

Application of the external PIXE analysis to ancient Egyptian objects

S. Nagashima^{a,*}, M. Kato^a, T. Kotani^a, K. Morito^a, M. Miyazawa^a, J. Kondo^b,
S. Yoshimura^b, Y. Sasa^c, M. Uda^{a,c}

^a*Dept. of Materials Sci. & Eng. Waseda Univ., Shinjuku, Tokyo 169, Japan*

^b*Egyptian Culture Center Waseda Univ., Shinjuku, Tokyo 169, Japan*

^c*Lab. for Materials Sci. & Tech. Waseda Univ., Shinjuku, Tokyo 169, Japan*

Abstract

Mural paintings with $\sim 20 \times 25 \text{ cm}^2$ in size excavated in Egypt were analyzed by the external PIXE technique. Colored layers were stacked with white, yellow, red and black pigments in sequence, which were composed of $\text{Mg}_3\text{Ca}(\text{CO}_3)_4$ (white), $\alpha\text{FeO} \cdot \text{OH}$ and As_2S_3 (yellow), $\alpha\text{Fe}_2\text{O}_3$ (red) and soot (black), respectively. A single particle of As_2S_3 was also found from the yellow colored part, which glistened in the sun. A thin paraffin layer did not disturb the PIXE analysis, which was a part of reinforcement materials for ancient remains and was flowed out from a back side to a surface region.

1. Introduction

Analyses of archeological objects bring us much information on the development and propagation of the cultures and the technologies of the human race. For conservation and restoration of these valuable and scarce materials, it is indispensable to understand the constituents and structures of these remains. Many kinds of physical and chemical methods have been used for a better appreciation of the ancient materials. Among these, PIXE is one of the most powerful and effective methods from the following reasons: high and almost equal sensitivities to all of elements measured, simultaneous analysis of the elements present, short data acquisition time, easy handling of specimens without tedious pretreatment, limited amounts of samples, almost the same analytical reliability to trace and main components and so on [1–6]. In addition, the external PIXE method is excellent in nondestructive and size free aspects, and is insensitive, especially for delicate materials, to temperature and/or pressure. These characters of the external PIXE technique have successfully been utilized in the elemental analysis of the archaeological materials [7–16].

In this study, excellencies of the external PIXE method have been confirmed by focusing on the stacking order and thickness of multi-colored layers on Egyptian mural paintings. Paraffin and several kinds of plastics applied to the back side of ancient materials are widely used nowadays in this field for protecting these fragile ancient materials from fracture. However, surfaces of the ancient remains are

sometimes covered with a thin layer of paraffin or plastics flowing out of the back side. In this experiment the possibility is discussed as to whether or not the chemical compositions of the objects of interest can be analyzed by external PIXE even through the paraffin layer.

2. Experimental

Two large fragments of mural paintings were submitted to the external PIXE analysis, which were excavated from a site at the Malkata South located on the West Bank of Luxor in Egypt by the Waseda University Egypt Archaeological Mission in the period of 1974–1979. They were found at the ‘‘Kom el-Samak’’ (Hill of Fishes) constructed by Amenhotep III in the 18th Dynasty. The paintings have been preserved in the Egyptian Culture Center at Waseda University. The first mural painting has a size of $\sim 20 \times 25 \text{ cm}^2$ and its whole surface was painted with a regular pattern of a lotus bloom which was color-decorated with five kinds of pigments; white, two types of yellow, red and black as schematically shown in Fig. 1. The second mural painting is schematically shown in Fig. 2, having a size of $\sim 20 \times 15 \text{ cm}^2$. Almost one half of the surface was painted with a geometrical pattern using three kinds of pigments; white, red and blue, and another half was decorated with two types of yellow pigments. A back side and periphery of the mural painting were reinforced 20 years ago with paraffin to prevent fracture caused by mechanical shocks. However, a part of the surface was also covered with a thin paraffin layer flowing out of the back side. Then two yellow colored areas in Fig. 2 were

* Corresponding author.

