

## Green color chemical recipes in stained glass windows of NE Spain and N Italy (XIII<sup>th</sup> to XV<sup>th</sup> centuries)

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A great number of medieval religious buildings in Europe contain stained glass windows. A number of original glass fragments (i.e. with original medieval lead framework) coming from restoration projects (Girona, Tarragona, Pedralbes Monastery at Barcelona (Spain); the Siena Cathedral, the San Petronio Basilica and the San Giacomo Maggiore church in Bologna (Italy)) have been analyzed in term of major, minor and trace elements. In contrast to the coeval glass windows of central Europe, most of the studied glass fragments are soda-glass of Mediterranean origin, whereas the imported K-glass were used only to realize some colors in the windows (in most of cases red ruby plaque glass). Concerning the technological aspects, these glass were realized starting from the colorless base glass, to which metal-transition elements were added to obtain the different colors. A first conclusion is that some elements, singularly REE associated to Nb and other trace elements characterize the source of silica, that is quartz sand or quartz cobbles. This allows to the identification of homogeneous sets of colored and colorless glass (i.e., original medieval glass) in the same windows and sites, even in the cases of subsequent widespread reposition of glass fragments over the centuries. Total content in Sr provides information on the calcium carbonate source (limestone or aragonitic shells). The different shades of the green color were obtained by using a Fe-Cu association. The study of green glass fragments by ICP-MS and laser ablation HR-ICP-MS allows to characterize different mineral salts taking into account the associated trace element metal associations. We acknowledge the technical support of the CCiT of the Universitat de Barcelona and the ICTJA-CSIC labGEOTOP, infrastructure co-funded by ERDF-EU (Ref. CSIC08-4E-001). This work has been carried out in the framework of the research group PEGEFA SGR2009 972 (Generalitat de Catalunya).

## Perturbing a field diffusion experiment: First results of the DR-A test in the Mont Terri Rock Laboratory (Switzerland)

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Clay-rich formations have repeatedly been shown to provide an appropriate environment to safely retain harmful solutes. However, a thorough understanding of diffusion of anions, cations and uncharged tracers through clay is fundamental to assess any long-term transport properties. A field diffusion experiment (DR-A) was recently started in the Mont Terri Underground Rock Laboratory (Switzerland). The aim of this experiment is to provide insights on coupled transport and sorption processes that are of central importance in clays, notably anion exclusion, competing sorption by cation exchange, anion and cation diffusion, and to test the predictive capability of transport codes.

The experimental design is based on established setups (DI-A1 and DI-A2 [1,2]) with a traced artificial pore water (APW) that should match the local geochemical conditions and which is circulated through a 1-m injection interval. The tracers included HTO, I<sup>-</sup>, Br<sup>-</sup>, Cs<sup>+</sup>, <sup>85</sup>Sr<sup>2+</sup>, <sup>60</sup>Co<sup>2+</sup> and Eu<sup>3+</sup>. However, unlike earlier experiments, the traced APW was exchanged after 6 months by a non-matching solution (~3 times higher ionic strength, strongly increased in K content compared to the original APW) still containing the tracers. This geochemical perturbation was expected to provoke responses that can be observed in the circulated solution.

The increase of the ionic strength and the K content led to a release of Cs from the exchanger and back-diffusion into the circulated solution. So far, no clear effect on anion exclusion was observed. The data will be interpreted by several modelling groups (IDAEA-CSIC, PSI, Univ. Bern, Univ. British Columbia, Lawrence Berkeley Natl. Lab.) using codes with different representations of the coupling between ionic strength and the transport and sorption properties.

[1] Van Loon *et al.* (2004) *Radiochim. Acta* **92**, 757. [2] Wersin *et al.* (2008) *Appl. Geochem.* **23**, 678.