

## SHORT COMMUNICATION

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## Touch-free in situ investigation of ancient Egyptian pigments

Received: 8 October 1999 / Accepted in revised form: 10 March 2000

**Abstract** Some of the pigments painted on the Funerary Stele of Amenemhat (ca. 2000 B.C.) exhibited at the Egyptian Museum, Cairo and on the walls of the Tomb of Userhat (ca. 1450 B.C.), a rock-cut tomb in Thebes, Egypt, were investigated in situ using both a convenient home-made hand-held type of X-ray diffractometer and a commercial X-ray fluorescence spectrometer in a complementary way under touch-free conditions.  $\text{CaCO}_3 \cdot 3\text{MgCO}_3$  (huntite) was found in the white-painted parts of these two ancient monuments. An arsenic (As)-bearing phase was detected in the yellow-painted parts of the latter monument. The occurrence of huntite in Egypt has not been reported previously.

The pigments used in ancient monuments provide information on past technologies and possible trades. Ancient Egyptian pigments have been analyzed extensively in laboratory studies (Barbieri et al. 1974; Riederer 1974; Noll 1981; Jaksch et al. 1983; El Goresy et

al. 1986; Saleh 1987; Riederer 1988; Lucas and Harris 1989; Schiegl et al. 1989, 1990, 1991a,b; Stulik et al. 1993; Uda et al. 1993; Green 1995; Weatherhead 1995; Nagashima et al. 1996; El Goresy 1997; Uda 1998), but not in the field. In order to perform a touch-free in situ investigation of ancient Egyptian pigments, we used, for the first time, a hand-held X-ray diffractometer together with an X-ray fluorescence spectrometer as a complementary tool. These can be useful for a quick preliminary survey in the field. The X-ray diffractometer was designed and made by K.T. in line with the specifications written by M.U. One of the objects for the X-ray measurements was chosen from the exhibits at the Egyptian Museum, Cairo; namely the painted limestone (height: 30 cm, length: 50 cm) shown in Fig. 1. This is the Funerary Stele of Amenemhat (JE 45626) which is exhibited in gallery # 21, case A, on the ground floor, and which was taken from Assasif (Tomb R.4), Thebes, 11th Dyn. Middle Kingdom (ca. 2000 B.C.). We also made measurements on wall paintings in a rock-cut tomb in Thebes, Egypt; the Tomb of Userhat who lived during the reign of Amenophis II (TT 56, height: ca. 2.5 m, width: ca. 2.5 m), New Kingdom (18th Dyn. ca. 1450 B.C.), which is located in the west bank of Thebes. The tomb's walls are decorated with beautiful scenes of offering, hunting and farming as well as a funeral procession. The pigments which decorate the Stele and the tomb's walls still exist in excellent condition.

The home-made X-ray diffractometer is approximately 25 cm wide, 12 cm long and 20 cm high. It is equipped with a Cr X-ray tube which emits Cr  $K\alpha$  and  $K\beta$  X-rays, and is operated at 50 kV and 1 mA (i.e., 50 W). The diffraction angle,  $2\theta$ , which ranges from  $35^\circ$  to  $90^\circ$  (i.e., from lattice spacing  $d=3.8\text{--}1.6 \text{ \AA}$ ), can be altered by a pulse motor. Diffracted X-rays from the surface layers of a few  $10 \mu\text{m}$  in thickness were measured using a scintillation counter and recorded on paper. Materials characterized only with high  $d (>3.8 \text{ \AA})$  values and bulk materials or inner layers covered with surface layers of a few  $10 \mu\text{m}$  or more are beyond the

