The browning phenomenon of medieval stained glass windows.

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Manganese is a chemical element which has long been used as a colouring or a bleaching ingredient [1] in the glass industry. Its existence at various oxidation states is at the origin of a large variety of colours. This colour can evolve according to environmental parameters such as UV radiations or the atmospheric pollution. In some ancient stained glass windows, the simultaneous presence of manganese and iron, coupled with the alteration by water and micro-organisms [2], can induce a browning and, consequently, a loss of transparency in stained glass windows. Among the diverse alteration observed on stained glass windows, the browning phenomenon is still poorly documented and its occurrence among stained glass is not precisely known.

Small pieces of ancient stained glass windows presenting brown zones at their surface have been collected mostly from French workshops (Troyes and Tours). Samples have been characterized using optical microscopy, Scanning Electron Microscopy coupled with Energy Dispersive System (SEM-EDS) and microprobe analysis. In order to get insight into Mn environment in altered zones, XAS experiments (chemical maps, XANES and EXAFS) have been performed at the Mn K-edge on the LUCIA beamline (Soleil synchrotron) [3] using a Si(111) double crystal monochromator and fluorescence detection mode using a focused beam of 4x4 μm^2. XANES and EXAFS spectra of reference compounds of inorganic and biogenic origin containing Mn under various oxidation states (II, III and IV) and in different cristallographic environments have been collected in order to be compared to the spectra of alterated zones.

The historical glasses that present an alteration phase enriched in Mn appear to be potassic glasses and more precisely calco-potassic. Chemical maps recorded on historical samples show that the Mn-rich alteration phases develop in Ca- and K-depleted zones. The XAS spectra of the alteration zones show evident differences with the Mn K-edge of fresh glass ensuring that a modification of the Mn environment occurred. No clear identification of the alteration phase is possible from a fingerprint analysis of XANES spectra. EXAFS data analysis lead to the identification of Mn environment in this alteration phase.

Reference:
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