Yellow, red and blue pigments from ancient Egyptian palace painted walls

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Abstract

Yellow, red and blue pigments from the painted walls of the Malqata palace, founded by Amenhotep III, 18th Dynasty, were analyzed using PIXE and X-ray diffraction (XRD). From most of the yellow, red and blue parts, goethite, hematite and Egyptian blue, respectively, were found on the basis of diffractometry results. From some yellow parts, As was detected together with Fe spectroscopically, suggesting the use of orpiment as a yellow pigment. The red pigment seems to be natural and not man-made. This assumption is deduced from the dehydration experiment of a synthesized goethite. © 2000 Elsevier Science B.V. All rights reserved.

PACS: 32.30.Rj; 41.75.Ak; 71.24.+q
Keywords: Ancient Egypt; Pigment; X-ray analysis; Red; Blue

1. Introduction

Ancient remains are expected to provide information on past technologies. Pigments used in ancient Egypt are among the most attractive targets to be investigated, because ancient Egyptians prepared many kinds of pigments artificially [1]. A representative one is the Egyptian blue, i.e. calcium copper silicate, $CaCuSi_4O_{10}$.

PIXE is one of the most sensitive analytical methods applied under non-destructive and touch-free conditions [2]. It can be used for analyzing elemental concentrations of a specimen both in vacuum and in air. The "in vacuum" use is advantageous to detect low atomic number elements. The "in air" use, however, is suited for analyzing fragile or volatile or non-heat resistive specimens of a irregular shape and of a large size as in the

case of our present analysis of ancient remains. Chemical formulae and grain sizes of pigments, which cannot be determined by PIXE, were estimated here using diffractometry.

Specimens investigated here are fragments of the Malqata palace wall founded in ancient Egypt (ca. 1390 BC), on which yellow, red and blue pigments are painted. Laboratory-made iron oxyhydroxide and its dehydrated oxide have been studied using diffractometry, for estimating whether an ancient red pigment with poor crystallinity is artificial or not.

2. Experiments

PIXE and X-ray diffraction (XRD) measurements were performed in air. This is because the fragments of the Malqata palace wall made of a sun-dried brick are very fragile, not suitable for investigation in vacuum. A 2.0 MeV proton beam was generated in the Pelletron accelerator at the Radiation Laboratory of the Tokyo Metropolitan Industrial Technology Research Institute. The beam was collimated to 2×3 mm^2 through two graphite slits. The proton beam was extracted to air through an exit foil made of Al (6 μm in thickness). The beam spot size on the specimen was 3×5 mm^2. A proton beam current was 100 nA or less on the Al exit foil. The energy of the proton beam was reduced to 1.6 from 2.0 MeV after passing through the Al foil and 10 mm air between the exit foil and a specimen [3,4]. The emitted X-rays were detected by a Si(Li) semiconductor detector placed at 135° relative to the incident beam direction after passing through 70 mm air between the specimen and the detector window (an 8 mm thick Be foil). The energy resolution of the detector was 180 eV for the Mn Kα (5.89 keV) X-ray energy.

XRD data were taken using an automated X-ray diffractometer [11] equipped with a Cu Kα source. The accelerating voltage and the electric current at the Cu anode were 40 kV and 30 mA, respectively. The scanning speed of the goniometer ($2\theta°$ s^{-1}) and the scanning step ($\Delta 2\theta°$) were 0.005 and 0.025, respectively.

3. Specimens

The Malqata palace wall or staircase located on the West bank of Luxor (670 km south from Cairo), Egypt, was excavated by the Waseda University Egypt Archaeological Mission in 1974. The palace was constructed by Amenhotep III in the 18th Dynasty (ca. 1390 BC). The fragments of the wall have been preserved in the Egyptian Culture Center at Waseda University. Simulation experiments for preparing an artificial red pigment were carried out by mixing a ferric chloride solution with a sodium hydroxide solution, followed by washing at room temperature and by heating at 300–900°C.

4. Results and discussion

A typical fragment of the Malqata palace wall and/or staircase is ca. 3×5 cm^2. The surface of the fragment is coated with white (bottom) and blue (top) layered pigments. A part of the blue colored surface is painted again individually with dark-blue and yellow pigments. The bottom white layer was identified as huntite ($CaCO_3 \cdot 3MgCO_3$), which shows fine white [5–7], using diffractometry. A PIXE spectrum taken from the yellow colored part is characterized by intense As and Fe Kα peaks. Orpiment (As_2S_3) and goethite ($\alpha FeO \cdot OH$) were found here in the XRD pattern taken from the same part analyzed by PIXE. Eight fragments coated with yellow pigments gave similar results to those mentioned above, though rather intense As Kα and Fe Kα peaks were found from brilliant and dark yellow parts, respectively.

