EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

	Experiment title: Study of the composition of various types of ink on ancient Egyptian papyri – determination of provenance	**Experiment number**: HG84
Beamline: ID21	**Date of experiment**: from: 13/4-2016 to: 15/4-2016	**Date of report**: 07/9-2016
Shifts: 6	**Local contact(s)**: Marine Cotte	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

In the spring of 2016, we were granted 48 hours of beam-time at ID21, ESRF, to study the chemical composition of ancient Egyptian inks and papyri from the Papyrus Carlsberg Collection. During the 48 hours we analyzed a group of 12 carefully selected papyrus fragments using µX-ray fluorescence (XRF) and µX-ray absorption near edge structure spectroscopy (XANES). We made macro and micro XRF-maps of all the fragments at Cu K-edge (9.05 KeV). We primarily focused on the black ink, though we also analysed the red ink present on three fragments at 3(+9) KeV – so as to get a good signal for S, Cl, Fe and Pb. The manuscripts that we analyzed can be subdivided into two groups.

One group comes from southern Egypt and primarily consists of the private papers of an Egyptian mercenary solider, Horus, who was stationed at a small military outpost in southern Egypt, Pathyris, located some 30 kilometers south of modern Luxor. Today this archive consists of 51 larger Greek and Egyptian papyri that date to the late second century BCE. Though thousands of papyri from Pathyris are preserved in papyrus collections around the world, this is the only archive from the military camp that have come down to posterity more or less intact.

The other group derives from the only large scale institutional library to survive from ancient Egypt. This assemblage includes some 300-400 papyrus manuscripts which span the first through the early third century CE with the bulk dating to the late first and second century CE. It was discovered within two small cellars inside the main temple precinct at Tebtunis, modern Umm el-Breigât, which is located in the south of the Fayum depression some 100 kilometers south-west of Cairo. The dry and brittle manuscripts are all poorly preserved and broken into several thousand smaller fragments. Whole columns or pages are only rarely preserved, and the difficult and time consuming process of sorting and identifying fragments of specific manuscripts is still ongoing.

As seen in figure 1, our synchrotron results were surprising, in as much as we encountered a hitherto unknown type of ink in a number of fragments coming from both Pathyris and Tebtunis, namely a copper containing carbon ink. The preliminary analysis of Cu-K edge XANES spectra collected on the inks displayed complex features, characteristic of different species, e.g. cuprite ($Cu_2O[Cu^{1+}]$) and azurite ($Cu_3[CO_3]_2[OH]_2$). Further these inks are the earliest examples in the history of writing of the conscious addition of metal compounds during the manufacture of black ink. From our results it seems that the raw material for some of the "refined" black inks in the ancient Mediterranean were obtained as byproducts of metallurgy, glaze and glass production.

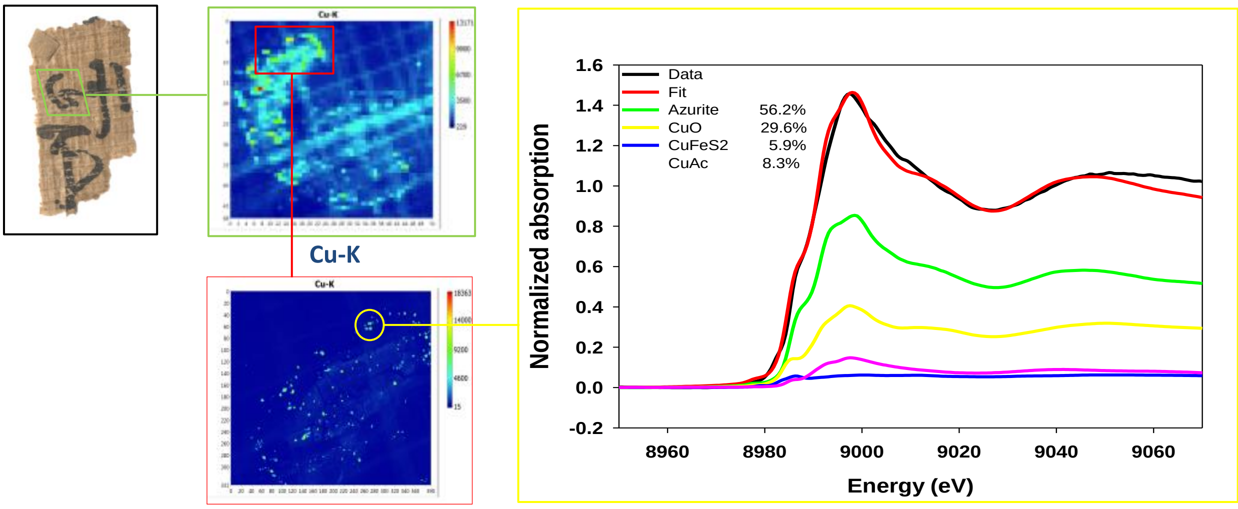

Fig. 1: Greek papyrus fragment from Pathyris dating to the 16th of October 101 BCE. The green and red inserts demarcate areas of the macro and micro XRF maps, which show the distribution of Cu in the sample. The yellow circle indicates the area from where the XANES spectra, seen to the right, were obtained.

In the papyrus fragments, where Cu was detected in the inks, it is present also in very low amounts along the fibrous structure. XANES measurements suggests that the Cu appearing along the fibers consists primarily of malachite ($Cu_3CO_3[OH]_2$). From the XRF maps, as seen in figure 1, it is clear that the Cu compounds are concentrated in the letters from where they seem diffuse out in the papyri. A possible explanation for this phenomena is the conservation history of the fragments. There is no detailed documentation on the method of conservation applied to the papyri, but it usually consists of a simple process, where the papyri are moistened with water in order to unfold them. Therefore it seems that copper containing carbon inks unlike both carbon ink and iron-gall ink are unstable and that particular Cu compounds are susceptible to migrate, if water is applied during conservation. This demonstrates the need for scientific analysis of ancient manuscripts, if better methods of papyrus conservation are to be developed.

The composition of the red inks is unattested in the history of writing. The XRF maps are characterized by the following elements in decreasing amounts of relative abundance: Si, Fe, P, Pb, S, Ca, Al and Cu. P and Pb are strongly co-localized and distributed along the edges of the letter. Micro-metric maps of relevant areas confirmed the correlation between the two elements and revealed further that they formed a cell-like structure. This perhaps indicates the use of an unknown dryer or binding agent in the ink. S seemed correlated with Ca, so likely gypsum ($CaSO_4$•$2H_2O$) was added as a white toner. The source of the red pigment is probably haematite (Fe_2O_3), goethite ($FeO[OH]$) or minium (Pb_3O_4); to which compounds Si and Al could be related? None of the analyzed black and red inks are completely identical, which could indicate that individual scribes concocted their own inks. However, it should be kept in mind that the papyri in question were written over a period of 300 years and that the composition and fabrication of inks are likely to have evolved over this span of years.

The results obtained so far using the synchrotron radiation from ID21in the study of the black ink on papyri provide exiting new perspectives on a decisive chapter in the history of science: the invention and evolution of ink. Further, the chemical and structural signatures obtained through the X-ray analysis reflect the physical properties of the manuscripts and thereby address one of the central challenges facing the historian: the fact that the majority of ancient manuscripts lack a recorded archaeological context. It is our expectation that these "finger-prints", we have found, in the future will contribute to the mapping of characteristic traits of ink and papyrus, which is of importance for their chronological and geographical origin.