

X-RAY ANALYSIS OF GREEK BRONZE AGE PIGMENTS FROM KNOSSOS

S. PROFI, L. WEIER, and S. E. FILIPPAKIS

Abstract—Analyses are reported of a number of Minoan pigments from wall paintings at Knossos, dating from c. 1700–1400 B.C.

1. INTRODUCTION

When Sir Arthur Evans [1] began his excavations at Knossos at the beginning of this century he uncovered vast numbers of painted frescoes. Those of the period of the 'Early Palaces' in Middle Minoan I and II (about 2000–1700 B.C.) were painted red or were decorated with simple geometric designs in red and white [2]. However, in the 'Last Palace' period (beginning in Middle Minoan III in 1700 B.C.) painted scenes became abundant and the artist's palette increased accordingly.

These paintings were first examined technically by Noel Heaton [3, 4] in 1910. Heaton ascertained that the paintings were executed in true fresco technique and that the pigments were simple earth pigments: the white was calcium carbonate probably in the form of lime hydrate; the black, a carbonaceous shale or slate; red and yellow were iron oxides. The blue was the only synthetic pigment: the copper-calcium silicate known as 'Egyptian Blue'. Since that time no further technical studies [5] have been carried out on these frescoes and thus closer scrutiny by means of X-ray analytical techniques may offer interesting additional information.

2. SAMPLES

Samples were taken from the Late Minoan II destruction deposit of the Unexplored Mansion and therefore can be no later than 1400 B.C. It is possible however that they are earlier than Late Minoan II, perhaps even as early as Middle Minoan III (1700–1600 B.C.). There are 24 samples: 23 monochromatic and 1 dichromatic. Among them are 1 white, 2 black, 3 blue, 3 beige, 7 red, 2 pink, 1 brown, 2 orange and 4 yellow. The painted plaster fragments vary in size from 1–2.5 cm², while the plaster varies in thickness from 0.4–0.8 cm.

3. EXPERIMENTAL TECHNIQUES

Since the samples were of an archaeological nature, the non-destructive methods of X-ray fluorescence analysis (XRF), X-ray diffraction analysis (XRD), and mineralogical microscopic examination with a polarizing microscope were used throughout the whole study. The equipment and techniques employed were identical to those of an earlier study reported in this journal [6] and will not be repeated here.

4. EXPERIMENTAL RESULTS

4.1 Plaster

As shown in Table 1, Ca, Fe and Ni (traces) were detected in the plaster with XRF, Ca being the major element. In the Debye-Scherrer pattern of the plaster the dominating lines belong to CaCO₃. There are also additional lines, some of them belonging to SiO₂ and

some which cannot be identified. Mineralogical examination shows the plaster to be mainly CaCO_3 with small amounts of quartz and clay, and some very small particles which may be gypsum, which is prevalent on the site. Fe and Ni appearing in the XRF spectra and the unidentified lines of the XRD patterns can be attributed to the small quantities of these minerals accompanying the calcite. There are also small quantities of straw.

