



	Experiment title: Investigating the role of iron and manganese oxides in colouring Post-Roman glass by XANES and micro-XRF spectroscopies	Experiment number: HG 183
Beamline:	Date of experiment: from: 05.04.2022 to: 08.04.2022	Date of report: 20.07.2022
Shifts: 9	Local contact(s): Marine Cotte	<i>Received at ESRF:</i>
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Report:

The experiment aimed to study the colouring technologies in Post-Roman glass by correlating the impact of iron (Fe) and manganese (Mn) ratios and oxidation states.

In particular, the study focused on: 1) influence of different glass production parameters (addition of reducing and oxidising agents, effects of mixing and re-melting glass batches produced in different redox conditions and changes in melting duration) in experimental glass samples; 2) study the variation of Fe and Mn oxidation states in honey coloured archaeological glass with purple stripes; 3) study of the dichroism of some archaeological samples.

Experimental natron-type glass and archaeological glass from Withorn (UK) and Tintagel (UK) were analysed using bulk Fe and Mn K-edge X-ray absorption Near Edge Structure (XANES) spectroscopy, micro-XANES and micro X-ray fluorescence (μ -XRF). Powders collected from minerals (almandine- Fe^{2+} , olivine- Fe^{2+} , hematite- Fe^{3+} , rhodochrosite- Mn^{2+} , manganite- Mn^{3+} and pyrolusite- Mn^{4+}) were used for calibration. Fe and Mn distribution and oxidation states in the samples was mapped by μ -XRF and micro-XANES, respectively.

1. Influence of different glass production parameters in experimental glass samples: experimental glass

samples were prepared following the composition of the archaeological samples (same manganese oxide content), but using different amounts of reducing agents (potassium bitartrate), in order to track its effect on Fe and Mn oxidation states. In presence of Fe, Mn can either act as a purple colourants when present as Mn^{3+} or can oxidise the bluish reduced iron to its yellowish oxidised form. The reaction that would occur between Fe and Mn is the following:

$\text{Fe}^{2+} + \text{Mn}^{3+} \rightleftharpoons \text{Fe}^{3+} + \text{Mn}^{2+}$. Fe XANES spectra obtained from the first sample set (S1, S1a, S1b, S1c and S1d)

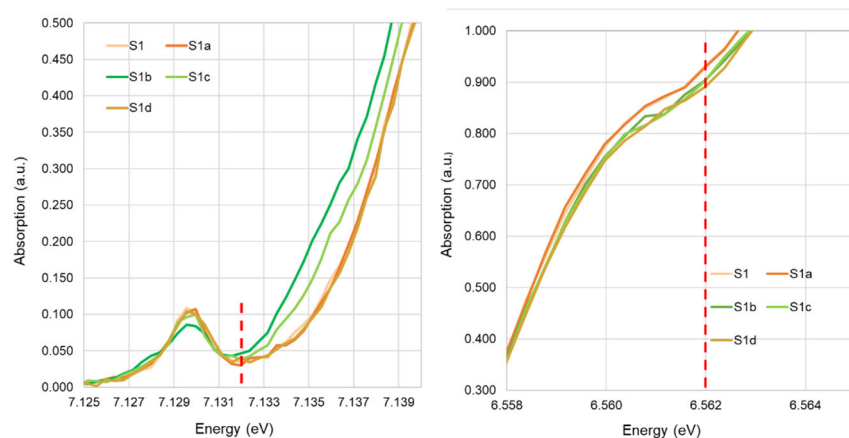


Fig 1. Fe (left) and Mn (right) K-edge XANES spectra of the first experimental glass set.

indicate that by increasing the amount of reducing agent in the melt, higher amount of reduced iron is produced (S1b and S1c samples) compared to the sample without reducing agent (S1), as a shift of the edge

position towards lower energies occurs (Fig.1). Mn XANES spectra show a shift towards higher energy (more oxidised Mn) in the samples containing the reducing agent compared to S1 (no reducing agent), indicating that this agent does not affect Mn oxidation state but mainly has an influence in the iron redox ratio.

2. Study of the variation of Fe and Mn oxidation states in honey coloured archaeological glass with purple stripes: Fe and Mn XANES spectra of the glass samples from Tintagel (T1-T5) and Whithorn (WH1-WH4) indicate that Fe and Mn are in a similar oxidation state in the yellow samples, while iron is reduced in the green samples (T2 and T4) (Fig.2). No difference in Mn and Fe oxidation state occurs in the purple stripes compared to the yellow glass bulk, proving that the change in colour is mainly due to Mn/Fe ratio. Micro-XRF maps helped mapping the distribution of Fe and Mn in the samples, proving that Mn concentrates in the purple stripes of the samples (Fig. 3).

