

were used from the beginnings of glass production through into the Roman period for the opacification of green, blue and white samples. Subsequently, they started to be replaced by tin-based opacifiers during the fourth century AD in glass produced from the eastern Mediterranean through into northern Europe. For the production of red and orange samples, it seems that across the centuries only Cu-based opacifiers were used.

In this work, the opacifiers identified in a series of mosaic tesserae coming from Mediterranean region and dated from the 6<sup>th</sup> to the 11<sup>th</sup> century are compared and employed to sketch the glass technology evolution on a chronological and geographical base. The coupling of the chemical data with the SEM-EDS and XRD investigations allows the identification of the opacifiers employed in the glass production.

In particular, the data relative to San Severo Basilica (VI century AD, Classe–Ravenna-Italy), represent a useful tool to understand the shift from Sb to Sn bearing opacifiers. The sample set coming from this site presents a peculiar characteristic: all the blue samples, colored mainly with copper, are lead and tin free and are opacified with calcium antimonates, on the contrary all the green samples are antimony-free and contain high levels of lead and rather high levels of tin.

On the whole, San Severo samples fit with the chemical composition of the coeval mosaic tesserae. The co-presence of Sb-based opacifiers and of tin bearing samples in the sample set, represent a rather peculiar trait, but, it is well known that in Italy, the tin based opacifiers have been found from the fifth century AD onwards, but at the same time, antimony-based opacifiers continued to be used, or reused, until the 13th century AD.

The simplified pattern of Sb and Sn bearing opacifiers is then complicated in some areas of the Mediterranean glass production by the occurrence of quartz crystals dispersed in the glass matrix. The study of the opacifiers could be an indirect method for dating and provenancing the mosaic glass.

**Keywords:** Sb based opacifiers, Sn based opacifiers, mosaic tesserae

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### Spectroscopic study of chromophores in ancient HIMT glass

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We have studied a series of Late Roman glass fragments belonging to the peculiar group called HIMT (High Iron Magnesium Titanium glass), characterized by different color nuances, and previously chemically characterized [1-3]. XANES, UV-VIS and luminescence spectroscopies [4-6] are exploited for determining the distribution of the oxidation states of the two chromophores Fe and Mn in the ancient finds and in two synthetic glass specifically prepared with selected chemically compositions.

Fe and Mn K-edge XANES spectra were collected in fluorescence mode at the GILDA-CRG beamline (ESRF, Grenoble, France). A dynamically and sagittally focussing monochromator with Si (311) crystals was used. Energy calibrations were achieved using Fe and Mn foils as references and the position of the first inflection point was taken at 7112.0 and 6538.0 eV respectively. The pre-edge region was extracted from the normalized spectra and analysed by least-square fitting of pseudo-Voigt functions of equal width to the pre-edge spectral

envelope. For each sample, the pre-edge centroid was calculated from the average position of the pseudo-Voigt functions, weighted by their respective integrated areas. UV-VIS absorption spectra were measured on a Varian Cary 100 double-beam spectrophotometer operated between 900 and 200 nm. Luminescence emission and excitation spectra were collected in a Spex Jobin-Yvon FluoroMax3 spectrofluorometer.

On the basis of both XANES and UV-VIS results, in all the ancient glass samples Fe results to be mostly in its oxidate state 3+. XANES data indicate that the prevalent Mn oxidation state is 2+, however the presence of minor amounts of Mn3+ has been proved by UV-VIS and luminescence spectroscopy. The different spectroscopic techniques, used in a combined approach, are able to interpret the apparent anomalous colour of some of the ancient glass samples.

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**Keywords:** XANES, UV/VIS, archaeological glass

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### μ-XRF study on unearthed ancient pottery at Au Thong, Thailand

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Pottery has been produced in Thailand for thousands of years. In this work, unearthed potsherds examined come from the Au Thong prehistorical site, Suphan Buri Province, Central Thailand. A multi-analytical approach was carried out on the same sample to reduce the sampling, including petrographic, mineralogical and chemical investigations by mean of micro-beam X-ray fluorescence (μ-XRF), optical microscope, scanning electron microscope coupled with energy dispersive X-ray fluorescence spectroscopy (SEM-EDS) and Particle induced X-ray emission spectroscopy (PIXE). X-ray diffractometer (XRD) analysis was also performed to confirm the presence of clay minerals. The composition analysis showed the heterogeneous matrices which were commonly associated with high concentrations of elements such as Ca, Fe, Al or Ti that used to be the pottery characterization.

**Keywords:** μ-XRF, ancient Thai pottery, Au Thong