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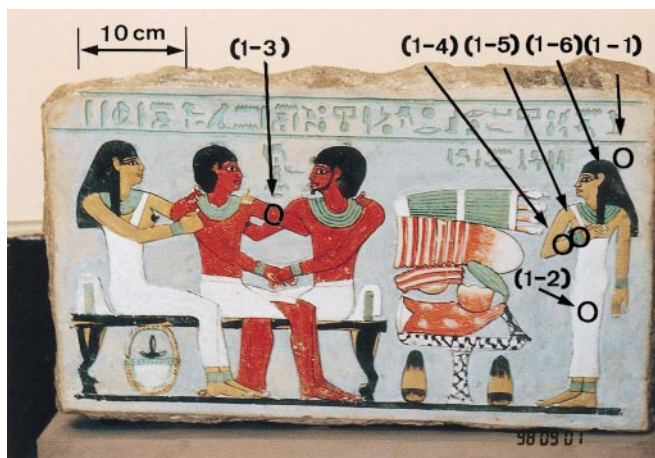
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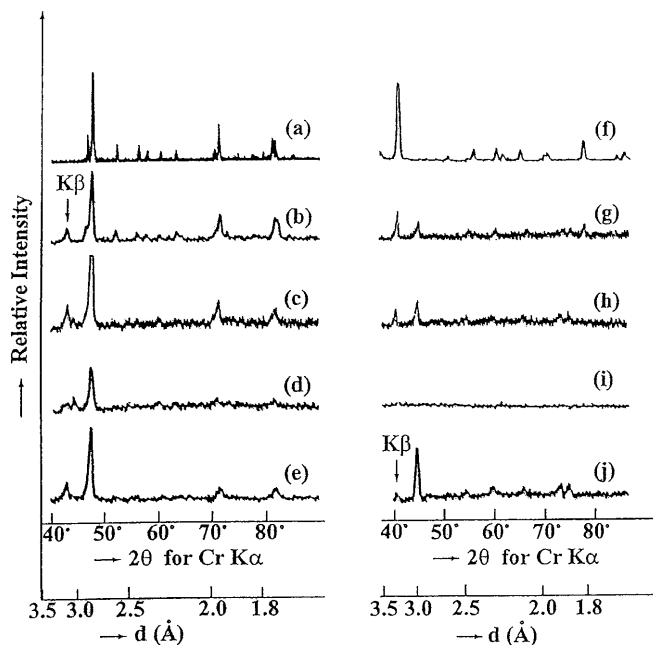
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**Fig. 1** The Funerary Stele of Amenemhat (ca. 2000 B.C.) exhibited at the Egyptian Museum, Cairo. *Open circles with arrows* show parts analyzed by X-ray diffraction and X-ray fluorescence methods. Here (1-1) is the background limestone matrix, (1-2) the white robe, (1-3) the reddish-brown (male) skin, (1-4) the light-yellow (female) skin, (1-5) the light-green bracelet, and (1-6) the black hair

reach of the X-ray diffractometer. A typical example is yellow orpiment ( $\text{As}_2\text{S}_3$ ), expected to be one of the yellow pigments present in the Funerary Stele, which is characterized with one intense diffraction peak at  $d=4.85 \text{ \AA}$ . Another example is the pigment on the tomb walls, which are covered with a thick secondary natural calcite layer deposited over the millennia or covered by thick secondary materials resulting from the deterioration of the original pigment (Jaksch et al. 1983; El Goresy et al. 1986; Schiegl et al. 1990; El Goresy 1997).

A typical diffraction pattern recorded with the diffractometer is shown in Fig. 2b. It was taken from the reference mineral, huntite, and compares with that shown in Fig. 2a which was taken using the X' Pert-MPD diffractometer commercially available from Philips, operated at 50 kV and 30 mA, i.e. 150 W. The former diffraction pattern was recorded for only 8 min. It compares well, in terms of quality, with the 60-min recording by the commercial diffractometer. This is because the former uses both Cr  $K\alpha$  and  $K\beta$  X-rays without filtering  $K\beta$ , and also because it employs wide slits which restrict the dispersion angle of the diffracted X-ray. This leads to high sensitivity with the sacrifice of certain amounts of angle-resolution and of depth information due to the low penetration depth of Cr K X-rays. Such high sensitivity is very advantageous for investigations in the field, where a deficiency in information obtained by the home-made diffractometer can be supplemented, at least in part, by micro-analytical results accumulated in laboratory experiments (Jaksch et al. 1983; El Goresy et al. 1986; Schiegl et al. 1990; El Goresy 1997). The diffractometer was placed in front of the painted area to be investigated using tripods, so that its position could be controlled in three dimen-