Five fragments painted with red pigments were analyzed by PIXE. All of them are characterized with high contents of iron, suggesting that the red pigments are anhydrous iron oxides (red iron oxide) or hydrated iron oxides (red ochre). Chemical formulae are expected to be αFe_2O_3 for the former, and $\alpha FeO \cdot OH$ or an intermediate between αFe_2O_3 and $\alpha FeO \cdot OH$ for the latter, respectively. Hematite (αFe_2O_3) and goethite ($\alpha FeO \cdot OH$) were found to be main components of the red pigment. These are spread on the sun-dried brick, i.e. a mixture of quartz and poorly crystallized

clay. From the broadening of the diffraction lines originating from αFe_2O_3, the grain size of the red pigment is also assumed to be small (see the following discussion).

Natural iron oxides occur plentifully in Egypt and then anhydrous and hydrated iron oxides could be used as the red pigments without any heat treatment. However, calcination of yellow ochre ($\alpha FeO \cdot OH$) has been pointed out to produce a deep red ochre [1]. Then we have attempted to check whether the red ochre studied here is produced by heating yellow ochre or not. For this purpose the yellow ochre was prepared in our laboratory, and was heated at elevated temperatures, i.e. 300–900°C. The goethite mineral is characterized with a needle-like shape, and is dehydrated to αFe_2O_3 by heating at 300°C or higher temperature. At the beginning of the dehydration, in our experiment, a grain shape of αFe_2O_3 formed from the needle-like shape of $\alpha FeO \cdot OH$ with the relationship of $\langle 0\,0\,1 \rangle$ of $\alpha FeO \cdot OH // \langle 1\,1\,0 \rangle$ of αFe_2O_3. Here $\langle 0\,0\,1 \rangle$ of $\alpha FeO \cdot OH$ is in longitudinal direction of the needle-like shape. After heating at 900°C for 1 h, the grain size of αFe_2O_3 became five times longer than the initial size or more, and the shape became almost spheric. An estimation was made by calculating sizes of the dehydrated grain, along with crystallographic directions, with the aid of Scherrer's formula

$$B = 0.9/t \cos \theta, \tag{1}$$

where B is the full width at half maximum of the diffracted line, t the size of grain, 2θ the diffraction angle and λ is the X-ray wavelength.

The estimated sizes of the αFe_2O_3 grains, along with crystallographic directions, are summarized in Table 1 both for the laboratory-made hematite and the hematite found in the pigment painted on the surface of the Melgata palace wall. It is easily understood that the shape of the hematite in the red pigment is almost isotropic and its size is approximately 300 Å. We could not find such shape and size of the dehydrated grain heated at any temperature (see Table 1). This indicates that the red ochre found in the red pigment is natural and not made by heating yellow ochre.

Seven fragments with surfaces coated with blue and their related pigments were analyzed by

PIXE. High and low concentrations of Cu and Fe, respectively, suggest that the blue pigment consists of Cu-rich chemical species. Therefore the possible contents of the pigment are the Egyptian blue or cuprorivaite ($CaCuSi_4O_{12}$), cuprowollastonite ($CaCuSiO_3$) and Cu-rich glass [8–10]. The atomic concentration ratios estimated from PIXE data [11] are summarized in Fig. 1 for all the blue and its related pigments. Here the X-ray intensity estimated from Ar in air is used for normalizing all the atomic concentration ratios concerned.

A particular blue pigment gave a chemical composition different from those of the other six

Table 1
The grain sizes along with crystallographic directions $\langle h\,k\,l \rangle$ of hematite in Å

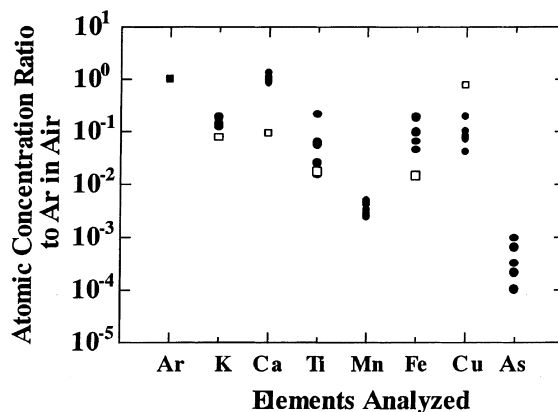|	012	104	110	024	116
300°C	80	78	290	79	130
400°C	120	120	290	110	140
500°C	140	140	290	130	140
600°C	210	180	290	190	170
700°C	250	250	410	240	240
800°C	440	340	450	320	290
900°C	440	400	510	410	360
Pigment	280	270	310	300	310

Fig. 1. Atomic concentration ratios of the blue pigments determined by PIXE. The number of fragments used is seven.

pigments, shown by the open squares in Fig. 1. The diffraction pattern taken from this pigment is characterized by quartz mixed with an amorphous phase. Variations in the atomic concentration ratios among the other six samples are mainly due to the fact that the thickness of the blue painted layers is different, and the sun-dried brick is exposed, in some parts, by breaking-down of the blue painted layers. This leads to a reduction in the concentration of Cu, and to an increase in those of Fe and Ti. A small amount of As is likely due to contamination from a yellow painted part because As_2S_3 can be easily removed by wiping when cleaning [11].

Acknowledgements

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