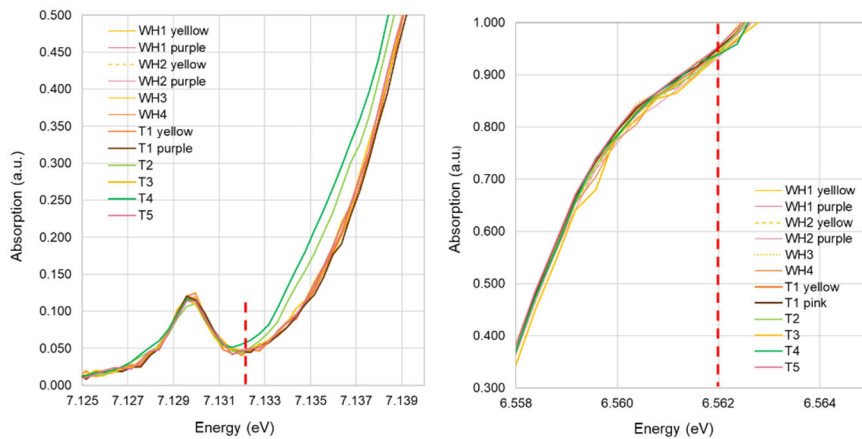


Fig 2. Fe (left) and Mn (right) K-edge XANES spectra of glass from Tintagel (T1-T5) and Whithorn (WH1-WH4).

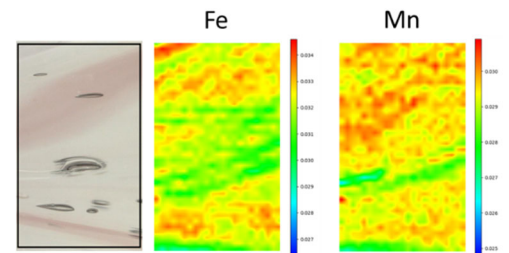


Fig 3. Micro-XRF Fe and Mn maps of a yellow glass sample with purple stripes (P1di).

3. Study of the dichroism of some archaeological samples: Many archaeological fragments display dichroism, as they appear pale green in transmitted light but honey-coloured in reflected light. Using a focused beam, XANES spectra were collected from the surface of the archaeological and experimental samples (within 20 μm) to evaluate any changes in Fe and Mn oxidation states of the surface compared to the bulk. Fig. 4 reports the intensity of the edge position in Fe and Mn XANES spectra collected within the first 20 μm in the samples from Tintagel and Whithorn and an experimental glass sample with similar composition (M2i). The archaeological samples show a trend: the intensity of the edge position increases from the surface to the bulk, indicating that manganese is more oxidised on the surface, while the oxidation state of Fe doesn't follow this trend. This surface layer containing Mn in a more oxidised form in some of the archaeological probably plays a role in scattering transmitted and reflected light differently and might be responsible for the dichroism. The fact that Mn in the experimental glass M2i is not more oxidised than the bulk can indicate that the formation of this thin layer in the archaeological samples occurs post-burial, rather than during the manufacture.

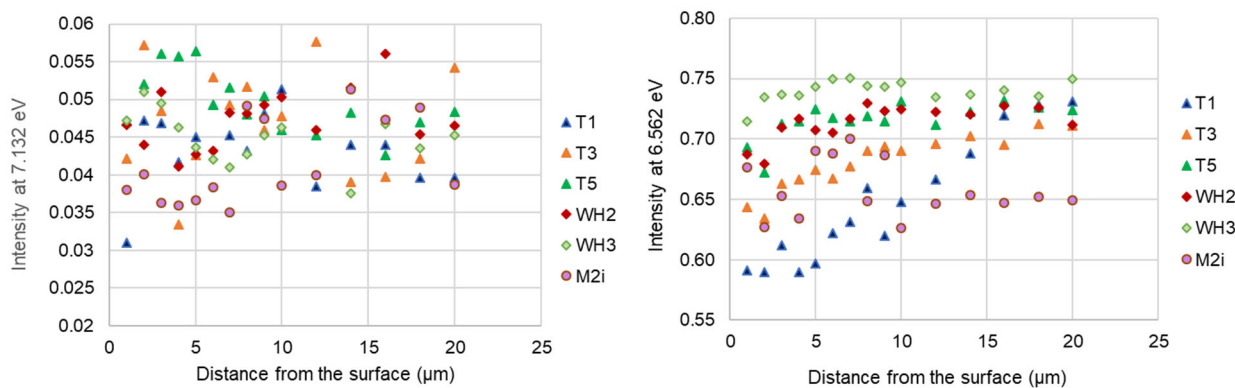


Fig 4. Intensity of the edge position in Fe (left) and Mn (right) micro-XANES spectra collected within the first 20 μm in the samples from Tintagel and Whithorn and M2i experimental glass sample.