Names and affiliations of applicants (* indicates experimentalists):

Simona Quartieri and Maurizio Triscari, Dipartimento di Scienze della Terra, Universita' di Messina (Italy)

Federico Boscherini, INFM and Dipartimento di Fisica, Universita' di Bologna (Italy)

Alessandra Sani, ESRF (France)

Report:

The XANES technique has been applied to the study of fragments of perfume bottles of the 2nd century AD, found in the Patti Roman Villa (Sicily), characterized by different color (from green: glass A, to pale brown: glass C, to uncolored: glass B). Ancient glasses often contain iron at levels which can impart a typical incidental green coloration. To minimize this problem, from around the middle of the first millennium BC, substances were added which tended to neutralize the colorant effects of the iron. Before the Roman period antimony was the main decolorant, while from the second century BC manganese become. Since the characterization of colorant and decolorant components is important in understanding the manufacturing technique of the ancient glasses, we have applied XAFS spectroscopy to study the oxidation state of iron and manganese in these glass samples.The aims of this work are: i) to confirm the Roman origin of the glasses found in the Patti Villa on the basis of their chemical composition; ii) to test the influence of iron oxidation state on the color of the studied glasses; iii) to identify the possible decolorant role of manganese oxide in the almost uncolored samples.

Before performing the XANES experiments, the glass fragments were investigated by electron microprobe analysis in the wavelength-dispersive mode. From the chemical point of view, the samples resulted to be 'low-magnesia' glasses, with a composition typical of the Roman period.

The Fe and Mn K-edge XANES spectra were collected directly on the glasses in the fluorescence mode on the GILDA-CRG beamline. A dynamically sagittally-focussing monochromator with Si(311) crystals and a 13-element high-purity Ge detector were used. Energy calibration was achieved with Fe and Mn foil standards; the position of the first inflection point was taken at 7112.0 eV for the former and 6539.0 eV for the latter. The following standards were used as reference compounds for iron: synthetic olivine (octahedral Fe^{2+}), synthetic hematite (octahedral Fe^{3+}) and natural magnetite (octahedral Fe^{2+} and both tetrahedral and octahedral Fe^{3+}). As reference compounds for Mn the following materials were used: synthetic MnO_2,

Mn_2O_3 and MnO for Mn^{4+}, Mn^{3+} and Mn^{2+}, respectively; natural rhodonite ($Mn^{2+}SiO_3$) and natural tephroite ($Mn^{2+}SiO_4$) as other standard compounds containing Mn^{2+} in octahedral coordination. The XANES region was scanned with energy steps of 0.1 eV. The raw XANES spectra of samples and reference compounds were subtracted of the pre-edge background with a linear function and then normalized on the high energy side of the curve. This normalization allowed the comparison of samples with different absorber content. The analysis of the pre-edge region was then performed by least-square fitting of Gaussian peaks to the pre-edge spectral envelope. The Fe- and Mn-XANES spectra are reported in Fig 1 and 2ab, respectively. A detailed analysis of the pre-edge peaks has also been performed (not shown).

The Fe-XANES spectra (Fig. 1) of glasses B and C are virtually identical, both in the general shape and in the energy positions of the various features. The XANES features of glass A occur at significantly lower energy values with respect to glasses B and C and to the reference compounds hematite and magnetite, while are near to those present in olivine spectrum, characteristic of iron in the oxidation state 2^+. We can conclude that our ancient glasses contain iron in different oxidation states: only Fe^{3+} is present in glass B, where virtually only a pre-edge peak at 7114.0 eV is present; Fe^{3+} is dominant in glass C, where together with the peak at 7114.0 eV a weak shoulder is present at 7112.4 eV; finally, the green glass A contains a high percentage of Fe^{2+}. Concerning Mn-XANES spectra (Fig. 2a,b), both the pre-edge and the main-edge energy positions of the glasses B and C, and the comparison of the shape of the XANES spectra of glasses and reference compounds, evidence a strong similarity between the glass samples and the standard compounds tephroite and rhodonite. This suggests that in the ancient glasses B and C manganese is present in the reduced form Mn^{2+} and confirms the hypothesis of a redox interaction between iron and manganese, as a result of a deliberate addition of pyrolusite as decolorant during the melting procedure.

This work shows that XAFS is a potentially very useful non-destructive technique which can be applied in archaeological studies on many different materials. In fact, it is a non-destructive method which can be applied in air; it virtually does not require any restriction on the type and size of the sample, which can be metal, ceramic, glass, cloth, wood, etc. and, finally, it is applicable to most of the elements of interest, even in very low concentrations. All these characteristics are particularly important in archaeological applications, in which samples are precious cultural heritage made of many different materials.
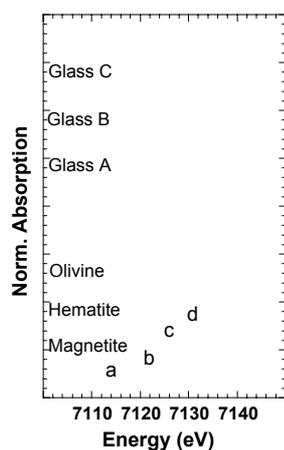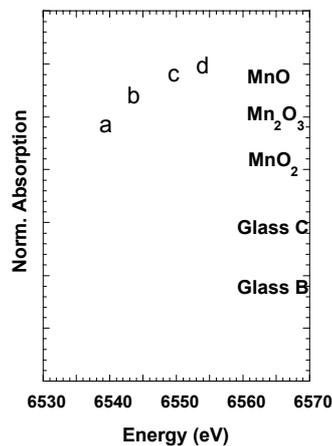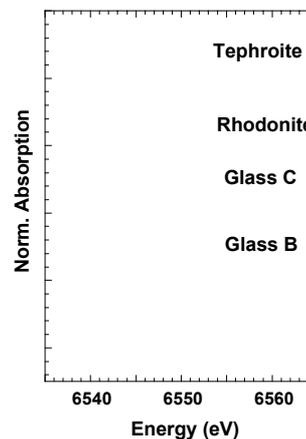

Fig. 1

Fig. 2a

Fig. 2b

Publications:

Triscari M., Quartieri S., Boscherini F., Sani A. (2000) Application of X-ray absoprtion spectroscopy with synchrotron radiation to the study of glasses of archaeological interest. Atti I Convegno AIAR, pp. 459-466, Patron Ed. Bologna.

Triscari M., Quartieri S., Boscherini F., Sani A. (2000) XAFS investigation of iron oxidation state in glasses of archaeological interest. 80° Convegno SIMP, Pavia, 11-13/9/200, Plinius 24:216 (abstract)

Quartieri S., Triscari M., Sabatino G., Boscherini F., Sani A. (2001) Fe and Mn K-edge XANES study of ancient Roman glasses. Eur. J. Mineral., submitted.