**Fig. 2** X-ray diffraction patterns. **a** is taken from the reference mineral huntite ( $\text{CaCO}_3 \cdot 3\text{MgCO}_3$ ) using a commercial diffractometer, and **b-j** are taken using the home-made diffractometer (Cr  $K\alpha$  and  $K\beta$ ); **b** is from the reference mineral huntite, **c** from the white robe (1-2) in Fig. 1, **d** from the background white on the wall of the Tomb of Userhat, **e** from the yellow offering table on the wall of the Tomb of Userhat, **f** from the reference mineral quartz, **g** from the light-yellow skin (1-4) in Fig. 1, **h** from the light-green (1-5) in Fig. 1, **i** from the reference microscopy glass, and **j** from the reference mineral calcite

sions. Measurements were thereby performed under touch-free conditions.

X-ray fluorescence measurements in air were also carried out under the same conditions as above using the XRF analyzer, Portarix, which is commercially available from Rigaku. The XRF analyzer was operated at 40 kV and 0.125 mA (i.e., 5 W), and the intensity of the X-rays emitted from the pigments was measured with the energy-dispersive type of Si PIN photodiode. The data that were thus accumulated were processed using Windows 95, which was also used for controlling the experimental setup. Here, just 5 mn measurements were sufficient to obtain well-resolved spectra (i.e.,  $\Delta E < 300 \text{ eV}$  at 5.9 keV).

From the white part of a robe painted on the Funerary Stele [Fig. 1 (1-2)] huntite ( $\text{CaCO}_3 \cdot 3\text{MgCO}_3$ ) (Faust 1953; Sasa and Uda 1995) was detected by X-ray diffraction, as shown in Fig. 2c. Using XRF, Ca, Fe and Sr were found to be the main components of this part. The atomic concentration ratios of Sr:Ca and Fe:Ca were spectroscopically estimated to be 0.01 and 0.003, respectively, taking into account the  $K\alpha$  X-ray emission yields of these elements excited with the Mo  $K\alpha$  X-rays employed here, and also taking into account the  $K\alpha$  X-ray absorption coefficients of these elements in the  $\text{CaCO}_3 \cdot 3\text{MgCO}_3$  matrix. Under our experimental conditions, however, quantities of Mg, O and C could

not be determined from the observed X-ray fluorescence spectra, because the experiment was performed in air, which absorbs X-rays of energy lower than 2.5 keV, i.e.,  $K\alpha$  X-rays emitted from elements with atomic number less than 17(Cl). The same rule also applies to the following measurements.

The reddish-brown skin color [Fig. 1 (1–3)] presumably originates from hematite ( $\alpha\text{Fe}_2\text{O}_3$ ), because diffraction lines from hematite, not shown here, were found. Hematite use is also expected from the moderate height of the Fe  $K\alpha$  peak which is observed in the X-ray fluorescence spectrum. The woman's skin is painted with a light-yellow pigment [Fig. 1 (1–4)]. Its X-ray diffraction pattern is shown in Fig. 2g, from which quartz,  $\text{SiO}_2$  (white in color if pulverized) was identified as one of the main components, together with calcite,  $\text{CaCO}_3$ . An Fe  $K\alpha$  X-ray peak was clearly found in the X-ray fluorescence spectrum taken from the same part, though no distinct diffraction peaks characteristic of iron-bearing compounds were found in Fig. 2g.

From the light-green part of a bracelet (Fig. 1 (1–5)) an intense Cu  $K\alpha$  peak, accompanied by weak Ca, Fe, As and Sr  $K\alpha$  peaks, was found in the X-ray fluorescence spectrum, though only crystalline phases of quartz and calcite were found by X-ray diffractometry (Fig. 2h). This is perhaps because poorly crystallized materials give ill-defined diffraction patterns, when recorded with the same sensitivity as that for Fig. 2b–j. An example is shown in Fig. 2i which was taken from the reference spectroscopy glass. The green pigment could be an amorphous Cu-bearing compound (Jaksch et al. 1983; El Goresy et al. 1986; Schiegl et al. 1990; El Goresy 1997).

