ESRF	**Experiment title:** **Synchrotron Diffraction Mapping of a Gallo-Roman Painting**	**Experiment number**: CH1123
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Report:

Identifying the pictorial materials composing an ancient artwork and determining the artist's know-how are important recurrent issues in archaeological science. One needs to determine the availability of the pigments over certain periods and regions, and how they have been prepared and used. It helps the restorator diagnosing any transformation or degradation. X-ray diffraction (XRD) is frequently used, although often penalised by i) the width and depth of probe, ii) the constrained angular alignment of the object analysed, and iii) the difficulty in interpreting *quantitatively* the diffraction diagrams. In the present test experiment, we show that it is possible to produce a pixelised picture (fig. 1) from the XRD data which mimics the major features of the painted raw surface, scanning a synchrotron point beam at low incidence and using a large-area detector. Tuning the energy, size and incidence angle of the synchrotron beam makes it possible to examine fine details, to scan over large areas, or to probe superficial or buried layers of paint. We obtain relevant structural information on the crystalline pigments used and their relative proportions at the surface. The graininess of the constituent powders is also examined, in relation with the methods of preparation and application on the support.

The work was carried out on an exceptional remain of a painted Roman wall showing a cherub's face (fig. 2). The 9x12 cm^2 fragment was supplied by the Museum of Metz (France), as part of an ensemble of pieces dated of the Roman period and excavated from the Pierre Hardie street in Metz in 1994. It offers the opportunity to analyse the chemical compositions of the pigments and the artists' fresco techniques in the 2^{nd}-3^{rd} century AC.

The mural fragment was first submitted to a PIXE elemental analysis carried out at the AGLAE accelerator at Le Louvre. A 0.1mm beam of 3 MeV protons is extracted in air through a 0.1μm thick Si_3N_4 window and impinges on the surface. The proton-induced fluorescence radiation is emitted at characteristic wavelengths which reveal the elemental composition of the top 10-20 μm painted surface. From the intensity of the fluorescence radiation lines are constructed the elemental abundance maps which clearly show the presence of Ca, Fe, Cu and Pb (fig. 3). The method fails in identifying the chemical state of the fluorescing elements, and hence the phases they belong to, and it is not sensitive to underlying layers of paint.

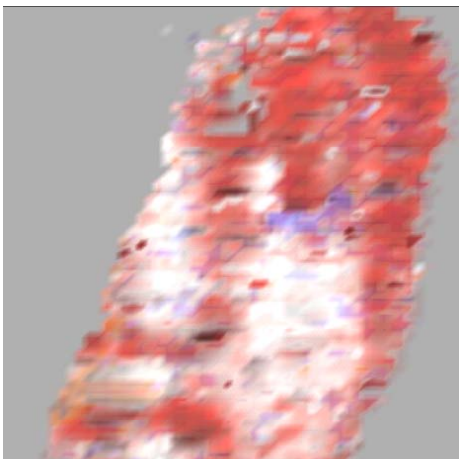
The diffraction signal from the painted surface was recorded at the ID11 beamline by the means of the 2D MUX-FRELON CCD camera fitted with a large-area X-ray image intensifier. The object was positioned in reflection geometry at a low fixed incidence angle ω, and x-y step-scanned with a focussed beam (≤ 0.1 by 1

mm^2) at λ = 0.991Å. ω=5° was found to be a sensible value, for minimising the signal from the support, and for reducing the truncation and shadowing of the Debye-Scherrer rings by the object itself. The exposure time was 40sec per step (i.e. per mm^2 pixel), including detector overhead and data transfer to the computer unit. The machine was operating in the single bunch mode, and therefore this time can be substantially decreased.

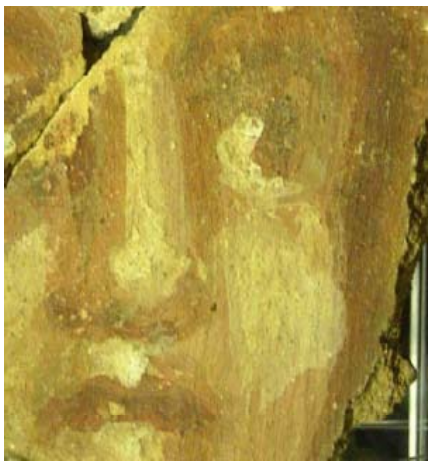
Combining different ESRF software packages (*FIT2D*, A. Hammersley, *kcorcake*, G. Vaughan), the diffraction rings on the 2D patterns (9.7Gb for a $(60 \text{ pixels})^2$ map) were processed through a semi-automatic computed procedure. After transformation into 1D patterns, two procedures have been implemented: either each major single peak of the respective present phases is individually integrated over a relevant region of interest (ROI method), or the entire pattern is fitted as a whole using a scale factor for each phase and constraining the peak intensities by the structural model of each phase (whole pattern Rietveld fitting). The former method gives the individual peak intensities versus the position (x,y) at the surface; the latter gives the scale factor of each phase (proportional to the mass present) versus (x,y). Both methods eventually give comparable maps. The whole pattern fitting is a more robust method and yields more quantitative figures. In particular the respective mass proportions can be derived from the scale factor of each component in the diagram and the peak shape parameters can be interpreted in terms of grain size and strain. This method is prone to more errors in the final phase abundance maps if a pigment exhibits a non random distribution of crystallites (preferred orientation or limited number of X-ray illuminated crystallites).

The XRD map (fig. 1) reveals the presence of: quartz (SiO_2), cuprorivaite ($CaCu(Si_4O_{10})$), hematite Fe_2O_3 and goetite FeO(OH), calcite $CaCO_3$ and a yet unidentified Pb-based phase. The non uniform distribution of the diffracted intensity over the diffraction arcs of rings suggests the first two silicates consist in a non isotropic distribution of big grains. Two different calcite abundance maps were obtained from the ROI method. One map shows the uniform presence of a finely divided powder of calcite. On the second map, one sees the contours of the nose and of the left cheek: it originates from a topmost layer of calcite superficially spread over those parts of the face which the artist wanted to highlight.

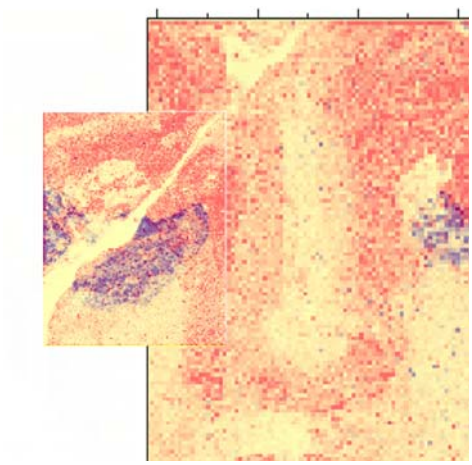
Cuprorivaite is the major compound in the Egyptian Blue: this pigment was found here in the form of large crystallites and was not visible to the naked eye. It was unexpectedly revealed by the XRD and PIXE analyses. The presence of Egyptian Blue as a pigment over the eye lids and in the hair is unusual over this period. XRD also reveals the existence of two main Fe oxides. Hematite is found in significant quantities, whereas goetite is sprinkled over the hair and at the lip corner. The surface repartition of both oxides could not be obtained separately from the fluorescence data only.



1. XRD phase abundance map



2. Painted Roman fragment



3. PIXE elemental presence map