Speciation of network modifiers (Na, K and Ca) and transition metals (Mn, Fe and Cu) in stained-glass windows of Tours and Strasbourg cathedrals (France)

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A series of XIVth century medieval glasses from Tours and Strasbourg cathedrals stained-glass windows were studied by µ-XRF and µ-XAFS at the K-edge 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 surface weathered phases for both sites. These red flashed glasses are composite: The red part of the glass consists of a multitude of micrometer-thick dark-reddish layers that are intercalated between some greenish layers. The red-green composite is layered on a gre. This composite (1 mm thick maximum) covers a much thicker layer (about 2 mm) of a greenish glass support. 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 μ^m. Cu K-edge XAFS and XRF (K-As) data were collected at the 10.3.2 beamline (ALS, Berkeley, USA) using a Si(111) monochromator and a 8x8 µm spot size. Special care was taken to ensure that the X-ray beam did not photo-reduced the samples.

The intensity of red color of the flashed glasses from Tours is directly correlated to the Cu-content at the probed area, Furthermore, the measurements reveal that the greenish glass is enriched in Fe and Mn. Cu speciation within the red regions indicates the presence of linear Cu(I) complexes, such as observed in cuprite (Cu_2O). No evidence for metallic Cu was found in any of these (which?) glasses. Reference glass samples were synthesized at variable oxygen fugacities and confirm the above results. In the greenish regions, Cu is highly depleted. Nevertheless, Cu speciation remained unchanged (2-coordinated Cu(I) complexes). On the inner glass surface (exposed to the inside), a weathered and pale green layer covering the red glass area is detected. Its origin is still unknown, but this weathered layer is enriched in Cu(II) and as well as in Na, K, Mn and Fe. The outer side of the glass shows different signs of weathering, made of craters enriched in Fe that is present as ferrihydrite. On the outer side of the glasses from Strasbourg, a black layer of unknown is present. In this layer, Mn is present as a birnessite-type oxy-hydroxide, whereas Fe is present as ferrihydrite-type compounds. Mn is highly correlated to Na, suggesting the presence of a sodic-birnessite. Surprisingly, the Mn redox in the Strasbourg sample changes as a function of the depth of the weathered layer from ~IV to from ~III.

For the first time, Na K-edge µ-XAFS spectra are reported the (LUCIA beamline at SOLEIL/SLS). The data suggest a variety of changes in Na speciation for Na present the non-corroded glasses and Na present in the weathered layers. As for K-edge data of K and Ca, the reduction of Na K-edge XANES data is challenging because of the difficulty to perform accurate *ab-initio* XANES calculations, which are mandatory to perform reliable assignments. Therefore, much work is still needed to fully conclude the above spectroscopic information, especially in the weathered layers.