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Micro-PIXE analysis of an ancient Egyptian papyrus: Identification of pigments used for the "Book of the Dead"

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Abstract

This paper reports a study of colours and inks of an ancient Egyptian papyrus using an external proton microprobe in PIXE mode. Representing the Book of the Dead, this papyrus is dated from the 19th dynasty, New Kingdom (c.1295–1186 BC). Elemental maps were obtained by moving the papyrus under a fixed focused external beam using a motorised support. The maps were compared to photographic pictures taken in visible light. Inks used in the hieroglyph text appeared to be based on carbon (black) and iron oxide (red). Coloured drawings illustrating the text showed a wider palette: hematite, ochre, orpiment, Egyptian blue, verdigris. Most intriguing was the observation in several parts of the drawing of a whitish pigment containing strontium. Deposits of strontium-rich minerals (e.g. strontianite, celestite) have been identified in Egypt. The exact nature and the archaeological implications of this pigment have still to be determined. Finally, fine powder and coarse grains of arsenic oxide were observed, probably remaining from an early preservation treatment against insect attacks after excavation. © 2001 Published by Elsevier Science B.V.

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1. Introduction

Analytical techniques based on high energy ion beams have been used in several studies of ancient documents and manuscripts. In particular particle-induced X-ray emission (PIXE) implemented with an external microprobe has shown great ability to infer the elemental composition of ink as well as paper, papyrus and parchment [1,2]. In combination with imaging techniques, PIXE allowed to reconstruct worn away characters [3].

In this study, an ancient Egyptian papyrus identified as originating from the Book of the Dead was analysed. The objectives were threefold:
1. study the elemental composition of the inks and paints in the document;
2. search for any anachronistic pigments that would reveal a forgery;

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3. identify undocumented preservation or restoration treatment.

2. The papyrus

The Papyrus Lund KM 21933 has been dated and identified from the text content by Egyptologists. This is the first time it has been studied using analytical techniques. It consists of written parts with a vignette segment which forms the right end of a Theban 19th Dynasty Book of the Dead, chapter 186 (c.1295–1186 BC). In Egyptology the label "Book of the Dead" is given to a number of religious funerary texts and spells for protection and guidance of the deceased entering the afterlife. The original owner of this papyrus was named Ash-au-hat "the pilot", a high-ranking man, possibly an official in charge for all the food supplies in Egypt. The papyrus is probably a so-called tomb robbery papyrus, dug out and brought to Europe approximately in the 1820s. Though only the lower half of the papyrus is preserved, the vignette can be seen as illustrating a deceased male at the western mountain meeting the hippopotamus childbirth goddess *Ipet*. The accompanying text located on the left was written in cursive hieroglyphs using two different inks, black and red. A red margin line, framing the text and the vignette, appears on the entire recto of the papyrus. The verso is left blank.

3. Experimental

The analysis was performed using the external micro-beam line of the AGLAE (Accélérateur Grand Louvre pour l'Analyse Elémentaire) 2 MV tandem electrostatic accelerator located in the Louvre palace in Paris. A 3-MeV proton beam was collimated and focused using three Oxford-style quadrupole lenses [4] and brought into air through a 0.1-μm thick silicon nitride foil. When passing through this extremely thin foil and the 2-mm helium path to reach the target, the beam energy loss and straggling are only about 8.5 and 4.5 keV, respectively [5]. Under these conditions, the beam can be focused on the target with a spot size estimated to be 50 μm.

The papyrus was mounted on a robust sample holder, with accurately motorised motion of $X/Y/Z$ axes. The beam was kept fixed while the papyrus was raster-scanned using stepping motors, enabling elemental mapping of large rectangular areas. For this study, images of 200×200 pixels of 40×40 mm^2 were acquired in a single pass, using a scanning speed of 3 mm/s. X-rays were detected using two Si(Li) detectors, mounted at 45° relative the beam direction [6]. The first detector is dedicated to the detection of light elements (Na–Ca). The active area is 10 mm^2, and the ultra-thin window (0.25 μm boron nitride) permits the detection of the low-energy X-rays down to the oxygen line (0.52 keV). Helium gas flows along the 60 mm path between the target and the crystal which is equipped with a magnetic deflector avoiding backscattered protons to reach it. A second Si(Li) detector simultaneously collects the X-rays emitted by heavier elements (Ca–Sr). The solid angle is larger (50 mm^2, 20 mm distance from the target) and a 50-μm Al foil was used to filter the intense signal from light elements (mostly Si) and to stop backscattered particles of the beam. The proton dose was monitored by measuring the X-ray emitted by Si atoms of the external beam foil with a compact Peltier-cooled silicon-drifted detector. Data were acquired using the Mpawin multiparametric system (Fastcomtec Gmbh). X-ray spectra were processed using the GUPIX software package [7]. The beam intensity was 0.6 nA, yielding a count-rate varying between 1 and 4 K counts/s. The average irradiation time was about 2 min for a spot analysis and 45 min for an elemental map. The non-destructivity of the experiment was carefully checked by imposing a ten-fold beam dose (by varying either the intensity or the time) on a minor part of the papyrus without noticing any damage.

