ESRF	**Experiment title:** Micro chemical study of Egyptian blue pigment balls from an archaeological workshop on the island of Kos (Greece)	**Experiment number**: HG-116
Beamline: ID21	**Date of experiment**: from: 25/10/2017 to: 27/10/2017	**Date of report**: 3/10/18
Shifts: 3	**Local contact(s)**: Dr. Wout De Nolf	*Received at ESRF:*

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Report:

We investigated four cross-sections of samples of Egyptian Blue (a synthetic analogue of the naturally occurring cuprorivaite mineral, $CuCaSi_4O_{10}$) from the ancient workshop of Kos (Greece). Egyptian Blue (EB) is the first synthetically produced pigment and was obtained by firing a mixture of copper, silica, calcium carbonate, and an alkali flux at temperatures between 850 °C and 1050 °C. The analyzed cross-sections were obtained by casting unsuccessfully produced EB samples that featured high heterogeneity. The aim of our experiment was the characterization by micro-XRF and Cu K-edge micro-XANES of such cross-sections to shed more light on the production technology of EB.

Spatially-resolved information on the chemical composition and crystal chemistry of the Cu-containing compounds was obtained. The Cu species were localised at a sub-micrometric resolution (Figure 1). The obtained data were analyzed by the PyMca software and the dark field correction and image alignment were performed by the Spectrocrunch library.
The micro-XRF maps revealed the heterogeneity of the material. EB crystals were found alongside a Cu-bearing glassy phase and unreacted materials (Fig. 1).

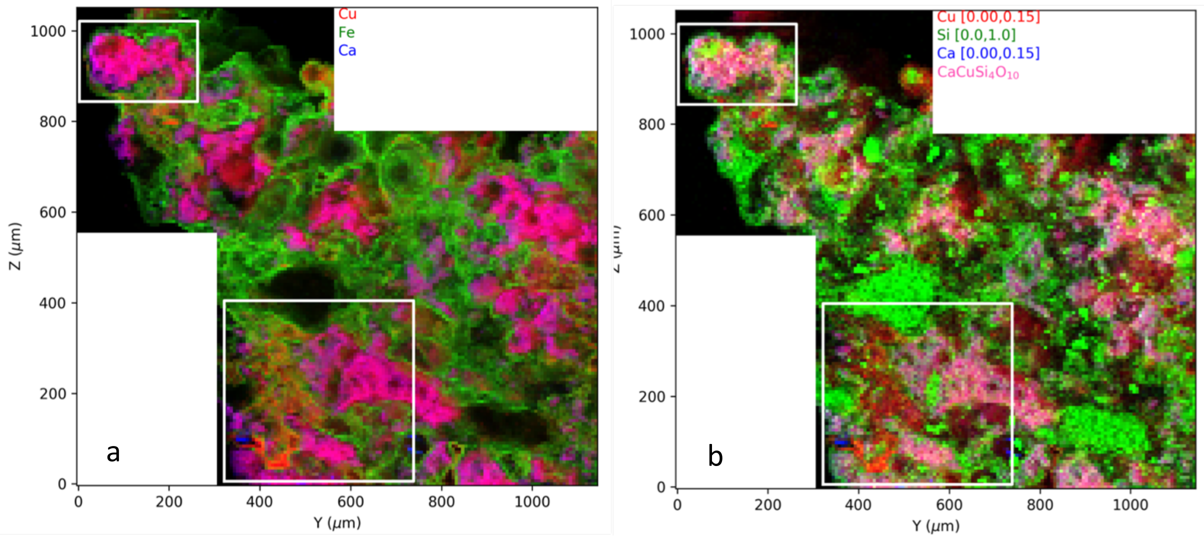

Figure 1 – a. micro-XRF map obtained on one of the samples for Cu, Fe, and Ca, where we can observe the Fe-containing phase (green) surrounding the cuprorivaite crystals (magenta), unreacted Ca- (blue), and Cu-containing phases (red). b. micro-XRF map obtained on the same sample for Cu, Si, and Ca. In green, the unreacted Si-containing grains are visible.

XANES spectra of standard copper compounds (atacamite, dioptase, malachite and tenorite) and commercially available EB were also obtained. The recorded spectra were normalized and Principal Component Analysis (Figure 2) was carried out on a matrix of the intensity of six energy values, chosen to have high variability in the spectra.

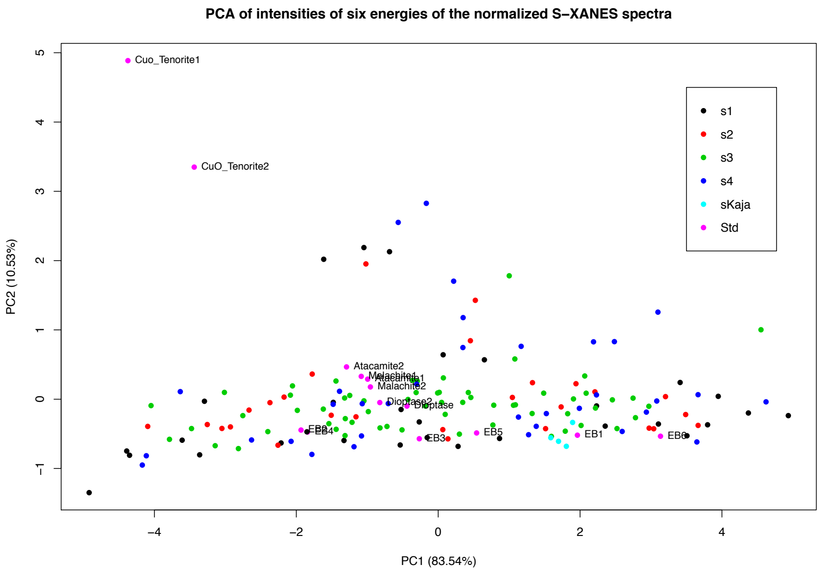

Figure 2 – Score plot of all the samples and the reference materials projected in the first two principal components. In the computing of the PCA, all the data were normalized and scaled.

The results shed light on the local chemical environment of the Cu^{2+} species, providing structural and chemical insight on the nature of this material. The absence of Cu^{+} species in our samples was confirmed.