



Synchrotron X-ray micro-beam studies of ancient Egyptian make-up

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Abstract

Vases full of make-up are most often present in the burial furniture of Egyptian tombs dated from the pharaonic period. The powdered cosmetics made of isolated grains are analysed to identify their trace element signature. From this signature we identify the provenance of the mineral ingredients in the make-up and we observe different impurities in products, which have been demonstrated as synthetic substances by previous works. Focused X-ray micro-beam ($2 \times 5 \mu\text{m}^2$) is successively tuned at 11 keV, below the L_{III} absorption edge of Pb, and 31.8 keV for global characterisation of the metal impurities. The fluorescence signal integrated over each single grain is detected against the X-ray micro-diffraction pattern collected in transmission with a bi-dimensional detector. Furthermore, for galena grains rich in Zn, the XANES signal at the K-absorption edge of Zn shows its immediate nearest-neighbour environment. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The extensive use of green, white and black make-up has been known since the earliest periods of Egyptian history for their aesthetic and therapeutic purposes [1,2]. In previous works [2,3], we have studied the inorganic and organic contents of

the cosmetics dated between 2000 and 1200 BC, kept in their original containers and preserved in the Louvre Museum. Two well-known natural lead-based compounds were identified: the crushed ore of black galena (PbS) and the white cerussite (PbCO₃). In addition, our analyses have revealed two unexpected white synthetic products: laurionite (PbOHCl) and phosgenite (Pb₂Cl₂CO₃).

Archaeological data and ancient texts [4] provide information about the origin and trade of the lead ores. Different mines, located at the Red Sea coasts, have been exploited during the pharaonic

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period. Moreover, some trade of galena took place between Egypt and “The Punt country” (Yemen, Somalia or Ethiopia), as shown in various representations of different expeditions organised in foreign countries [4]. From the identity and respective abundance of the trace elements present (Fe, Ni, Cu, Zn, Ag, Sb), it is possible to classify the samples according to their extraction provenance.

For synthetic compounds, the trace elements have to be linked to the minerals used during the preparation process (natron, sea or rock salt, etc.). Indeed, *De Materia Medica* of Dioscoride and *The natural history* of Pliny the Elder [5] provide a detailed description of laurionite and phosgenite as prepared from the silver foam (litharge PbO), two thousand years ago: the lead oxide was crushed, washed and mixed with rock salt and sometimes with carbonated salts of natron (mainly Na₂CO₃). These recipes are complex and require a long preparation time that may affect in turn the trace element composition.

Proton-induced X-ray emission (PIXE) tests have been carried out at the Laboratoire de Recherche des Musées de France using the AGLAE tandem accelerator. A focused proton beam is extracted in air (about 10 μm diameter) to analyse single grains of galena. The high background in the spectra due to the strong Pb L and Pb M fluorescence emission greatly reduces the detection sensitivity for transition metals. Good results can be obtained by micro-PIXE though, but only in the case of inclusions inside the bulk of galena (ZnS crystals in this work or silver-containing inclusions in other galena ores [6]). Consequently, we have used the synchrotron X-ray micro-fluorescence technique, in order to analyse metal impurities with a monochromatic beam below the Pb L edge.

2. Experimental

The micro-fluorescence, imaging and diffraction (FID) beamline ID22 at the ESRF (Grenoble, France) using hard X-rays is dedicated to the determination of the elemental concentration (including trace element analysis), to absorption spectroscopy, imaging, tomography, holography

and to diffraction studies of samples with a micrometer spatial resolution.

We have used two experimental set-ups with different X-ray focusing conditions, respectively, tuning the energy at 11 keV, below the L_{III} absorption edge of Pb, and at 31.8 keV, above the K absorption edge of Ag and Sb:

- For the low-energy set-up, Fresnel zone plates are used with high demagnification factors (about 50). At the sample location, the beam was focused on a $2 \times 5 \mu\text{m}^2$ spot with about 1.5×10^{10} photon/s. Measurement can be carried out with very high-sensitivity for K edges from S up to Zn. Using a Si[1 1 1] monochromator, the third order of diffraction induces the L-fluorescence of lead. This signal can be used to monitor the flux on the sample.
- In the high-energy set-up, the energy is limited by the mirror (coated strips of Pt on Si substrate) cut-off at 32 keV. Compound refractive lenses (CRL) are used to focus the beam and a pinhole limits the spot size to $2 \times 5 \mu\text{m}^2$ with about 1.5×10^9 photon/s.