TABLE 1
ANALYTICAL DATA OF PIGMENTS FROM KNOSSOS

Sample	Colour	X-ray fluorescence XRF	X-ray diffraction XRD	Mineralogical examination	Identification
Plaster	White	Ca, Fe, Ni (tr.)	CaCO_3 , SiO_2 , unidentified lines	Calcite, quartz, clay	Lime plaster
Knossos 1	White	Ca, Fe, Ni (tr.)	Plaster	Plaster, iron hydro- xide, haematite	Unpainted plaster
Knossos 2	Black	Ca, Fe, Ni (tr.)	Plaster	Black particles, quartz	Carbon (?)
Knossos 3	Black	Ca, Fe, Ni (tr.)	Plaster, unidentified lines	Black particles, brown iron oxide	Carbon (?)
Knossos 4	Blue	Cu, Sn (tr.), Ca, Fe, Ni (tr.)	Plaster, $\text{CaCuSi}_4\text{O}_{11}$	Blue particles, quartz	Egyptian Blue
Knossos 5	Blue	Cu, Sn (tr.), Ca, Fe, Ni (tr.)	Plaster, $\text{CaCuSi}_4\text{O}_{11}$	Blue particles, quartz	Egyptian Blue
Knossos 6	Blue	Fe, Ca, Ni (tr.)	Plaster, glaucophane	Amphibole crystals, quartz, iron oxide, calcite, mica, chlorite, black particles	Glauco-phane
Knossos 7	Beige	Ca, Fe, Ni (tr.), Cu (tr.)	Plaster, quartz, unidentified lines	Quartz, iron hydroxide, haematite	Ochre diluted by quartz
Knossos 8	Beige	Ca, Fe, Ni (tr.), Cu (tr.)	Plaster, quartz, unidentified lines	Quartz, iron hydroxide, haematite	Ochre diluted by quartz
Knossos 9	Beige	Ca, Fe, Ni (tr.), Cu (tr.)	Plaster, quartz, unidentified lines	Quartz, iron hydroxide, haematite	Ochre diluted by quartz
Knossos 10	Red	Fe, Ca, Ni (tr.)	Plaster, haematite	Haematite, quartz, calcite, biotite	Red ochre
Knossos 11	Brown		—	Blue particles, haematite, iron hydroxide, quartz	Ochre and Egyptian Blue
Knossos 12	Red	Fe, Ca, Ni (tr.)	Plaster, haematite	Haematite, clay, quartz	Red ochre
Knossos 13	Red	Fe, Ca, Ni (tr.)	Plaster, haematite	Haematite, clay, quartz	Red ochre
Knossos 14	Red	Fe, Ca, Ni (tr.)	Plaster, haematite	Haematite, quartz	Red ochre
Knossos 15	Red	Fe, Ca, Ni (tr.)	Plaster, haematite	Haematite, quartz, muscovite	Red ochre
Knossos 16	Red	Fe, Ca, Ni (tr.)	Plaster, haematite	Haematite, quartz	Red ochre
Knossos 17	Red	Fe, Ca, Ni (tr.)	Plaster, haematite	Haematite, quartz, muscovite	Red ochre
Knossos 18	Pink	Fe, Ca, Ni (tr.)	Plaster, haematite	Iron hydroxide, haematite, quartz	Red + yellow ochre
Knossos 19	Pink	Fe, Ca, Ni (tr.)	Plaster, haematite	Iron hydroxide, haematite, quartz	Red + yellow ochre

Table continued on page 36

TABLE 1 (continued)

Knossos 20	Orange	Fe, Ca, Ni (tr.)	Plaster, haematite	Haematite, iron hydroxide, quartz, clay	Yellow + red ochre
Knossos 21	Orange	Fe, Ca, Ni (tr.)	Plaster, haematite	Haematite, iron hydroxide, quartz, muscovite	Yellow + red ochre
Knossos 22	Yellow	Fe, Ca, Ni (tr.)	Plaster	Iron hydroxide, quartz	Yellow ochre
Knossos 23	Yellow	Fe, Ca, Ni (tr.)	Plaster	Iron hydroxide, quartz, haematite, muscovite	Yellow ochre
Knossos 24	Yellow	Fe, Ca, Ni (tr.)	Plaster	Iron hydroxide, quartz, haematite, clay	Yellow ochre
Knossos 25	Yellow	Fe, Ca, Ni (tr.)	Plaster	Iron hydroxide, quartz	Yellow ochre

4.2. Pigments

The plaster contaminates the XRF spectra of the pigments as well as their powder patterns. Thus, the characteristic constituents of each pigment were determined after comparison with its plaster by subtraction of the common peaks or lines.

White Pigments

Knossos 1 is the only white sample. The XRF spectrum shows only Ca to be present in great quantity, while the Fe content is slightly higher than in the plaster. The Debye-Scherrer pattern shows the plaster lines. Only under the polarizing microscope one can detect, apart from the plaster, also some iron hydroxide and haematite.

Black Pigments

The XRF spectra of the black pigments are very similar to the plaster spectrum, Knossos 3 having most probably some additional Fe. The powder pattern of Knossos 2 is exactly the plaster pattern, while the one of Knossos 3 gives some extra lines. The mineralogical examination revealed also two types of black: Knossos 2 shows black particles and some quartz, while the other black pigment consists of smaller and less black particles, having also some brown iron oxide particles surrounding the black with almost no quartz.

The black particles are most probably some form of carbon and thus beyond the detection capability of the methods employed.

Blue Pigments

Two types of blue could be recognized in all types of examination. Knossos 4 and 5 are the same in their XRF patterns, exhibiting Ca, Cu and traces of Sn along with some minor Fe, while in Knossos 6 Fe is major and Cu minor.

Under the microscope Knossos 4 and 5 showed large or medium-sized blue particles and small particles of quartz, which is the typical image of Egyptian Blue as known from the previous work on Mycenaean pigments [6]. Knossos 6 has a greyish tone produced by a mixture of quartz, some iron oxide, calcite, mica, chlorite and a very small quantity of black particles. Mixed with this are long crystals, very large when compared with blue particles of Egyptian Blue, some of which are blue, others being blue-violet or red-violet. The petrographic characteristics of these crystals indicate some sort of amphibole.