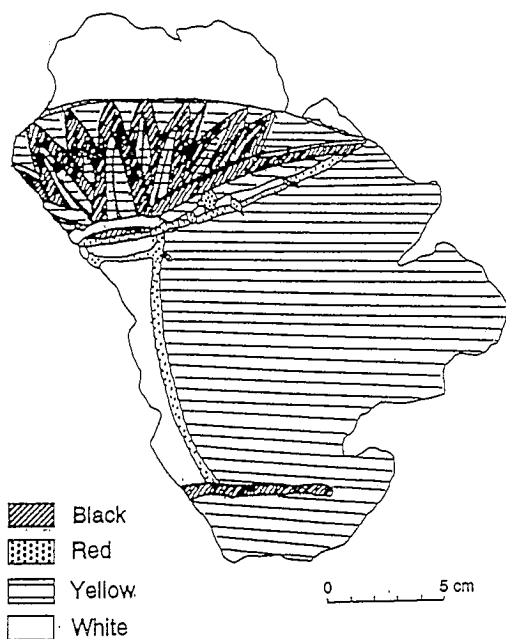


Fig. 1. A mural painting excavated from a site of Kom el-Samak on the west bank of Luxor, Egypt. A lotus bloom was painted with five kinds of pigments; white, two types of yellow, red and black.

analyzed, which were coated and non-coated with paraffin, respectively.

Proton beams accelerated to 2.5 MeV by a tandem

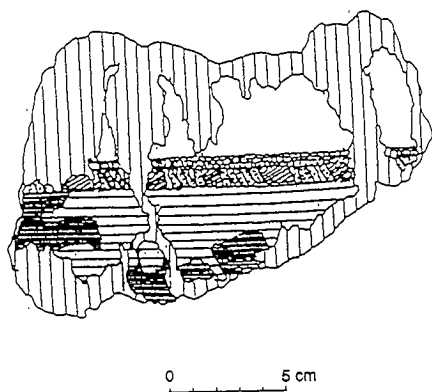


Fig. 2. A mural painting excavated from the same place with Fig. 1. Almost one half of the surface was painted with three kinds of pigments; white, red and blue, and another half was decorated with two types of yellow pigments. Darken areas on the yellow part were covered with paraffin.

Pelletron (NEC) in Waseda University were emitted to air through a 3 mm dia graphite aperture interfaced with a 6 μm thick Al foil. The energy of the proton beams on the specimen was reduced from 2.5 to 2.14 MeV by this Al foil plus the 14 mm of air between the exit foil and specimen. The emitted X-rays were detected in a Si(Li) detector placed at 135° relative to the incident beam direction and at a distance of 20 mm from the standard 0.7 μm Be window. The energy resolution of the detector was 180 eV at the energy of Mn K α (5.894 keV) X-ray. Signals from the detector were stored in a multichannel-pulse height analyzer and processed by a microcomputer, and recorded on a floppy disk. Backgrounds for PIXE spectra observed here were estimated empirically. After subtracting the backgrounds, elemental concentrations in weight were calculated by PIXAN BATTY and PIXAN THICK [17], and then converted to atomic concentrations.

3. Results and discussions

At a first glance PIXE spectra obtained in these experiments for white, yellow and red pigments on the mural paintings have a strong resemblance to previous spectra which were taken from small fragments of ancient Egyptian pigments excavated at the same place [18]. In previous work these pigments were identified by both PIXE and X-ray diffraction methods as: huntite $\text{Mg}_3\text{Ca}(\text{CO}_3)_4$ for white, goethite $\alpha\text{FeO} \cdot \text{OH}$ and orpiment As_2S_3 for yellow, and hematite $\alpha\text{Fe}_2\text{O}_3$ for red. In this experiment we assumed that these pigments were fundamentally the same as before except for degrees of contaminations from soil components originating from the mud brick, on which the pigments were painted.

An observation with the naked eye suggested the presence of multiply stacked layers of pigments on the sun-dried mud brick. The PIXE spectrum shown in Fig. 3(a) is representative of the spectra taken from a part, color-painted mainly by white but partially by yellow. This spectrum is fundamentally the same as that taken previously from a white pigment [18]. The PIXE spectrum taken from a natural huntite $\text{Mg}_3\text{Ca}(\text{CO}_3)_4$ produced from Tea Tree Gally in Australia is shown in Fig. 3(b) for comparison; small amounts of Al, Si, S, Cl, K, Ti, Fe, Sr and Ba can be seen as impurities. Mg and Ca are the main components in this mineral. However, as shown in Fig. 3(a) relative intensities of Al, Si, S, Ti, Mn, Fe and As from the painting are stronger than those expected from the huntite. The PIXE spectrum taken from the mud brick is shown in Fig. 3(c) from which most of the excess amounts of Ti and Mn, and a part of Fe in Fig. 3(a) can be understood by assuming that these are contributions from the mud brick. The elements Al, Si, S and As, part of the Fe and also small amounts of Ti and Mn, must have originated from the yellow colored part which was partial-