A video microscope helps to localise the grains and to visualise their colour and shape, characteristic of some minerals: the crystals of galena are coarse, grey and cubic, whereas the lead chlorides consist of small, white ovoid grains. X-ray micro-diffraction patterns are collected with a high-resolution CCD camera (1152 × 1242 pixels, dynamic range 16 bits, Princeton Instruments, set up at 10 cm from the sample) and allow the phases to be identified (Fig. 1). Galena cubes present highly textured diffraction patterns, because they tend to be packed up on the top of one another face to face along the $\langle 100 \rangle$ direction. Then, X-ray micro-fluorescence measurements are carried out at both energies with a 12 mm² Si(Li) solid-state detector (Eurysis Mesures). Acquisition times were 600 and 300 s, respectively, for the low- and high-energy measurements.

Scanning the energy from 9.6 to 9.8 keV, the X-ray absorption of Zn²⁺ is determined from the fluorescence signal and the immediate nearest-neighbour environment of Zn²⁺ in galena is given by the XANES post-edge oscillations. A current integration detector (silicon PIN diodes) monitors the incident beam flux.

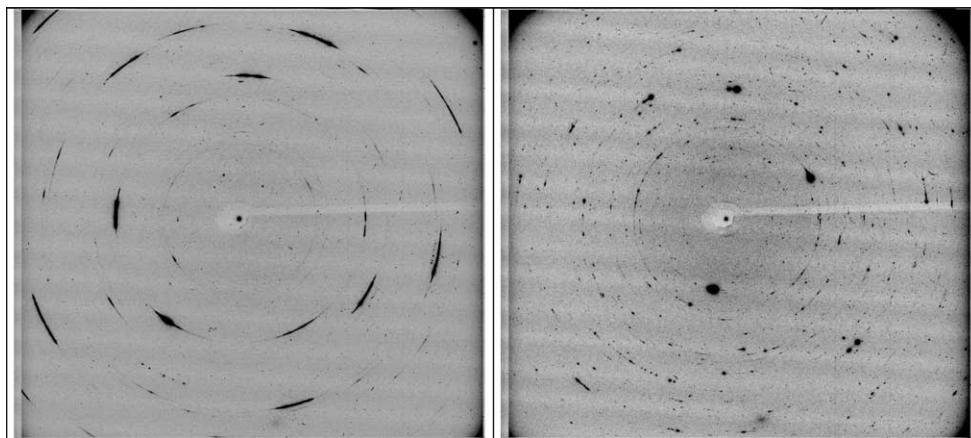


Fig. 1. X-ray diffraction patterns of galena (left) and phosgenite (right) grains. $\lambda = 1.127 \text{ \AA}$, sample/CCD camera distance = 10 cm, beam size = $2 \times 5 \mu\text{m}^2$.

The powdered cosmetic samples made of isolated grains are spread on $8 \mu\text{m}$ thick Kapton foils. A small droplet of acetone attacks the surface of the polymer and allows maintaining the grains on the foil. Five Egyptian cosmetics are analysed: galena is the main component in four of them (AF167, E11048b, E20514, E23106). Only sample MG14400b is rich in phosgenite (Table 1). Previous analyses of their respective lead isotopic compositions showed that the lead ore was mainly extracted from the Red Sea mines [7,8]. Nevertheless, sample E23106 presents a particular signature, characteristic of a different geochemical history.

3. Results and discussion

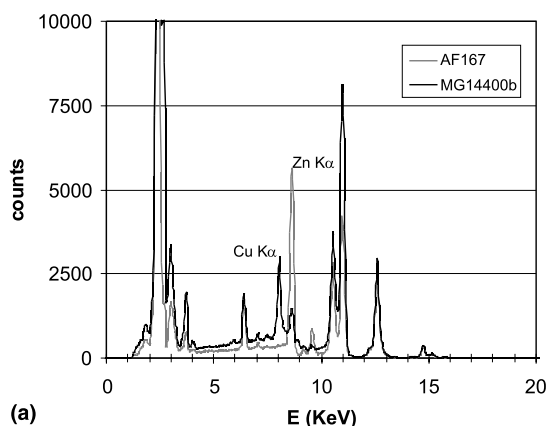
All the three samples (AF167, E20514, E11048b) show a relatively high content of zinc

and the presence of iron traces. Exploitation of Pb–Zn ores is well known in Antiquity and several of these ancient mines are located in Egypt along the Red Sea coasts. However, we have observed a high-proportion of antimony in galena grains of sample E23106 (Fig. 2(b)). Sb in a lead ore cannot originate from an Egyptian mine. The anomalous occurrence of Sb in galena shows that either the ore was imported in Egypt to prepare this make-up or this make-up was marketed across the borders. These preliminary results are in agreement with the lead isotopic compositions: the crushed ore contained in the make-up powder E23016 has been extracted from a foreign source.