The papyrus was analysed in 40 spots for quantitative results. These spots were selected on the cardboard backing, bare papyrus, hieroglyph inks, drawing lines, and various colours of the drawing: black, red, yellow, blue, white.

4. Results and discussion

Table 1 gives the chemical analysis for the spots the location of which are indicated in Fig. 2. The papyrus and the pigment layers were assumed to be thin targets, and this is confirmed by the areal density values obtained (<100 μg/cm^2). For quantitative analysis, the sensitivity of the set-up was calibrated using thin reference targets (50 μg/cm^2) from Micromatter. The papyrus itself contains considerable amounts of Ca and Si (spot b). While Si is coming from the papyrus plant itself, Ca is more likely a constituent of a preparation layer for the drawing. These results are in agreement with previous studies of ancient papyri [8].

4.1. Inks used for hieroglyphs

The PIXE spectrum from the black ink (see spot c) shows no noticeable element. This ink is probably carbon-based (soot). This diagnostic is confirmed by the observation of the 0.523 keV oxygen line emitted by the cellulose of the papyrus, the intensity of which is attenuated by a factor 4 when overlaid by the carbon layer from the ink. The red ink (spot a) has a simple fingerprint: it contains a high amount of iron. The very saturated red hue discards the yellowish pigment goethite (FeOOH) and the low silicon content disagree with an ochre pigment. Thus this ink is likely to be hematite (α-Fe_2O_3).

4.2. Pigments used for the vignette

Red lines (spot e): Having a high Fe content, the red drawing lines are likely made of hematite-based pigment (α-Fe_2O_3). Other elements are attributed to the underlying preparation layer.

Orange red (*spots g, i, k*): Several areas exhibit a yellow to brown colour. Quantitative analysis shows large amounts of Fe combined with Si, Al and Ca. This result is consistent with a yellow ochre pigment which is a mixing of various iron oxides (goethite α-$FeO \cdot OH$, limonite $FeO \cdot nH_2O, \ldots$) with clay and silica. The composition varies according to the different shades.

Yellow (*arsenic map of Ipet*): Maps collected on the legs of the goddess Ipet (Fig. 3) clearly show that As is present in the yellow colour used to paint the feet, indicating the use of orpiment (As_2S_3).

Blue (*spot j*): There is evidence of the well-known Egyptian blue pigment. Indeed, the PIXE spectrum of this spot reveals the major constituents of this artificial pigment ($CaO \cdot CuO \cdot 4SiO_2$).

Green (*spot l*): The copper map shows a spot located on the border of a large hole in the papyrus. Point analysis of this spot l shows that Cu and As are major constituents. Presence of Cu is attributed to the verdigris pigment $(CH_3COO)_2 \cdot Cu(OH)_2$, while As is linked to a preservation treatment (see below). It therefore seems that the papyrus has been damaged by the very corroding pigment which has almost disappeared. This is commonly observed for ancient papyri, where most of the green-painted area have been destroyed by this very acidic pigment.

White (*spots d, h, m*): Elemental maps as well as quantitative point analysis indicate that the white pigment contains magnesium and strontium. Indeed, Mg and Sr maps closely follow the white drawing of the kilt of the character (Fig. 2). A more detailed analysis of this white layer was performed in view to separate the signal from the white layer and from the papyrus substrate. The spectrum of the white layer (Fig. 3) was obtained by subtracting the spectrum of an unpainted zone from the spectrum of a whitish zone (square areas in Fig. 1). The processing of the resulting PIXE spectrum led to a pigment containing mostly Mg, Sr and to a lesser extent S and Ca (last line in Table 1). A small Ca and S content was observed; it was masked in the elemental maps by the papyrus signal. At first sight, the Si map would wrongly lead to the conclusion that silicon is involved in the pigment. Actually, the signal on which is based the Si map is coming from both the strontium Lα-lines (1.806 keV) and the silicon K-line (1.740 keV). Similarly, the presence of As affects the Mg results because of the overlap of Mg K-lines (1.254 keV) and As Lα-line (1.282 keV). This can be observed in Table 1, where the spots f, i and m show an apparently high Mg content which in fact is related to the high As content. Nevertheless, the Mg map shows a clear correlation with the white pigment.

