. Who took part in the experiments? (Please indicate names and affiliations)
Gert Nuyts (University of Antwerp)
Steven De Meyer (University of Antwerp)

2. Were you able to execute the planned experiments?
NO - No historical samples could be analysed, due to the reason described in section 3.

3. Did you encounter experimental problems?
YES - During the Mn XAS acquisition the ROI of the XRF detector changed at some point due to an unknown cause. As a result the counts of the Mn Kb lines were used instead of the Mn Ka, which caused a drastic lowering of the sensitivity (14X) resulting in a longer measuring time and lower quality. This issue was resolved after the second day.

4. Was the local support adequate?
YES

5. Are the obtained results at this stage in line with the expected results as mentioned on the project proposal?

YES – It is well known that the colour of silicate glass is influenced by the redox state of Mn and Fe. Fe(II)-ions give glass a green-blue hue while Fe(III)-ions colour it a typical yellow. Mn(II)–ions have a very faint yellow colour, while Mn(III) provides glass with a purple tint.

One of the aims of the experiment was to (1) test the possibility of using Mn/Fe-K edge XAS in order to determine the oxidation/coordination of Mn/Fe in calco-potassic glasses and (2) the influence of the furnace atmosphere on the obtained hue during the production of medieval window glass.

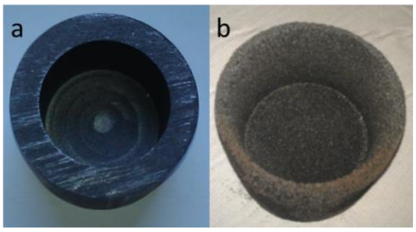

Figure 1: Example of a graphite crucible (without the lit) in which the glasses shown in Figure 2a and 2e were fused; (a) before and (b)after 7h in a furnace at 1250°C plus an additional annealing step of 2h at 800°C.

For this purpose several Mn and Fe containing glasses (~53 wt% SiO_2, ~28 wt% K_2O, ~17 wt% CaO) were fused under different types of atmospheric conditions. With increasing pO_2, glasses were fused inside a closed graphite container, under pure nitrogen (6.0), ambient and pure oxygen (5.0) atmosphere (furnace parameters can be found in Table 1). As for the graphite container, graphite oxidises at higher temperature consuming oxygen and releasing CO_2 (Fig. 1). Therefor it was hypothesised that this should result in a low pO_2.

Atmosphere	Heating ramp (°C/min)	Fusing time (h)	Temperature (°C)	Cooling rate (°C/min)
graphite	10	7	1250	max
nitrogen	15	7	1100	20
ambient	10	24	1100	max
oxygen	15	12	1100	20

Table 1: Furnace parameters of the fused glasses shown in Figure 2.

Figure 2 shows 8 lab-made calco-potassic glasses 4 having only Mn (Fig. 2a-d) and 4 having only Fe (Fig. 2e-h) as a colouring agent. Figure 3 shows the respective XANES spectra of these lab-made glasses.

In the Mn series (Fig. 2a-d) it can be observed visually that only glass fused inside a graphite container is colourless, while a faint purple hue is observed for the glass fused under nitrogen atmosphere. In the Mn-K edge XANES spectra almost no difference is observed between these two glasses. This is an indication that only a very small amount, below the detection limit, of Mn(III)-ions already results in a slight purple hue. Both glasses fused under ambient and oxygen atmosphere have a deep purple colour. From the XANES spectra it can be concluded that the average oxidation state of the Mn in the glass fused under ambient atmosphere is in between that of glass fused under pure nitrogen and pure oxygen.

In the Fe series (Fig. 2e-h) the expected colours are observed, ranging from green-blue (nitrogen) to yellow (ambient and oxygen). This trend is also seen in the XANES spectra, with a similar average oxidation state of glasses fused under ambient and oxygen atmosphere. It is important to stress out that the glass fused inside the closed graphite container is even more reduced then the glass fused under nitrogen atmosphere. The brown-yellow colour (Fig. 1e) is most likely caused by the Fe(III) – S(-II) complex, which can form in very strong reducing environments.

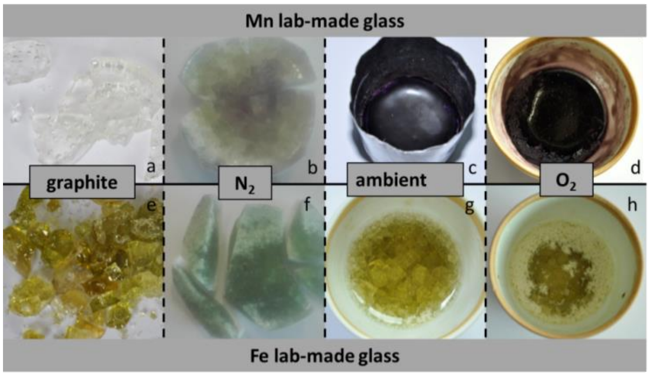

Figure 2: (a) Mn K-XAS spectra of Mn containing lab-made glasses and (b) Fe K-XAS spectra of Fe containing lab-made glasses fused under 4 different atmospheres.

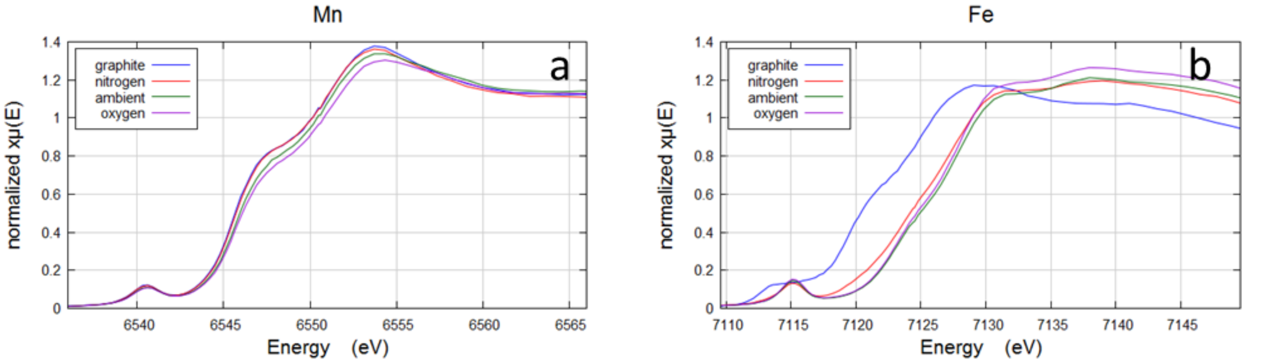

Figure 3: Lab-made calco-potassic glasses containing (a) 0.5, (b) 1.5, (c,d) 1.0 wt% MnO and (e) 0.5, (f-h) 1.0 wt% of Fe_2O_3. Glasses (a,e) were fused in a graphite container, (b,f) under nitrogen atmosphere, (c,g) in ambient air and (d,h) under oxygen atmosphere.

The results are still under process and should be validated by EPR, but some preliminary conclusions can already be drawn. In the pO_2 range of the 4 atmospheres the average oxidation state of Fe ranges from +II (graphite) to +III (ambient/oxygen), while it appears that only a small fraction Mn actually is present as Mn(III) even in glasses fused in pure oxygen.

6. Are you planning follow-up experiments at DUBBLE for this project?

NO – not in the immediate future.

7. Are you planning experiments at other synchrotrons in the near future?

YES – In order to have investigate the historical samples.

8. Do you expect any scientific output from this experimental session (publication, patent, …)

YES if additional data is obtained through EPR all the results will be written down in a publication.

9. Additional remarks

None