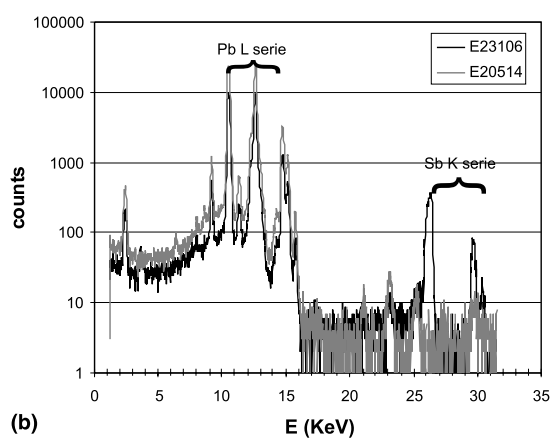
Moreover, we have noted that synthesised phosgenite exhibits impurity patterns different than those of natural Pb ores (Fig. 2(a)). The observed trace elements in synthetic grains are Cu and Fe. They have to correspond to impurities

Table 1
Quantitative analysis in % (Rietveld method) from X-ray diffraction diagram of about 10 mg of powder

Sample	Galena	Cerussite	Phosgenite	Laurionite	Anglesite	Sphalerite	Smithsonite	Cotunnite	Gypsum	Quartz	Palmierite
AF167	82				13.3	4.7					
E11048b	46.7	11.5	33.4								8.4
E20514	72	3	8.9	1	4.1	9.5	1.5				
E23106	52.1	12.6	18.5	3.8	10.1				2.2	0.7	
MG14400b	3.6		88					2.2	3.7	2.5	



(a)



(b)

Fig. 2. (a) μ -XRF analysis. Impurities in galena (AF167) and phosgenite grains (MG14400b) – acquisition at 11 keV, 10 min, beam size = $2 \times 5 \mu\text{m}^2$. (b) μ -XRF analysis. Impurities in both galena ores – acquisition at 31.8 keV, 5 min, beam size = $2 \times 5 \mu\text{m}^2$.

present in the minerals used during the preparation process (natron, sea or rock salt). Analyses of different kinds of natron showed that the proportion of iron oxides could reach 0.3% [1]. A more precise study of these data will allow us to find the origin of the raw products involved in the chemical synthesis.

Furthermore, for galena grains rich in Zn, the XANES signal at the K absorption edge of Zn can show the immediate nearest-neighbour environment. This is important if one needs to distinguish between Zn in ZnS nanocrystalline inclusions embedded in PbS, and Zn^{2+} substituted in the PbS

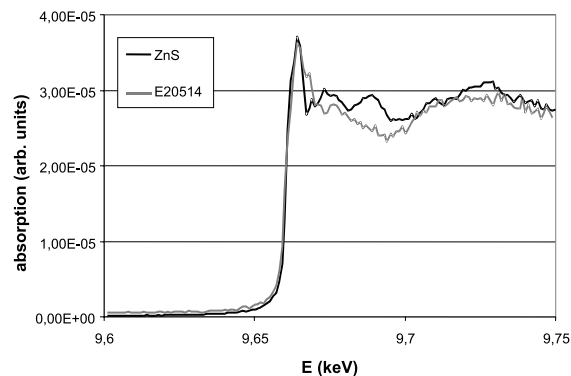


Fig. 3. XANES signal at the K absorption edge of Zn in a reference powder ZnS (Prolabo) and in Egyptian galena (sample E20514).

lattice. The difference in the Zn site can also be relevant for the description of the mineral source. For sample E20514, the absorption signal of Zn atom was compared to that produced by a reference powder of ZnS (Prolabo). Fig. 3 shows that the two environments are different: Zn^{2+} is therefore probably substituted to Pb^{2+} in PbS in the case of sample E20514.

4. Conclusion

The combination of μ -XRF, μ -XRD and μ -XANES synchrotron techniques enables one to identify the trace elements and to approximately evaluate their quantities, in order to classify the samples according to their origin. The comparison of the respective impurity contents in Egyptian cosmetics has shown two origins for the galena ores. The impurity pattern of the synthetic lead chloride compounds is different from that of galena: it is related to the preparation process using various salts in solution.

This study illustrates the capability of synchrotron micro-beam techniques to study non-destructively samples of high archaeological value. Moreover, the high X-ray flux makes it possible to detect low-levels of impurities. Enough data can be collected over many grains of different powders, which are statistically and archaeologically repre-

sentative for the understanding of complex manufactured materials.

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