The strontium clue: The presence of strontium in Egyptian white pigments has already been

Table 1
Element content in μg/cm^2 at various locations

Spot	Colour	Material	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Cu	As	Sr
			Detector #1									Detector #2			
a	Red	Ink	1.0	0.2	2.6	8.7	0.4	2.1	1.6	1.2	9.0	**20.0**	0.4	2.7	0.3
b	Backg	Papyrus	0.0	0.1	0.1	5.2	0.0	1.4	0.8	0.7	4.3	0.4	0.4	1.1	0.1
c	Black	Ink	0.0	0.7	0.1	4.7	0.0	1.3	0.8	0.7	6.8	0.9	0.5	1.3	0.1
d	White	Col	0.8	3.1	0.3	9.8	0.5	5.7	5.9	1.8	23.0	2.3	1.9	2.8	4.3
e	Red	Line	1.5	1.0	2.0	8.6	1.7	14.5	6.6	2.3	22.0	**17.0**	1.2	6.3	0.8
f	White	Grain	0.7	*42.4*	1.6	7.9	5.5	4.9	0.0	0.6	4.7	0.7	0.2	**188.0**	0.0
g	Pink	Col	3.6	*12.1*	6.3	51.0	0.9	15.5	6.4	5.1	21.0	17.0	2.7	10.0	4.3
h	White	Col	3.7	2.8	2.1	26.0	0.9	21.5	9.3	5.6	29.0	19.0	3.0	29.0	**25.0**
i	Red	Col	2.0	*16.0*	8.5	95.0	1.0	6.6	3.6	4.6	26.0	**26.0**	12.0	63.0	1.4
j	Blue	Col	2.4	0.0	5.9	**172.0**	1.5	6.8	5.5	4.4	**160.0**	6.6	**173.7**	4.6	0.2
k	Red	Col	6.0	1.9	5.0	62.0	1.2	18.0	13.4	7.4	37.0	**50.0**	2.9	23.0	3.0
l	Green	Col	1.6	*2.8*	3.6	49.4	1.1	8.7	2.4	3.8	21.5	7.6	**22.3**	29.3	1.1
m	White	Col	6.0	*22.0*	1.6	27.0	3.2	12.5	5.4	5.5	35.0	9.3	8.6	116.0	**24.0**
LOD			0.05	0.08	0.05	0.10	0.10	0.08	0.10	0.10	0.20	0.05	0.02	0.03	0.05
Area	White	Col	0.00	**0.46**	0.04	0.14	0.12	0.30	0.12	0.09	0.19	0.68	0.00	0.04	**0.75**

K-lines were used for all elements. LOD are the limits of detection given by the GUPIX program. In the last line, elemental content are given in arbitrary units. For this specific case, the determination of Sr and As relies on L-lines.

