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Acta Cryst. (2011) A67, C197**Degradation studies of cultural heritage materials using μ -XANES and μ -XRD**

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The mission of cultural heritage institutions is to preserve and protect artifacts from the distant or more recent past for the enjoyment and education of current and future generations. In order to fulfill this mission in a professional manner, detailed knowledge on alteration phenomena of various kinds that gradually and unobtrusively are taking place at or below the surface of these objects is required. In order to be able to investigate the nature of these chemical transformations, that sometimes lead to the formation of microscopically thin alteration layers, the use of state-of-the-art microanalytical methods is required. Next to being able to provide information on the composition of various materials at or just below the surface, these methods also must be able to deliver highly specific information on the nature of the chemical compounds that are locally encountered. In this respect, our recent experience shows that the use of a combination of synchrotron X-ray based spectroscopic and imaging methods such as X-ray fluorescence analysis, X-ray absorption spectroscopy and X-ray diffraction can reveal significantly new information of certain alteration processes that have remained enigmatic for a long time. Concrete examples to be discussed is the darkening of originally yellow lead chromate paint layers, as encountered in paintings of V. Van Gogh [1,2] and the blackening of red cinnabar-based paint layers in works of Rubens [3]. In both cases, one or more microscopically thin alteration layers were encountered that are responsible for the colour and that contain resp. the metals Cr and Hg in other chemical environments that what they were originally.

[1] L. Monico, G. Van der Snickt, K. Janssens, W. De Nolf, C. Miliani, J. Verbeeck, H. Tian, H. Tan, J. Dik, M. Radepont, M. Cotte *Analytical Chemistry* **2011**, 83, 1214-1224. [2] L. Monico, G. Van der Snickt, K. Janssens, W. De Nolf, C. Miliani, J. Dik, M. Radepont, E. Hendriks, M. Geldof, M. Cotte *Analytical Chemistry* **2011**, 83, 1224-1231. [3] M. Radepont, W. de Nolf, K. Janssens, G. Van der Snickt, Y. Coquinot, L. Klaassen, M. Cotte *Journal of Analytical Atomic Spectrometry*, **2011**, DOI: 10.1039/c0ja00260g.

Keywords: synchrotron radiation, cultural heritage, pigment alteration

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Acta Cryst. (2011) A67, C197**X-ray computed tomography: a powerful diagnostic technique for art and cultural heritage**

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Born in the early Seventies for medical applications, X-ray Computed Tomography is currently playing an increasingly important role in the field of Cultural Heritage diagnostics. In fact it represents a powerful non-destructive investigation technique, capable of displaying in a three-dimensional way the volume and the internal structure of the investigated objects, also thanks to modern 3D rendering techniques. This kind of information is very important for determining adequate

conservation and restoration procedures [1] [2].

The first attempts in adopting this technique for Cultural Heritage analysis have been done by means of medical CT scanners, usually with courtesy and permission of an hospital. However, medical scanners are optimized for the human body (composed mainly by water) and cannot be successfully used on dissimilar objects like those of interest in the Cultural Heritage field. Moreover, it is difficult to move valuable works of art outside the museum in which they are located.

The great variety of size, shape and composition that is typical of archaeological findings and art objects requires the development of tomographic systems specifically designed for Cultural Heritage analysis and movable on-site, if necessary. In order to fulfill this request, our research group has set-up several CT systems, that make us able to perform high resolution micro-tomography of small objects (voxel size of few microns) as well as CT of large objects (up to 2 m of size). In fact, in order to perform good non-destructive evaluations, the most suitable CT system (source, moving equipment, detector and elaboration software) must be carefully chosen to avoid obtaining meaningless results. For small objects (i.e. fossil teeth and ancient jewels) radiation sources having a very small focal spot size and high spatial resolution detectors are required. For big or thick objects it is necessary to use highly penetrating radiation sources, very efficient detection systems and advanced mathematical methods for the reconstruction of the 3D images. Commonly X-ray tubes up to 450 kV are used, but a certain interest in high energy CT (more than 1 MV) is now growing up.

In order to highlight the versatility and the potential of Computed Tomography as a tool of knowledge in the field of Art and Cultural Heritage, we will present the results of several diagnostic investigations carried out by our research group, in collaboration with major restoration and conservation centers, both in Italy and abroad. Among the case studies that will be treated, it is worth mentioning the "Goldfinch Madonna" by Raffaello (CT carried out at "Opificio delle Pietre Dure" in Florence), two Japanese wooden statues of the XIII and the XVII century (CT performed at the Conservation and Restoration Center "La Venaria Reale" in Turin) and a Roman bronze Eros statue dating to the 1st century A.D. (CT scanning carried out at the Getty Conservation Institute, Los Angeles CA, USA).

[1] F. Casali, *X-ray and Neutron Digital Radiography and Computed Tomography for Cultural Heritage*, in: Physical Techniques in the Study of Art, Archaeology and Cultural Heritage, ed. by D. Bradley and D. Creagh, Elsevier, **2006**, 41-123. [2] M.P. Morigi, F. Casali, M. Bettuzzi, R. Brancaccio, V. D'Errico, *Applied Physics A: Materials Science & Processing* **2010**, 100, 653-661.

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Acta Cryst. (2011) A67, C197-C198**Investigations of ancient Egyptian faience using XAS and PD**

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Egyptian faience was produced over a period of approximately 5000 years, with the first examples dating to ca. 4000 BC. Faience is a glazed, quartz-based material that was commonly used to make objects such as beads, pendants, rings, tiles, bowls, jars, gaming pieces and specialist funerary equipment (e.g., [1, 2]). The most common colors are light and dark blue, probably developed to imitate valuable stones, such as turquoise and lapis lazuli, but other colors also occur, albeit less frequently. Faience is relatively common on archaeological sites

dating from *ca.* 1550 BC onwards; of particular interest is the site at Armana which was occupied for a very short period of time (1350-1325 BC). Armana is located in middle Egypt and was the seat of reigning God-King Akhenaten and Queen Nefertiti. Despite the prevalence of faience, the chemical makeup and manufacturing techniques used to produce it remain somewhat enigmatic.