The XRD patterns of Knossos 4 and 5 present the lines for Egyptian Blue, while the pattern

of Knossos 6 shows those for glaucophane, a sodium magnesium (or iron) aluminum hydroxide silicate, previously unreported as a pigment of the Greek Bronze Age. Table 2 gives the lines presented by Knossos 6 Blue along with those of a natural glaucophane from Syros Island, Greece, provided by the Museum of Mineralogy and Petrology, Univ. of Athens, and those of ASTM card no. 15-58, a synthetically produced glaucophane.

TABLE 2
XRD PATTERNS FOR GLAUCOPHANE

<i>Knossos 6 Blue</i>		<i>Natural glaucophane from Syros, Greece</i>		<i>Synthetic glaucophane ASTM card no. 15-58</i>	
<i>d Å</i>	<i>I_{rel.}*</i>	<i>d Å</i>	<i>I_{rel.}*</i>	<i>d Å</i>	<i>I/I₁</i>
9.29	m	8.94	m	9.00	10
8.32	m	8.16	m	8.38	30
4.44		4.85		4.82	
3.85	s (calcite)	4.44		4.48	
3.33	(quartz)	3.84		4.05	
3.12	s	3.38	s	3.89	
3.02	s (calcite)	3.20	s	3.42	70
2.71	s	3.07	m	3.26	65
2.59		2.91		3.12	90
2.52	s	2.68	s	2.98	50
2.49	(calcite)	2.57		2.91	
2.28	(calcite, quartz)	2.52	s	2.79	
2.09	(calcite)	2.28	m	2.71	100
1.91	(calcite)	2.14		2.68	
1.87	(calcite)	2.05		2.58	
1.65		1.99		2.50	80
1.63		1.84		2.30	
1.53	(quartz)	1.68		2.27	
1.42		1.63		2.17	50
1.34		1.58		2.08	
		1.55		2.03	
		1.48		1.89	

**I_{rel.}* is given as: m = medium, s = strong.

Beige Pigments

The components presented by the beige pigments in the XRF spectra are Ca, Fe and traces of Ni and Cu, with Fe exceeding slightly the quantity of Ca. In the XRD powder patterns the dominating lines belong to the plaster and quartz, some less intense unidentifiable lines also being present. Under the microscope iron hydroxide, an abundance of quartz, and occasional small particles of haematite could be detected in all samples.

Red Pigments

XRF showed all red pigments to contain large quantities of Fe. This was confirmed by XRD which indicated the presence of haematite. Microscopic examination revealed in almost all the samples haematite, clay, and a small or occasionally very small quantity of quartz. Knossos 10, contained in a dichromatic sample with brown pigment and exhibiting more a beige than a red colour, contains additional calcite. In Knossos 10, 15 and 17 brittle mica particles could be clearly detected among the clay minerals; this was biotite in Knossos 10, and muscovite in Knossos 15 and 17.

Pink Pigments

Fe was again the major constituent of these pigments as revealed by the XRF analysis. However the presence of haematite was not clear in the powder patterns of the samples. Under the microscope both pink samples exhibited mainly iron hydroxide, some haematite and a small quantity of quartz.

Brown Pigments

The only brown pigment was Knossos 11, contained in a dichromatic sample along with Knossos 10 Red. Thus nothing could be concluded from the XRF spectrum which presented mainly Fe. Microscopic examination indicated a layer of Egyptian Blue covered by, rather than mixed with, a layer of haematite, a practice noted previously with a brown from Mycenae. There was also some iron hydroxide and quartz [7].

Orange Pigments

Fe is the major constituent of the orange pigments as shown by the XRF analysis. This is due to the haematite contained in the samples as indicated by the XRD patterns. However the microscopic examination reveals also iron hydroxide, some quartz and clay, possibly mica in Knossos 20, but certainly muscovite in Knossos 21.

Yellow Pigments

Again the major constituent in the XRF spectra is Fe, but haematite could not be detected in the Debye-Scherrer patterns which exhibited simply the plaster lines. As determined by the microscopic examination of these pigments they consist mainly of amorphous iron hydroxide. Quartz is also present. Knossos 23 and 24 contain a small quantity of haematite and clay, which is mainly muscovite in Knossos 23.

5. CONCLUSIONS

The results of the X-ray analysis of the Knossos pigments indicate a strong similarity to those previously examined from Mycenae [6].

