X-RAY ANALYSIS OF PIGMENTS FROM PELLA, GREECE

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Abstract—Samples of pigments from a wall-painting of a house of the first Pompeian style (400 BC–168 BC) found in Pella, Greece, were analyzed by the non-destructive methods of X-ray fluorescence and X-ray diffraction. Red pigments were identified as cinnabar and iron oxide pigments (haematite and goethite). Blue was the well-known Egyptian blue and yellow was identified as goethite. A characteristic feature of the wall-painting was the presence of green earth, i.e. celadonite and glauconite, encountered for the first time in this series of investigations.

1 Introduction

With the present work our intention is to extend our study of the wall paintings and raw material used for pigment production by the ancient Greeks. In previous works pigments of wall-paintings from different ancient sites of important centers of civilization covering chronological dates from 3300 BC (early Minoan) up to the fourth century BC (Vergina tombs) were examined [1–6].

Pella, in Western Macedonia, Greece, was an important center of civilization from 400 BC up to 168 BC; during that time it was the capital of Macedonia, which had been transferred to Pella from Aegae.

Limited excavation works conducted by the Archaeological Ephorate of Edessa, south of the main archaeological site of Pella, brought to light fragments of multicolored stuccoes. This led to the commencement of a systematic excavation, which uncovered a large house of typical antique form with a peristyle court in the center, around which were developed the individual parts of the house. The discovery was of great importance because it was a confirmation of the hypothesis that the first Pompeian style was already known in Greece during the classical and hellenistic ages. Furthermore, it was the first time that such a large decorated surface area had been revealed which also gave an idea about the height of the rooms.

The multicolored stuccoes were found in a room (Figure 1) situated in the northern part of the house. After the removal of the stuccoed fragments and their processing in the laboratory it was possible to reconstruct the entire decoration of three walls (7m × 7m) of the room to the height of the ceiling, exactly 5 meters. The decoration of the room is rendered in a pure architectural arrangement of the surfaces in the first Pompeian style with its main architectural elements in relief.

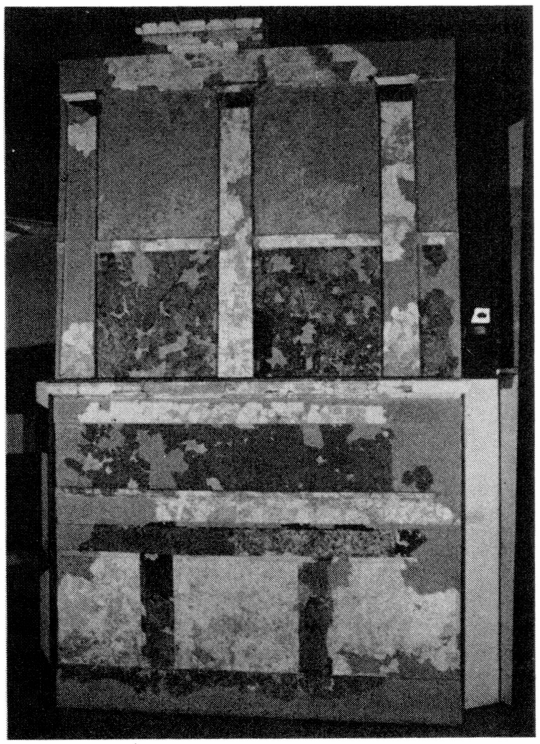

Figure 1 Wall-painting of the room in the house of Pella.

The decoration begins at the bottom with a toichobate 35cm high, decorated with large oblique strokes to suggest the veining of colored marble. The decoration is continued upwards with orthostates, white stretchers and colored binders, crowned by a string course, 20cm high, which imitate colored marble. A narrow black scotia, 4mm high, separates the string course from a white hepistyle topped by a geison, above which is set a course of yellow blocks. The course of these yellow blocks is crowned by a hepistyle on which the exceptionally protruding geison rests.

Over this is a decorative gallery of pilasters separated by red parapets, over which are light blue sur-

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faces imitating the open sky. The entire decoration ends at the top with yet another large geison. All the blocks of the stuccoed composition are drafted with margins 3cm wide.

From a technical point of view the stuccoes were made as follows. At the bottom of the walls a loosely made layer was preserved *in situ* to a height of 50cm, 0·2cm to 2·5cm thick. Its scattered fragments are relatively few, apparently because it was used only in the protruding decorative elements such as antas, hepistyles and toichobate. The second layer is compact, hard, and its thickness varies from 1·5mm to 4mm where the black scotia is found. The third layer is pure white and contains no sand at all. Its thickness varies from 1mm to 6mm and is made up of one to three sub-layers.