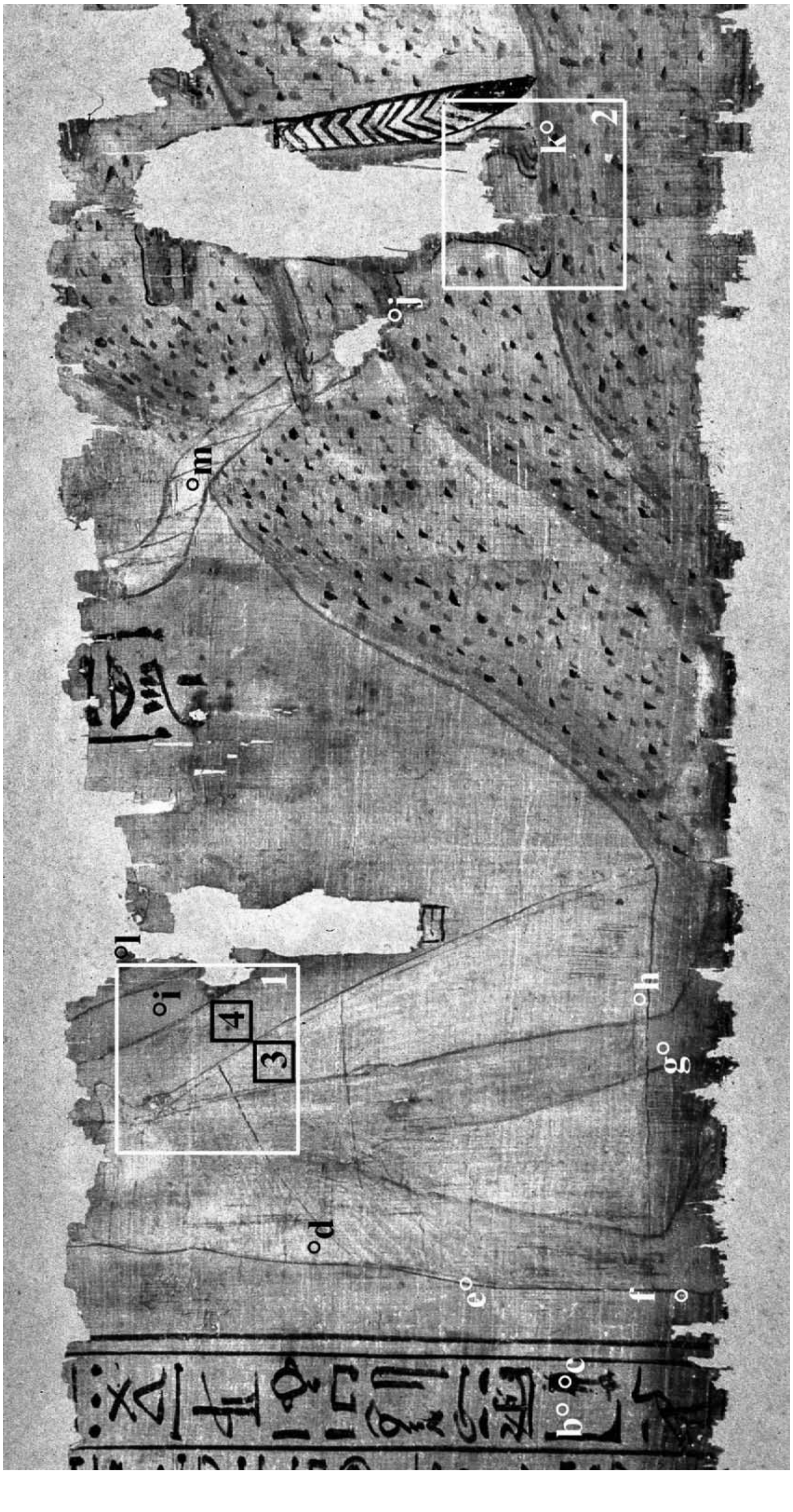
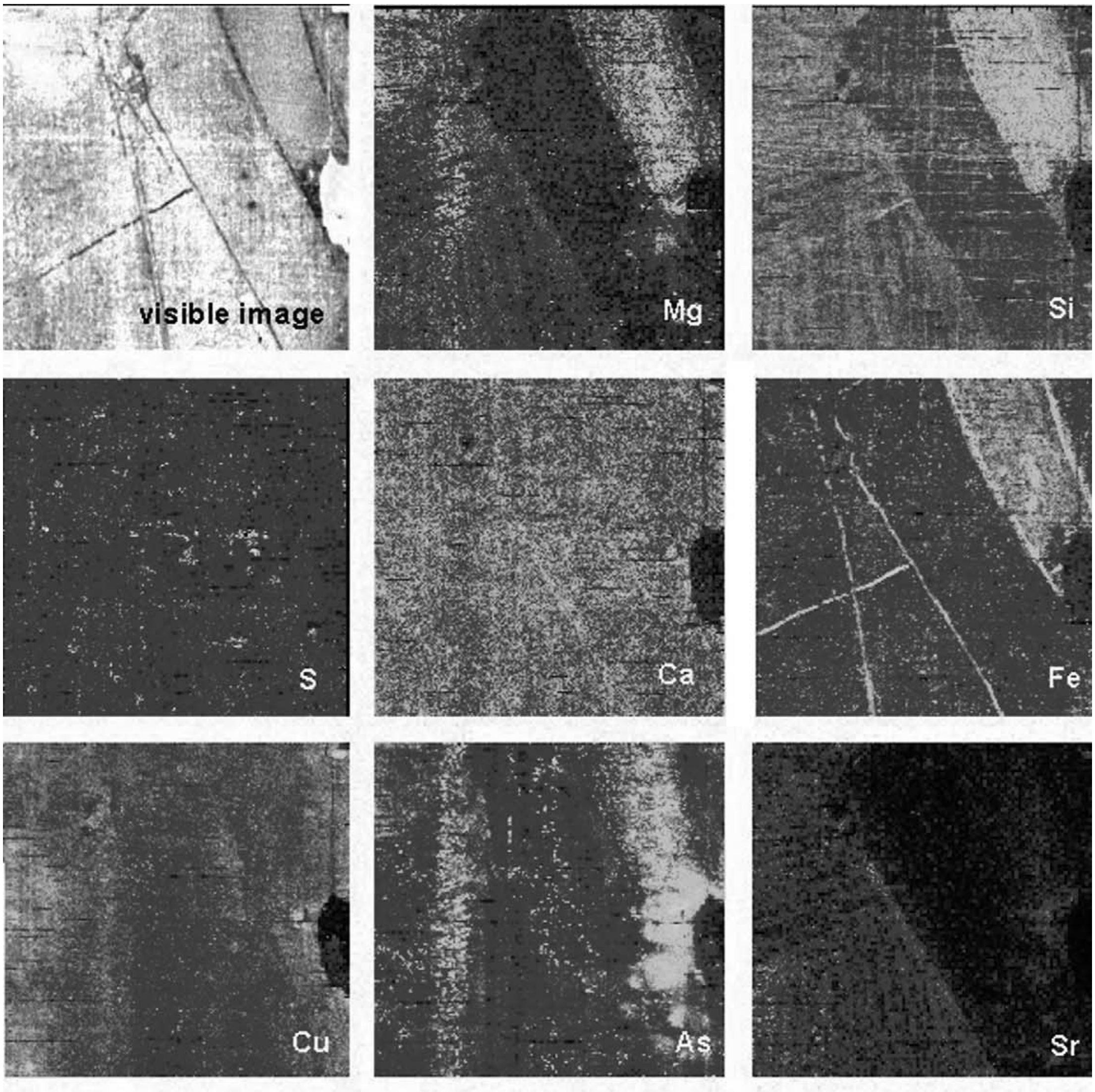


