The browning phenomenon of medieval stained glass windows

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In some ancient stained glass windows, the presence of manganese, coupled with the alteration by water and micro-organisms [1], 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 completely known.

Small pieces of ancient stained glass windows presenting brown zones at their surface have been collected mostly from French workshops. 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 alterated zones, chemical maps and X-ray Absorption Near Edge Structure (XANES) experiments have been performed at the Mn *K*-edge on the LUCIA beamline (Soleil synchrotron) [2] using a Si(311) double crystal monochromator and fluorescence detection mode. XANES spectra of reference compounds of inorganic and biogenic origin containing Mn under various oxidation states (II, III and IV) have been collected in order to be compared to the spectra of alterated zones.

Chemical maps recorded on historical samples show that the Mn-rich alteration phases develop in Ca- and K-depleted zones. The XANES spectra of the alteration zones show significant differences with the Mn K-edge of fresh glass ensuring that a modification of the Mn environment and oxidation state occurred.

[1] G. Orial *et al*, (2007), L'actualité Chimique 312-313, 34-39. [2] A. M. Flank *et al*, (2006), Nuclear Instruments and Methods in Physics Research 246, 269-274.

The Pedregal granitoid: a peculiar diatexitic rock (?) in a granite-migmatite complex

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The Pedregal granitoid, exposed of an area with of *ca* 3 km^2, is located in the Central Iberian Zone, northern Portugal and belongs to a synorogenic variscan granite-migmatite complex sub-concordant with the regional structures. It has an elongated shape with NW-SE trending sub-concordant with country rocks, and is a fine-grained biotite-rich granitoid with abundant small biotitic nodules (1 to 2 cm) which exhibit a internal foliation, and also metasedimentary xenoliths. The country rocks are represented by a metapelitic sequence of Edicarian age, the "Complexo Xisto-Grauváquico" (CXG).

The Pedregal granitoid is an homogeneous rock, without metamorphic differentiation, and has a isogranular texture without preferred orientation. Besides, the intergranular boundaries are consistent with a metamorphic texture marked by textural reequilibrium in solid state. Accordingly, this rock has peculiar structural/textural features, point out to a diatexitic character. The mineralogical composition of this granitoid is quartz + biotite + plagioclase + k-feldspar + zircon + apatite +titanite ± rutile, and secondary muscovite.

It is noteworthy the presence of pegmatites veins both in the granite and in the host rocks which are concordant with the main foliation of the CXG (NW-SE to NNW-SSE).

Geochemically is a peraluminous granitoid, with low SiO_2 (65 to 69 wt%) and very high Zr (390 to 435 ppm) contents. The Pedregal granitoid REE patterns show LREE enrichment much higher than the associated synorogenic granites and pegmatites (fig. 1).

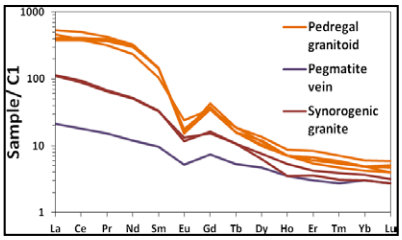

Figure 1 – REE normalized patterns.

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