The plaster is a lime plaster (CaCO_3). The content of quartz and clay is so low that it was probably not a purposeful addition. Straw which appears in about half the samples may have been added as a filler but it too exists in small amounts.

The red, yellow, orange, and pink pigments are natural earth ochres; i.e. haematite and/or iron hydroxide. The beige is also a natural earth ochre diluted with quartz, while the brown contains ochre and Egyptian Blue. The black is apparently carbon; the white, bare plaster. The blue pigments are of the greatest interest. As at Mycenae, the Egyptian Blue contains tin and again the question arises as to whether or not any connection exists between the production of bronze and of the Egyptian Blue pigment.

Another interesting observation is that there appears to be a relationship between the amount of quartz and the depth of colour of each individual particle of blue regardless of size; i.e. the greater the amount of quartz in the sample, the lighter each individual blue particle, and the less the amount of quartz, the deeper the colour of each blue particle. This phenomenon was also noted during the examination of the Mycenae pigments and is most likely a result of the method of manufacture.

The most important discovery was the existence of glaucophane. The mineral, $\text{Na}_2\text{Mg}_3\text{Al}_2[\text{Si}_8\text{O}_{22}](\text{OH})_2$, belongs to the amphibole group of chain silicates. Replacement of Mg by Fe^{2+} and of Al by Fe^{3+} is always present in natural minerals. As Fe is very abundant in the XRF spectrum of Knossos 6 Blue, we probably have glaucophane with a tendency to ferroglaucophane. Glaucophane-bearing metamorphic rocks exist on Crete, both on

the Western and Eastern part of the island, but not in the neighbourhood of Knossos. The critical mineral assemblages described in literature as commonly additional to glaucophane (calcite, mica, quartz, chlorite, etc.) are also present in our pigment sample, as revealed by the microscopic examination.

Since the completion of the present study more detailed work on the Knossos pigments has begun, and approximately 50% of the blue pigments examined thus far have been glaucophane. This is particularly interesting in the light of the fact that, during some preliminary work in this laboratory in 1973, glaucophane was identified in a blue pigment sample from the Thera frescoes from Santorini. To our knowledge, this is the first time glaucophane has been reported as a fresco pigment.

ACKNOWLEDGEMENTS

The authors are grateful to Mr Mervyn Popham and Mr Mark Cameron of the British School of Archaeology at Athens for providing the samples and are also very indebted to Dr E. Dimou of the National Institute for Geological and Mining Research for the mineralogical examination of the pigments and to Mr J. Elpiziotis of the N.R.C. Democritos for his invaluable technical assistance and help in collecting the experimental data.

REFERENCES

- 1 EVANS, SIR ARTHUR, *The Palace of Minos at Knossos, I*, MacMillan and Company, London 1921.
- 2 CAMERON, MARK, and HOOD, SINCLAIR, *Catalogue of plates in Sir Arthur Evans' Knossos Fresco Atlas*, Gregg Press Ltd, London 1967.
- 3 HEATON, NOEL, 'The mural paintings of Knossos—An investigation into the method of their production', *Journal of the Royal Society of Arts*, 58 (1910), 206–212.
- 4 HEATON, NOEL, 'Minoan lime plaster and fresco painting', *Journal of the Royal Institute of British Architects*, 18 (1910–11), 697–710.
- 5 DUELL, P., and GETTENS, R. J., 'A review of the problem of Aegean wall painting', *Technical Studies*, 10 (1941, 1942), 179–223.
- 6 PROFI, S., WEIER, L., and FILIPPAKIS, S. E., 'X-ray analysis of Greek Bronze Age pigments from Mycenae', *Studies in Conservation*, 19 (1974), 105–112.
- 7 It has been suggested that the appearance of two layers need not indicate necessarily two painted layers and could be the result of the larger blue particles being more closely bound to the plaster as it set. Ascertainment of this, however, was beyond the scope of the techniques employed.

Received 21 August 1975

Authors' address: N.R.C. Democritos, Aghia Paraskevi Attikis, Greece.

S. E. FILIPPAKIS, born 1933, Ph.D. crystallography, Weizmann, Institute of Sciences, Israel. Present position: Senior scientist, group leader of X-ray Crystallography Laboratory, N.R.C. Democritos.

S. PROFI (Mrs), M.Sc. Natural Sciences, University of Athens. Present position: Scientific collaborator, Physics Department X-ray Laboratory.

L. WEIER, B.A., University of North Carolina; Certificate in Museology, Louvre, Paris; Diploma in Conservation of Antiquities, University of London. Present position: Conservator, Archaeological Museum of Athens.