Fig. 1. Location of the analysed spots of the papyrus (labelled from b to m). The square zones 1 and 2 indicate the scanned areas used for elemental maps of Fig 2. The zones 3 and 4 were used to determinate the composition of the white pigment. Zone 3 contains the white pigment, while zone 4 contains the preparation layer only. Note that point "a" is not there in this picture, being located on another part of the papyrus.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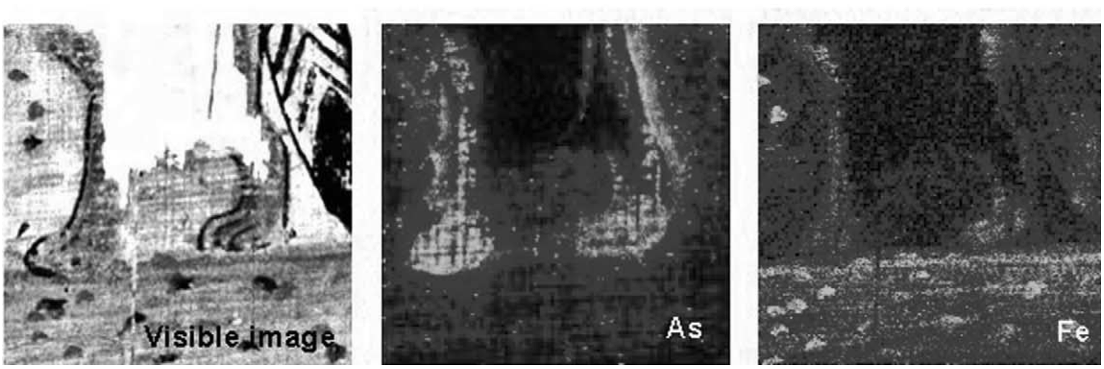
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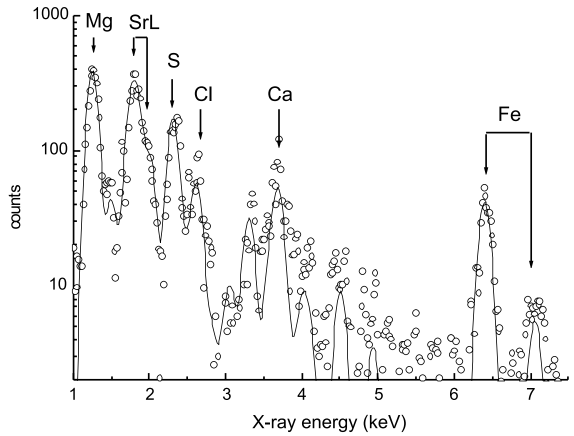