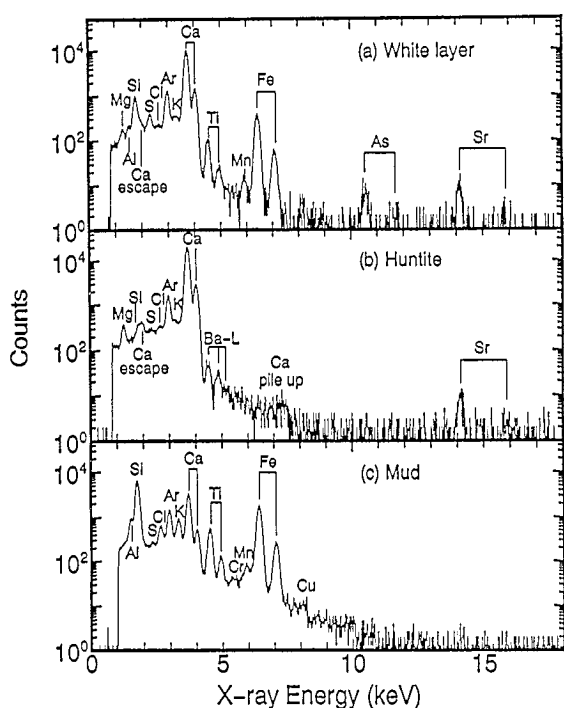


Fig. 3. PIXE spectra taken from the white colored part indicated in Fig. 1 (a), a natural mineral, Huntite (b), and a part of the ancient Egyptian sun-dried mud brick (c). Proton energy: 2.14 MeV.

ly mixed with the white part in the observed area. Thickness of the white layer was estimated to be $17 \mu\text{m}$ from the reduction in X-ray intensity of Ti in Fig. 3(a), comparing to that in Fig. 3(c). If we consider that a small amount of the Ti $K\alpha$ X-ray was contributed by the contaminated yellow pigments, the thickness should be larger than $17 \mu\text{m}$. Here both reductions in proton energies and characteristic X-ray intensities were taken into account.

From yellow and red parts, S, Fe and As, and Fe were clearly detected, respectively. These elements are characteristics of the yellow and red pigments, i.e. As_2S_3 and $\alpha\text{FeO} \cdot \text{OH}$ for yellow, and $\alpha\text{Fe}_2\text{O}_3$ for red. The existence of As_2S_3 as a single phase was confirmed here for the first time as follows. The yellow paintings in Fig. 1 looked like a mixture, through a careful observation, composed of a dark yellow part widely spread and brilliant small particles of 1 mm or less in size. Only one particle was stripped off from the yellow part and coated with a carbon thin layer to make it conductive, and then was analyzed by EPMA. The particle was mainly composed of S and As, i.e. As_2S_3 .

Sr was also detected from the yellow and red parts. Sr comes in naturally with Ca. Then this suggests that Sr comes from the white layer underneath the yellow and red layers. From this assumption the thickness of the yellow and red layers were estimated to be 8 and $8 \mu\text{m}$ or more,

respectively, considering both the energy loss of protons and absorption of X-rays through these layers; the intensities of the Sr $K\alpha$ X-rays through the yellow layer, and the yellow and red layers were observed to be 0.43 and 0.12 or less, respectively, as compared with those of the white layer. Since no characteristic black pigments were observed it is suggested that charcoal or soot was used as the black pigment as in the case reported elsewhere [19] and was painted as a topmost layer.

Paraffin-coated and non-coated yellow parts shown in Fig. 2 were analyzed by PIXE, giving fundamentally the same spectra shown in Fig. 4. This suggests that the PIXE analysis can be done even if the mural paintings were covered with a thin paraffin layer, however the color tone was darker and all the characteristics X-ray intensities weaker for the former than for the latter. This is because a part of both the visible-light and X-rays were absorbed, and because of loss in the proton energy on passing through the paraffin layer. However, degrees of reductions in $K\alpha$, β X-ray intensities of Fe were larger than those of Ti. This kind of reductions should mainly be caused by energy loss of incoming protons through the paraffin layer, leading to more intense reductions in the K ionization cross sections for elements with the larger atomic numbers under the experimental conditions here employed. From these assumptions the thickness of the paraffin layer and the energy loss of the protons were estimated to be $23 \mu\text{m}$ and 0.24 MeV ($2.14 \rightarrow 1.90$ MeV), respectively. Here the absorption of Fe and Ti K X-rays through the paraffin layer was ignored because paraffin is composed only of C and H with transmissivities of ≥ 0.96 for the Fe and Ti K X-rays.