A special technical feature is the mixture of pink pigment with the plaster of the wall, while all the other colors are placed on the surfaces with a brush.

Similar stuccoed fragments were found in the adjacent room in a simpler form as well as in the entrance of the house. The stuccoes of the latter have a different disposition of the decorative elements and are of lower height than those of the first room described above. Technically, however, all the stuccoes are similarly made.

2 Samples

Twenty-four samples were examined, among them three from the corresponding layers of the stuccoes, belonging to the big room and the entrance. We tried to analyze representative samples of all pigments, e.g. five red, two green, two light-blue, three white, three yellow, two grey, three black and one pink.

3 Experimental techniques

The experimental techniques of X-ray fluorescence and X-ray diffraction were used for the present study. The equipment and methods employed are described in a previous paper [1].

4 Experimental results

The experimental results of XRF and XRD analysis are summarized in Table 1. The plaster contaminates the XRF spectra of the pigments as well as their powder patterns. Therefore the evaluation of the pigment spectra was achieved by analyzing each sample on both sides and subtracting the corresponding lines of the plaster.

4.1 Plaster

The corresponding stuccoes of all three layers were examined. The plaster of the third layer was identified as pure $CaCO_3$ with no α-SiO_2 while in the other two layers the presence of α-SiO_2 with $CaCO_3$ was characteristic.

Table 1 Analytical data on pigments from Pella

Sample	*Colour*	*X-ray fluorescence (XRF)*	*X-ray diffraction (XRD)*
1	Plaster, 1st layer	Ca,Fe,Sr,Ti (trace)	Calcite, α-quartz
2	Plaster, 2nd layer	Ca,Fe,Sr,Ti (trace)	Calcite, α-quartz
3	Plaster, 3rd layer	Ca,Fe,Sr,Ti (trace), Ni (trace)	Calcite
4	Red	Fe	Haematite (Fe_2O_3), calcite
5	Red	Hg	Cinnabar (HgS), calcite
6	Red	Fe	Haematite, calcite
7	Red	Fe	Haematite, calcite
8	Red	Fe,Pb	Haematite, goethite (α-FeO(OH)), goethite, calcite
9	Green	Fe	Glauconite and/or celadonite, calcite
10	Green	Fe	Glauconite and/or celadonite, calcite
11	Light blue	Cu,Pb	Calcite, α-quartz, weak lines
12	Light blue	Cu,Sn (trace), Pb	Egyptian blue ($CaCuSi_4O_{10}$), calcite, α-quartz
13	Yellow	Fe,Pb	Goethite, calcite, unidentified lines
14	Yellow	Fe,Pb	Goethite, calcite
15	Yellow	Fe,Pb	Goethite, calcite
16	Pink	Ca,Pb	Calcite
17	White	Ca	Calcite
18	White	Ca	Calcite
19	White	Ca	Calcite
20	Black	Ca	Calcite, α-quartz
21	Black	Ca,Mn (trace)	Calcite
22	Black	Ca,Cu (trace)	Calcite
23	Grey	Ca	Calcite, α-quartz
24	Grey	Ca,Cu (trace)	Calcite

