Study of archaeological glass based on elemental imaging by laser ablation ICP-MS

J.T. van Elteren[1]*, S. Panighello[2], V.S. Šelih[1], N.H. Tennent[3], E.F. Orsega[2], A. Izmer[4], M. Šala[1] and F. Vanhaecke[4]

[1]National Institute of Chemistry, Ljubljana, Slovenia
    (*correspondence: elteren@ki.si)
[2]University Ca'Foscari Venezia, Venice, Italy
[3]University of Amsterdam, Amsterdam, Netherlands
[4]Ghent University, Ghent, Belgium

The study of ancient glass is predominantly focused on retrieval of its chemical composition to trace the provenance of raw materials, to unravel fabrication technologies and to investigate degradation phenomena. Techniques such as laser ablation ICP-MS are frequently used for multi-elemental microanalysis of glass in spot or raster mode. This work focuses specifically on the development of laser ablation ICP-MS techniques for lateral (2D) and volume (3D) imaging of glass to enhance the information retrieval. Spatial distribution analysis offers superior insight into the colocalization of elements to elaborate and advance archaeological hypotheses.
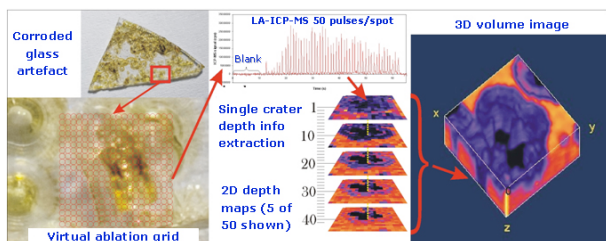

Fig. 1: 3D laser alblation ICP-MS protocol illustrated for imaging of Mg in a corrosion pit of an ancient glass artefact.

Laser ablation ICP-MS imaging techniques will be presented for 2D imaging based on rastering and quantification of the elements in the map using a so-called sum normalization technique which corrects automatically for drift and defocusing issues. Recently an innovative 3D imaging procedure was introduced based on laser drilling on a virtual grid on the surface using a burst of 50 laser pulses on each point of the grid (Fig. 1). After integration of the elemental peak areas, stacks of 50 2D depth maps with a depth resolution of 150 nm were retrieved which could be visualized as volume images. The application of the latter laser ablation ICP-MS imaging procedure will be demonstrated for the study of glass weathering mechanisms involved in the corrosion of some ancient glass artefacts.

Structure of Fe(III) precipitates formed by Fe(0) electrolysis in the presence of groundwater ions

Case M. van Genuchten[1], Susan E. Amrose[1], Ashok J. Gadgil[1,2] and Jasquelin Peña[3]

[1]University of California, Berkeley, USA
    cmvangenuchten@berkekey.edu
[2]Lawrence Berkeley National Laboratory, USA
[3]University of Lausanne, Switzerland

Oxyanions and bivalent cations influence the polymerization and precipitation of Fe(III) (oxyhydr)oxides, thus modifying the mineral structure in terms of local coordination environment of Fe, mineral phase, crystallinity, and oxyanion uptake mechanism. Few studies have investigated the interdependent effects of these ions on the formation of Fe(III) precipitates generated from Fe(II) oxidation, despite the co-occurrence of oxyanions and bivalent cations in natural waters. Such studies are essential to understand oxyanion mobility at both natural and engineered redox boundaries.

We combine wet chemical measurements and complementary synchrotron-based X-ray techniques (high energy X-ray scattering and Fe, As, and Ca K-edge X-ray absorption fine structure (EXAFS) spectroscopy) to investigate the interaction between oxyanions (PO_4^{3-}, AsO_4^{3-}, SiO_4^{4-}) and bivalent cations (Ca^{2+}, Mg^{2+}), and their subsequent effect on the formation of Fe(III) precipitates. Fe(III) precipitates were produced by the electrolytic dissolution of an Fe(0) electrode in an electrolyte consisting of oxyanion concentrations ranging from 0.05-0.5 mM and the presence or absence of 1 mM Ca^{2+} or Mg^{2+}.

Our results suggest a systematic decrease in the strength of bivalent cation:oxyanion interaction in the order of Ca>Mg and P>As(V)>>Si. We find that 1 mM Ca^{2+} enhances the uptake of As(V) (per mass of Fe) more than 1 mM Mg^{2+}. Whereas Fe(0) electrolysis leads to 2-line ferrihydrite-like material in the presence of 0.05 mM As(V) alone (initial As/Fe = 0.1), the presence of 1mM Ca^{2+} with 0.05 mM As(V) promotes the formation of more crytsalline lepidocrocite-like material. These results are consistent with a strong Ca-As(V) interaction that can modify the extent of As(V) uptake and the resulting Fe(III) precipitate structure. Ca K-edge XAS data in the Ca:As concentration series display features consistent with second-shell As(V) scattering. No discreet As(V)-Ca surface-precipitate is observed. Our results indicate that direct Ca-As(V) interactions must be considered when assessing iron and arsenic biogeochemistry.