

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.

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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

cases causes problems during complementary SEM/EDS analyses when the sample is not transferred onto a different sample holder with regard to minimization of risk of its damage, loss or contamination. Therefore monocrystalline silicon plates with indicated conductivity of $5 \Omega \cdot \text{cm}^{-1}$ were tested in practice. This value is sufficient for SEM (based on measurements – carbon conductive strips specially intended for SEM have the conductivity of approx. 500 k Ω and higher). The plates with thickness of 300 μm ($\pm 15 \mu\text{m}$) can also be used for subsequent direct FTIR analysis even in transmission mode, without the need of plate exchange. A method employing the image analysis system was introduced for precise sample adjustment for microdiffraction and the choice of the area to be measured. The trace of the primary beam on a fluorescent disc was scanned for different angles 2θ and subsequently saved as binary overlay images. A camera reads the live image of the sample through the focusing microscope and the operator can choose a spot for the analysis in ergonomic conditions (the second monitor was placed directly into the diffractometer chamber). This procedure is very convenient for heterogeneous samples, various abrasions, etc.

The system is further used for quantitative drug analysis. Both Rietveld method or method with the scale factor and the RIR (Reference Intensity Ratio) values (also called I/I_c values) are used. The results are cross-checked by standard methods of organic analysis (GCMS, FTIR), XRD analysis, in addition, enables precise phase analysis of inorganic components.

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Strategies in the crystallization of a glycoallergen and a F1-ATPase complex

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Hypersensitivity reactions mediated by immunoglobulins E (IgE) are considered an important public health problem in developing countries. The IgE response against an allergenic protein is the sum of specific responses against each of its allergenic epitopes, which vary in intensity. Natural rubber latex (NRL) from *Hevea brasiliensis* contains several proteins and glycoproteins involved in this type of allergy. In general, these are involved in cross-reactivity against fruits, pollens and insect venoms. The structural information about this type of proteins is scarce and the cascade of events leading to allergy symptoms is also poorly understood. Among NRL allergens there are β -1,3-glucanases (Hev b 2), lectins (Hev b 6.02), class I chitinases (Hev b 11) and profilin (Hev b 8). We recently solved the structure of two polymorphic crystals of one glycosylated natural form of the Hev b 2 [1], at 2.5 Å and 2.8 Å resolution. One of them presented clear density for the oligosaccharides. Interestingly, two glycosylation sites were found in the electron density maps. Appropriate buffers modified the solubility of the proteins. We have also solved the structure of two natural isoforms of Hev b 6.02 and three-dimensional studies for a recombinant Hev b 11 and Hev b 8 is underway.

We are also interested in the study of F1-ATPase from mitochondria, which is regulated by a low molecular weight inhibitor protein IF1. It has been reported that the endogenous complexes of F1 with IF1

exhibit a behavior that is different from that of complexes that had been reconstituted with exogenously added IF1. To get insight into the mechanism of action of IF1 we crystallized the endogenous complex F1-IF1 using two different approaches. Homogeneous preparation was fundamental; some preliminary results will be discussed.

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Lipid-Driven molecular complexes

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We describe three different self-assembled structures that are formed by lipid sequestration. The first two are designed lipopeptides that assemble into cylindrical micelles. The third is a two-component system consisting of an amphipathic protein forming a belt around a lipid assembly in discoidal lipoprotein particle.

Lipopeptide detergents (LPDs) are 25 residue peptides designed to form an alpha-helix with fatty acyl chains coupled to each end of the helix. LPDs form small 25-30 kDa micelles with aggregation number of 8-10, depending on the peptide sequence and the length of the acyl chains. We have previously described the 1.20 Å structure of LPD-12 [1], which forms octameric micelles with all anti-parallel helices. We now report the 2.0 Å structure of LPD5Q-14, which is based on a different peptide sequence coupled to 14-carbon acyl chains. Crystals of LPDQ-14 contain 18 molecules per asymmetric unit, arranged into two 9-mer micelles. Both micelles have similar structures, and are made of up three units of “up-up-down” trimers. There are considerable differences between the LPD-12 and LPD5Q-14 micelles, but both consist of an outer alpha-helical shell surrounding an acyl chain interior, as designed.

We also report the 1.9 Å structure of saposin A in a discoidal assembly with interally-bound detergent molecules. Saposin A is an alpha-helical protein that exists in both soluble and lipid-bound states, and has superficial similarities to the exchangeable apolipoproteins. Our structure show a belt of two “open-state” saposin A molecules forming a belt around 40 detergents arranged in a bilayer-like arrangement. The structure gives insight into the biological functions of the saposins, as provides a high resolution view of a discoidal lipoprotein particle.

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