ESRF	**Experiment title:** New insight on the fabrication techniques of calcium antimonates opacified glass by μ-XANES	**Experiment number**: EC-281
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Report:

Purpose

This experiment was part of a PhD thesis aiming at re-discovering the technological processes used throughout History to opacify glass using calcium antimonates[1]. These oxides ($Ca_2Sb_2O_7$ and $CaSb_2O_6$) have been used as glass opacifiers at least from Ancient Egypt to the present time, with periods of interruption. The micrometric white crystals, dispersed in the vitreous matrix prevent light from passing through the glass object. To produce these opacifiers, three methods are proposed:

1- addition in a translucent glass of opacifying crystals synthesized separately,
2- addition in a translucent glass of an opacifier-rich glass,
3- *in situ* crystallization.

Calcium antimonate crystals can be easily analyzed and identified thanks to chemical analyses, XRD or Raman. Conversely, getting information on the antimony in the glassy matrix is much trickier. Contrary to voltametric techniques which are global and destructive methods, μ-XANES appeared as a key way to non-invasively and selectively probe matrix and crystals, and to obtain 2D mapping of Sb oxidation state.

As explained in the proposal, this experiment had two main objectives:

1- To characterize each ancient glass production by the Sb^{3+}/Sb^{5+} ratio of their vitreous matrices (homogeneity, heterogeneity of the ratio), in order to evidence specific conditions of fabrication for the different productions.

2- To correlate these results with measurements performed on reference powders of Sb_2O_3 and Sb_2O_5, and on vitreous matrices of synthesized glass, which elaborating conditions are known (firing temperature and duration, ingredients and concentrations of Sb compounds introduced), in order to evaluate the elaborating conditions of ancient glass.

Experiment

Around 60 samples were studied: 10 reference powders; ~25 synthetic glasses made using the methods 1 and 3 mentioned above; 7 ancient glasses from Egypt18th dynasty (1570 - 1292 av. J.C.), 7 from Roman mosaic tesserae from Aquilea and Rome (1st c. B.C. - 4th c. A.D.), 7 from Nevers lampworking glass (18th c. A.D.), 7 from Limoges medieval enamels (mid-12th c. A.D. to the beginning of the 13th c. A.D.), and finally 2 mosaic tesserae from a contemporary company (Venice). These samples were prepared by polishing after embedding in resin. When no crystals were present (in some synthetic glasses) and for powders, XANES spectra were acquired with a beam size from 50 to 200μm. In the other cases (most), analyses were performed with a micrometer-probe (1.1μm(hor)×0.2μm(ver)). Visible luminescence under X-ray excitation appeared as a good way to locate and identify the different calcium antimonite crystals.

We started by exploring the Ca K-edge, Sb L_3 and Sb L_1 edges. The first ones enable an easy distinction of the two calcium antimonates oxides ($Ca_2Sb_2O_7$ and $CaSb_2O_6$) (Figure 1). On the other hand, the Sb L_1-edge rapidly came out as the best probe of Sb oxidation state. The shift of the white line from Sb^{3+} to Sb^{5+} (+4.5eV) was significant enough to get a direct identification of antimony in both crystals and matrix (Figure2).

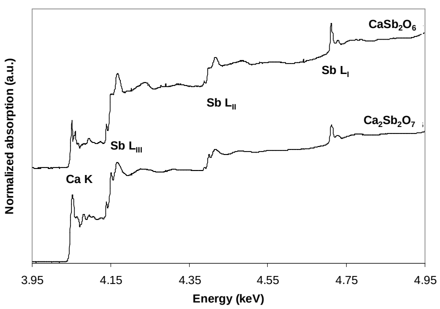

Figure 1: XANES spectra at the Ca K, Sb L_I, L_{II}, L_{III} edges of the references $CaSb_2O_6$ and $Ca_2Sb_2O_7$.

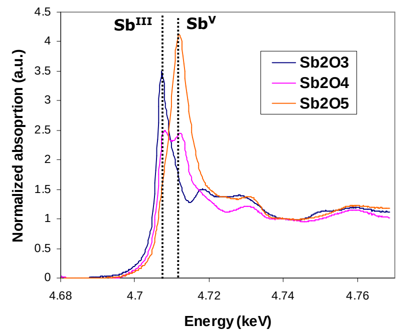

Figure 2: XANES spectra at the Sb L_I edges of different antimony oxides.

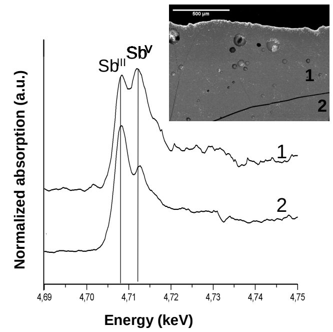

Figure 3: evolution of XANES spectra from the surface to the core of the glass.

Results

The two previous objectives were successfully reached.

1- The different ancient glass productions (Egypt, Roma and Nevers) showed characteristic XANES signatures. The Sb^{3+}/Sb^{5+} ratio is a clear marker of the productions. For each production, 7 samples were studied and for each sample, 3 spectra were acquired. The intra-group variability of these spectra is unambiguously smaller than the one between each group. For the Limoges production, the consistency is lower which can be explained by the fact that these glasses were obtained by mixing different opaque and translucent glasses. XANES and fluorescence analyses clearly reveal this heterogeneous mixture. Additional analyses of this particular production would be necessary.

2- A large set of synthesized glasses was studied as well, to follow the effect of various parameters (such as Sb source, Sb concentration, curing time and temperature, distance from the surface) on the crystallisation and on the oxidation state of antimony inside glass matrix. For example, reduction of Sb^{5+} into Sb^{3+} is easily evidenced with increasing temperatures. Similarly, we could follow the effect of air vicinity on Sb oxidation. The proportion of Sb^{5+} is higher near the surface (Figure3).

By comparing data obtained by µ-XANES, chemical analyses, microstructure observations and XRD on ancient and synthesized glasses, it was possible to propose hypotheses about the opacification techniques of the Egyptian, Roman and Nevers glass productions. As these phenomena can be both kinetically and thermokinetically affected, assumptions have to be made about curing time and temperature. Taking into account these hypotheses, the opacifying methods can be identified, and suggestion of Sb source can be made. As an article is in preparation, we cannot give here more details. All the results are presented in S. Lahlil's thesis[1].

Technical problems and perspectives

The ID21 X-ray microscope is particularly adapted for such studies, as it provides a unique tool to both identify and to image the different Sb oxidation states with a micrometer probe. The possibility to probe selectively matrix and crystals was essential. However, the dispersive detector was a clear limitation. Background signal from Si and Ca forced us to accommodate beam flux and detector position, detrimentally to Sb detection. We hope to continue these studies with the new spectrometer developed at ID21, which will be crucial for the deeper characterization of antimony in glasses.

We have now evidenced that Sb oxidation state is an unambiguous signature of glass production and has a direct effect on the crystallization process. But, in addition to the simple Sb^{3+}/Sb^{5+} ratio, we have observed that the white line of the XANES spectra present characteristic features (width and shape), varying in the different productions. We do believe that the deeper analysis of the XANES data, obtained with a more appropriate detector, could offer incomparable information on the Sb chemical environment in glasses, and consequently on ancient opacifying techniques.

[1] Lahlil, S. (2008). "Redécouverte des procédés d'opacification des verres à l'antimoine à travers l'Histoire. Etude des antimoniates de calcium." Thèse de l'Université P&M Curie, Paris VI.