The external PIXE technique was used successfully in analyzing big ancient Egyptian mural paintings in a nondestructive manner. Layer structures on the paintings were also studied without vandalizing the ancient remains. A thin paraffin layer did not disturb the external PIXE

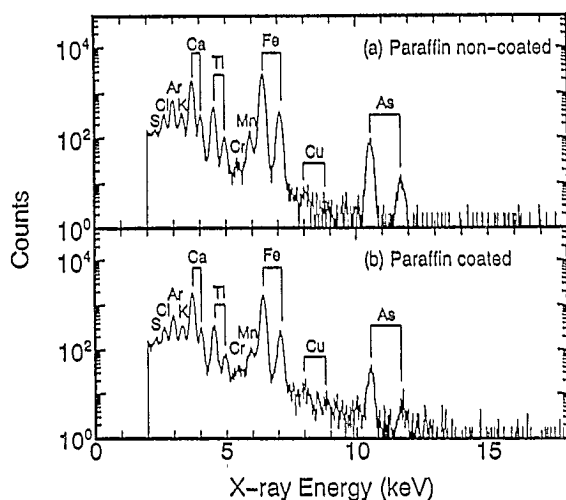


Fig. 4. PIXE spectra taken from the yellow parts with and without paraffin coatings indicated in Fig. 2.

analysis, which was a part of reinforcement materials and flowed out from a back side to a surface region.

References

- [1] S.A.E. Johansson and J.L. Campbell, PIXE, A Novel Technique for Elemental Analysis (Wiley, Chichester, New York, Brisbane, Toronto, Singapore, 1988).
- [2] C.P. Swann and S.J. Fleming, Scanning Microscopy 2 (1988) 197.
- [3] S.J. Fleming and C.P. Swann, Nucl. Instr. and Meth. B 75 (1993) 440.
- [4] C.P. Swann, P.E. McGovern and S.J. Fleming, Nucl. Instr. and Meth. B 75 (1993) 445.
- [5] Y. Sasa, K. Maeda and M. Uda, Nucl. Instr. and Meth. B 22 (1987) 426.
- [6] E. Hamilton, C.P. Swann and S.J. Fleming, Nucl. Instr. and Meth. B 85 (1994) 856.
- [7] B. Kusko, T.A. Cahill, R.A. Eldred and R.N. Schwab, Nucl. Instr. and Meth. B 3 (1984) 689, Archaeometry 26 (1984) 3.
- [8] M. Peisach, Nucl. Instr. and Meth. B 14 (1986) 99.
- [9] B. Kusko and M. Menu, Nucl. Instr. and Meth. B 49 (1990) 288.
- [10] M. Menu and P. Walter, Nucl. Instr. and Meth. B 64 (1992) 547.
- [11] J. Räsänen, Int. J. PIXE 2 (1992) 339.
- [12] Xiankang Wu, Xiangzhou Zeng and Fijia Yang, Nucl. Instr. and Meth. B 75 (1993) 458.
- [13] M. Menu, Nucl. Instr. and Meth. B 75 (1993) 469.
- [14] P. Del Carmine, F. Lucarelli, P.A. Mandò and A. Pecchioli, Nucl. Instr. and Meth. B 75 (1993) 480.
- [15] R. Cambria, P. Del Carmine, M. Grange, F. Lucarelli and P.A. Mandò, Nucl. Instr. and Meth. B 75 (1993) 488.
- [16] L. Jacobson, C.A. Pineda, D. Morris and M. Peisach, Nucl. Instr. and Meth. B 75 (1994) 901.
- [17] E. Clayton, PIXAN: The Lucas Height PIXE Analysis Computer Package AEEC/M113, Australian Atomic Energy Commission (1986).
- [18] M. Uda, T. Tsunokami, R. Murai, K. Maeda, I. Harigai, Y. Nakayama, S. Yoshimura, T. Kikuchi, K. Sakurai and Y. Sasa, Nucl. Instr. and Meth. B 75 (1993) 476.
- [19] A. Lucas and J.R. Harris, Ancient Egyptian Materials and Industries, 4th ed. (Arnold, London 1989).