The X-ray diffraction pattern characteristic of calcite,  $\text{CaCO}_3$ , not shown here, and an intense Ca  $K\alpha$  fluorescence peak were found from a black hair part [Fig. 1 (1–6)]. We suppose that both are basically from the calcite matrix, because the X-ray fluorescence spectrum was the same as that emitted from the matrix or background [Fig. 1 (1–1)]. This suggests that amorphous carbon or soot or soot mixed with calcite was painted on limestone to make the black color.

All the walls of the Tomb of Userhat were painted with a white pigment which we identified here as huntite,  $\text{CaCO}_3 \cdot 3\text{MgCO}_3$ , by X-ray diffraction, as shown in Fig. 2d. Ca, Fe, As and Sr were, to a greater or lesser degree, found in the X-ray fluorescence spectra from all the painted parts such as white, the pink of a tunic, the pink of a woman's skin, reddish-brown skin, yellow, red, blue and so on. From the pink part of a tunic, large amounts of huntite ( $\text{CaCO}_3 \cdot 3\text{MgCO}_3$ ) and small amounts of hematite ( $\alpha\text{Fe}_2\text{O}_3$ ) were found by X-ray diffraction (not shown here). The same combination of these two pigments was also found in the pink of a woman's skin and the reddish-brown skin part.

From the brilliant and thickly painted yellow part of an offering table or vessel, an intense As  $K\alpha$  peak was found in the X-ray fluorescence spectrum, although the X-ray diffraction pattern characteristic only of huntite

( $\text{CaCO}_3 \cdot 3\text{MgCO}_3$ ) was found in the yellow. Fe and Cu  $K\alpha$  peaks were found in the X-ray fluorescence spectra of the red and blue colored parts, respectively, though no well-resolved crystalline peaks could be detected in the diffraction patterns. This is because the home-made diffractometer is insensitive to orpiment characterized with the most intense peak at  $d=4.85 \text{ \AA}$ .

In all our investigations, completely non-destructive in situ X-ray measurements were performed on representative parts of ancient Egyptian monuments. Only XRF data are reliable for the blue, light-green, light-yellow and black parts, because these parts include, at least in part, amorphous phases insensitive to X-ray diffraction. Thus, the crystal structures and chemical formulae of the above colored parts could not be determined by the XRD method employed here. However, the finding of huntite ( $\text{CaCO}_3 \cdot 3\text{MgCO}_3$ ) from the painted Stele (11th Dyn.) and from the walls of the Tomb of Userhat (18th Dyn.) by X-ray diffraction, and the detection of large amounts of As from the yellow part of the latter by X-ray fluorescence are both interesting. Huntite is not known in Egypt as a primary mineral. The first use of huntite and orpiment in wall decoration is believed to have already occurred by the New Kingdom (18th Dyn. ca. 1400 B.C.) (El Goresy et al. 1986; El Goresy 1997) or earlier times (Heywood 1996). For identifying the yellow pigment, the home-made diffractometer is currently undergoing reconstruction, in order to make it capable of detecting the diffraction line at  $d=4.85 \text{ \AA}$ , the most intense line for orpiment.

**Acknowledgements** We would like to express our thanks to the Supreme Council of Antiquities in Egypt for granting permission to carry out this project; in particular to Prof. G.A. Gaballa (the Secretary General), Dr. Zahi Hawass (General Director of al-Giza), Dr. Mohamed Saleh (General Director of the Egyptian Museum), Dr. Mohamed al-Soghayer (General Director of Luxor), Dr. Mohamed Nasr and Mr. Sabri Abd al-Aziz. We acknowledge Mrs. T. Fujita for her help in performing the X-ray measurements.

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