The work presented herein utilized X-ray absorption spectroscopy (XAS) and synchrotron powder diffraction (PD) techniques to examine a range of faience objects obtained from collections acquired in Amarna, in addition to a selection of faiences prepared in the laboratory. The artifacts for this study were provided by the Aegyptisches Museum, Berlin. Faience for comparison was synthesized using a base mix of 80 wt-% SiO₂, 14 wt-% NaHCO₃ and 3 wt-% CaCO₃. Before firing at 900°C, Cu colorant was added to the equivalent of 3 wt-% Cu. Copper sources included bronze, corroded bronze, various natural minerals (malachite, azurite, turquoise, diopside, chrysocolla, atacamite, etc), and laboratory chemicals (CuO, Cu₂O, CuCO₃, CuSO₄, etc).

XAS data were acquired at Beamline C, DORIS, HASYLAB. These data showed that all spectra acquired from the faiences were very similar, regardless of color, Cu concentration, or Cu source. However, analysis of the subtle differences between spectra reveal Cu coordination can be described as, either, i) a distorted Cu-O octahedron with some Si present in a fairly weak second coordination sphere, or ii) exhibiting a Cu-Cu second sphere of coordination. The former is consistent with data from glasses or related materials and the latter suggests incomplete transformation to a glassy state. Such results may open avenues to use XAS to assess firing temperatures of ancient Egyptian faiences and to provide context on levels of control in ancient faience making.

PD data were acquired using the powder diffraction beamline at the Australian Synchrotron which allowed the non-destructive examination of these precious artifacts. Data from the Egyptian faience show that the dominant crystalline phases present are quartz and tetragonal cristobalite. These results are suggestive of different maximum firing temperatures. Data acquired from samples synthesized in the laboratory, to different temperatures, affords additional information as to the mineral chemistry and thermodynamics of faience formation.

This presentation will discuss the use of synchrotron techniques for the characterization of Egyptian faience and the subsequent outcomes.

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Evidence of the role of Zn AND Fe cations as dopants in lead antimonate yellow by x-ray absorption spectroscopy (XAS)

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Naples yellow (Pb₂Sb₂O₇) is one of the oldest known synthetic pigments. It shows a cubic pyrochlore structure, obtained by roasting mixtures of Pb and Sb oxides. Recent studies demonstrate that Naples yellow may exist also in a modified form obtained from a ternary mixture of Pb, Sb and Sn oxides (Pb₂Sb_{2-x}Sn_xO_{7-x/2}).

X-ray diffraction and Raman spectroscopy investigations of standard doped yellow pyroantimonates provided evidence that, in general, doping cations (such as Sn⁴⁺, Zn²⁺, Fe³⁺ or exceeding Pb⁴⁺) induce significant structural modifications of the pyrochlore lattice of the pigment, suggesting that ternary cations enter the octahedral sites replacing Sb⁵⁺ ions.

Here we report on the results obtained by XAS investigations carried out at the GILDA beam-line of ESRF (Grenoble, FR) on the role played by Zn and Fe cations in modified Naples yellow, characterising the ions' local properties (interatomic distances, coordination number and oxidation state). The XAS study has been non-destructively carried out on different standard yellow pyroantimonates, as well as on Renaissance ceramic shards from the collection of the *Musei Civici di Pesaro* (Italy). XAS measurements at the Zn-K and Fe-K absorption edges evidenced that Zn and Fe enter the antimonate structure. *Ab-initio* structural simulations based on Density Functional Theory were used to simulate both the structure around the metal (via a conventional structural relaxation) and the EXAFS spectra via a DFT Molecular Dynamics. The latter represents a novel and promising method for the analysis of point defects in crystals by EXAFS. The comparison with theory permitted to establish that in both cases the metal occupies the site of Sb. The same structure has been also observed for Zn cations in the yellow pigment of a Renaissance ceramic shard.

The study has been carried out within the joint research activities of the CHARISMA project supported by the 7th F.P. of EU.

Keywords: archeometry, EXAFS, defect

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Practical experience with powder XRD microdiffraction in forensic science field

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X-ray powder microdiffraction is a very valuable method for exact phase analysis. The size of the area being analyzed – approx. 100 μm is roughly comparable to areas that are studied by methods of optical and electron microscopy.

Most of the examinations in forensic science deal with determination, description and comparison of practically any substances that can come into contact with persons or objects. In this context the potential of X-ray methods is critical. Of course, not even XRD methods are a panacea and are routinely used in combinations with other methods (namely SEM-EDS/WDS, Raman microspectrometry, optical microscopy, XRF, FTIR etc.).

A recent trend in the forensic sphere is determination of the phase by at least two independent methods. The outcomes of the examinations are the grounds for bodies responsible for penal proceedings; i.e. for deciding the issues of guilt and punishment, and therefore they have to possess maximum credibility. The role of XRD methods is irreplaceable here because they allow phase analysis on a physically different basis than the majority of standard analytical methods for inorganic and organic bases.

Thorough testing of the potential and comparison with other possible diffraction arrangements was carried out - classic reflection (including collimators), rotary capillary, and transmission arrangement - during the introduction of the X-ray powder microdiffraction into the analytical routine use. Tests have been carried out for the arrangement with rotary capillary in order to determine the optimal capillary diameter with respect to the signal strength and FWHM value. Zero-background silicon plates are commonly used for imaging in reflection geometry. Standard plates are non-conductive and this fact in some