LOCAL STRUCTURES AROUND Na, K, Ca, Mn ,Fe AND Cu IN MEDIEVAL GLASSES : EFFECT OF WEATHERING

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A series of XANES spectra have been collected at the K-edges of Na, K, Ca, Mn and Fe using the LUCIA beamline on medieval glasses from the stain glasses of the cathedrals of Tours and Strasbourg. These glasses are weathered on their surface (internal and external-faces). Combination of XRF and XAFS information for these network modifiers and metals help understanding the way these elements reacts as a function of a slow and long-term weathering. The main difficulty is to reduce reliably the XANES information for low-Z elements (Na-Ca) as comprehensive full MS calculations (either the FEFF8 or FDMNES codes) do not show consistent results that could help to exploit the results. Special attention is currently devoted to reliable calculations of the XANES region.

INTRODUCTION

A series of stain glasses from the Tours (XIII-XVth century) and Strasbourg (XIVth century) cathedrals were studied by µ-XRF and µ-XAFS at the K-edges of Na, K, Ca, Mn, Fe and Cu in order to understand first the origins of the color of the red glasses (Tours) as well as to study the formation of surficial weathered phases (Tours, Strasbourg). These glasses are composite: the “fresh” glass is made of multi-micronic layers of a dark-reddish glass, which are intercalated between some of greenish color. This composite (5 mm thick total) is covering a much thicker layer (3-5 mm) of a greenish glass. However, the color of the ensemble is dark-red.

RESULTS AND DISCUSSION

Na, K, Ca, Mn and Fe K-edges were measured at the LUCIA beamline, using beryl and Si(111) double crystal monochromators and a beam size of ~15x15 µm. Cu K-edge (XAFS and XRF information) was collected previously at the 10.3.2 beamline of the Advanced Light Source (Berkeley, USA). Special care was taken to ensure that the x-ray beam does not photo-reduce the samples.

The red color of the glasses is directly correlated to its Cu-contents, whereas the greenish glass is enriched in Fe and Mn. The speciation of Cu within the red regions is that of linear complexes of Cu(I), as in cuprite (Cu_2O). On the glass surface (exposed to the inside), a weathered layer, enriched in Cu(II) is detected (also enriched in Na, K, Mn and Fe) but its origins remains unclear. The face exposed to the outside show less signs of weathering, only craters enriched in Fe, as ferrihydrite. On the side exposed to the inside, Mn is present as a birnessite-type oxi-hydroxide, whereas Fe is present as ferrihydrite-type compounds.

Ab-initio XANES calculations show consistent results at the Mn, Fe and Cu K-edges. By contrast, the models at the Na, K and Ca K-edges do show inconsistent results. If some structures yield decent results, some others just do not converge (such as carbonates) suggesting that there is a major problem in the modeling of the XANES spectra. We used either the lst version of the muffin-tin FEFF code and the non-muffin-tin FDMNES code. Consequently, we are very cautious in the understanding of the XANES spectra to avoid data overinterpretation. We are still working on these models to improve their reliability.

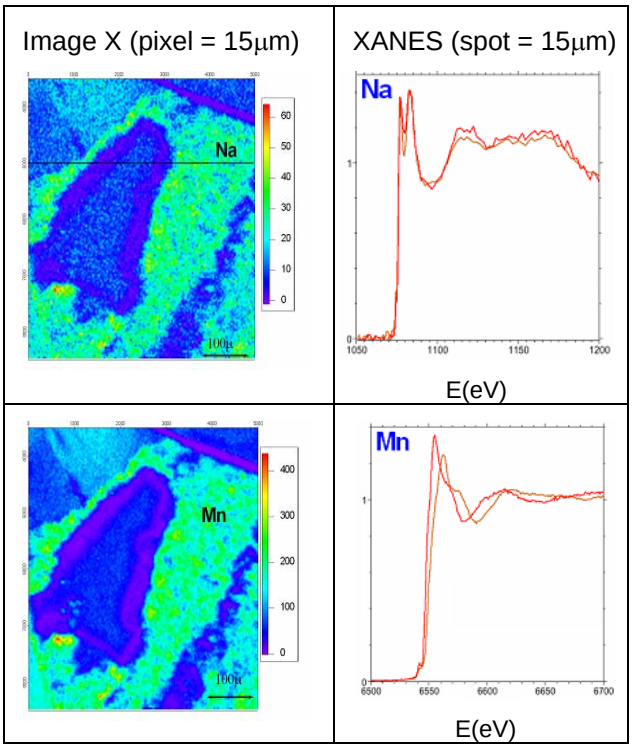

Fig. 1 — (left) XRF/elemental map of a glass from Tours showing the excellent correlation between Na and Mn on the weathered surface.(right) Na and Mn K-edges of selected spots shown on the left figure: (-) in the red non altered glass; (-) in the brown crust formed during alteration.

Mn is highly correlated to Na, suggesting the presence of a sodic-birnessite. Surprisingly, the redox of Mn changes highly (~ 4 to ~ 3) in the Strasbourg sample, as a function of the depth of the weathered layer.

In parallel, artificial weathering experiments of the fresh glass are conducted within a European (VIDRIO) and "Ile de France" program on the impact of tourism on the durability of patrimonial objects.