Fig. 3. Spectrum obtained by subtracting PIXE spectra from a whitish zone and a from an unpainted zone (papyrus only). The solid line indicates the fit using Gupix. The strong magnesium and strontium lines indicate that these elements are major components of the white pigment. Sr- and Mg-bearing minerals; celestite and huntite are possible candidates.

reported [9]. The measured trace level of Sr was attributed to natural substitution with Ca. The quantitative results obtained in spots m and h show that Sr is a major component of the pigment, at a level well above Ca. What is the mineral involved in the white pigment? The most widespread strontium ores are celestite ($SrSO_4$) and strontianite ($SrCO_3$). Such Sr-rich mineral deposits occur in Egypt, and evidence of ancient quarries exists such as in the *Wadi Mokattam* area [10,11]. What are the distinctive features of these minerals? Both have low hardness, facilitating the use as a pigment. While strontianite crystals are colourless, celestite crystals often exhibit an attractive sky-blue colour. Moreover, the measured S/Sr ratio of about 0.40 is in good agreement with the theoretical value of 0.37 for celestite (Table 1).

The presence of magnesium could possibly be related to dolomite $CaMg(CO_3)_2$ or huntite $(CaCO_3) \cdot 3(MgCO_3)$ minerals. The use of the uncommon huntite as a white pigment in artifacts from the New Kingdom is well established [12]. The measured Ca/Mg ratio is about 0.43; it fits with the theoretical value of 0.54 for huntite.

Grains of arsenic (*spot f*): We also observed grains of arsenic oxide As_2O_3. For instance, in spot f, we analysed a grain exhibiting almost only As-lines. Microscope observations revealed white grains, corroding the papyrus and forming small craters. It has been suggested that this As could have come from the degradation of the yellow pigment orpiment [13]. We do not think that it is the case here. Indeed, the map collected on the kilt of the character (Fig. 3) shows no correlation between As and the yellow colour nor with any part of the drawing. Arsenic is rather concentrated on damaged parts of the papyrus, as if it was applied to stop the deterioration of the document. Arsenic oxide is very poisonous; at the time of discovery of the papyrus, it was used as insecticide against phytophagous insects in natural history museums for the preservation of collections. We would then suggest that the arsenic grains scattered on various portions of the papyrus corresponds to such an early preservation treatment.

5. Conclusion

The palette for the vignette is in many parts characteristic of a religious funerary text from this period: iron oxide (hematite) and ochre for colours from pink to red and dark brown, orpiment for yellow, Egyptian blue for intense blue and verdigris for the green pigment. This last pigment is

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Fig. 2. Elemental maps. The Fe map follows the red drawing lines of the kilt and the colour of the skin of the arm. It indicates ochre or hematite. The Ca signal is almost uniform; it mostly arises from the papyrus itself. Mg and Sr are located in the white pigment used for painting the kilt of the character. A spot of Cu can be seen on the border of a big void in the papyrus, indicating that the papyrus has been damaged by the very corroding verdigris $(CH_3COO)_2 \cdot Cu(OH)_2$ pigment which has almost disappeared. Arsenic is concentrated around damaged parts and is not correlated with the drawing. The sulphur map has no correlation with arsenic nor with the drawing. Therefore, the presence of the pigment orpiment (As_2S_3) or a degraded form of it is unlikely. It is probably the remains of a preservation treatment for killing phytophagous insects. Two vertical bands observed in the As map are attributed to this treatment, as the papyrus was stored in rolled form.

missing in great part because of its highly acidic and corroding properties: for instance, the main inner part of the hippopotamus goddess has disappeared. There is also evidence of a ancient damaging treatment of the papyrus using arsenic oxide. The vignette has probably been painted in various blue, green and yellow colours – and thus had a sparkling and striking appearance. The appearance of the white parts of the characters' kilt and the sword-like item which the hippopotamus holds, must have been intended to be of an almost silvery, metallic shining white colour. We found that strontium and magnesium are the major components of this white pigment. Celestite and huntite are possible mineral sources for these elements. Further investigations are needed to determine the mineral species involved in the white pigment. Structural analysis methods such as Raman spectroscopy [14] and X-Ray diffraction [15,16] are well-established identification tools for this task. These techniques will be applied in a second phase of this study.

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