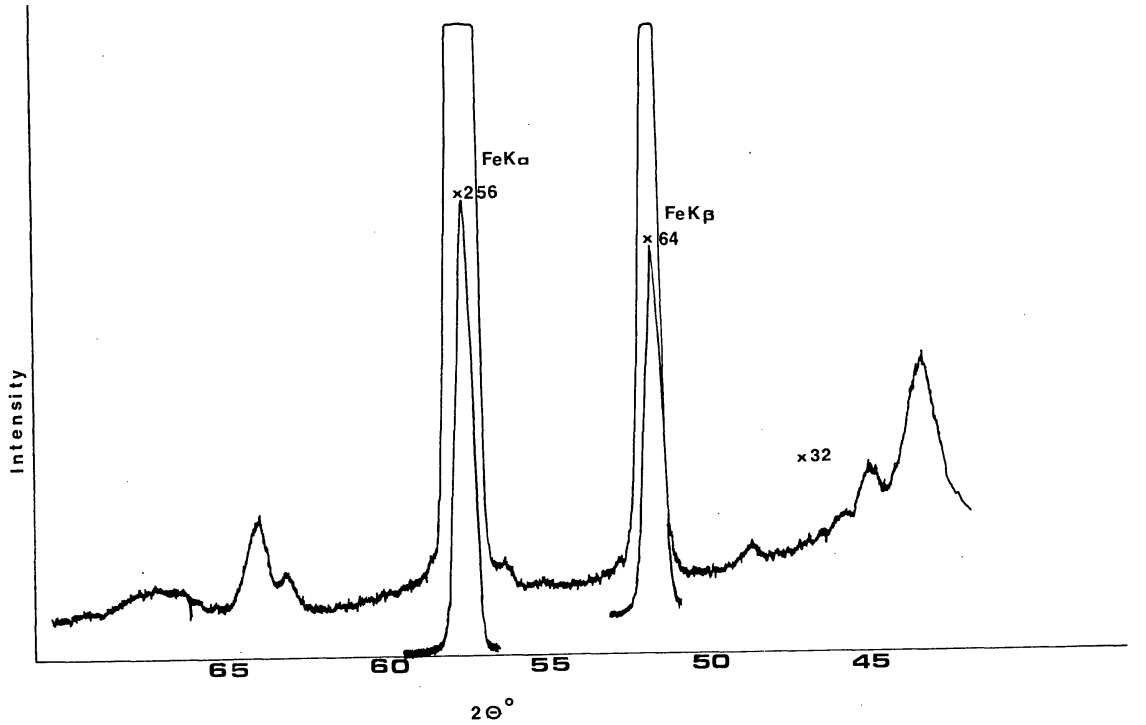

Figure 2 XRF spectrum of green pigment, Mo tube (40kV/20mA) LiF(200) analyzer.

4.2 Red

The XRF spectra showed that all the red pigments except one contained large quantities of iron and in sample 5 the major element present is mercury. The XRD pattern of the latter was identical with HgS (cinnabar) together with $CaCO_3$, which is present in all samples due to the plaster. The XRD patterns of the other samples showed the presence of Fe_2O_3 (haematite) and Fe_2O_3 mixed with α-FeO(OH) goethite (sample 8).

4.3 Green

From the XRF spectra, iron was identified as the major component in all samples while Cu was present only in trace quantities due to the plaster (Figure 2). The corresponding XRD pattern showed, besides the $CaCO_3$ presence due to the plaster, the characteristic lines of a ferrous silicate which could be either celadonite or glauconite. With the X-ray diffraction techniques used for the identification of the pigments, celadonite is not easily distinguished from glauconite. In Table 2 the d-spacings of these two minerals (ASTM-17-521 and ASTM 9-439) are listed together with the lines of our green sample.

Table 2 X-ray patterns for celadonite and glauconite in comparison with the green pigment (sample 10)

Sample 10	*Celadonite (ASTM card 17–521)*	*I/I_O*	*Glauconite (ASTM card 9–439)*	*I/I_O*
10·2	9·97	45	10·1	100
4·53	4·53	85	4·53	80
4·34	4·35	40	4·35	20
	4·14	35	4·12	10
3·62	3·64	80	3·63	40
	3·35	60	3·33	60
3·34				
	3·32	70		
	3·09	80	3·09	40
3·09				
	2·90	10	2·89	5
2·68	2·68	75	2·67	10
2·60	2·60	70	2·59	100
2·57	2·58	100		
2·40	2·40	75	2·40	60
	2·26	20	2·26	20
	2·21	25	2·21	10
	2·15	30	2·15	20

4.4 Blue

The major component of the XRF spectra was Cu along with Pb and Sn as trace element in sample 12. From the XRD pattern of sample 12, we identified Egyptian blue ($CaCuSi_4O_{10}$). It was difficult to measure the weak lines present in the XRD pattern of sample 11, probably due to the small amount of blue crystals present in the plaster.

4.5 Yellow

Fe is the major constituent in the XRF spectra of all samples along with Pb as minor element. The XRD pattern was identical with that of α-FeO(OH) (goethite) and $CaCO_3$.

4.6 Pink

The XRF spectrum showed the presence of Ca as major element with Pb as minor element, while no iron other than that of the plaster was present. The XRD pattern was identical with pure $CaCO_3$. No coloring crystalline material could be detected.

4.7 White

For the white pigments the XRF spectra showed Ca in large quantities and the XRD pattern showed all the characteristic lines of $CaCO_3$.

4.8 Black-grey

Ca was the only major element detected by XRF in all black and grey pigments, while the XRD patterns were identical with $CaCO_3$ or mixtures of $CaCO_3$ and α-SiO_2 The examination under the microscope showed opaque black particles similar to those observed in black pigments from other sites.

5 Conclusions

The results of this study extend our investigation of ancient Greek pigments chronologically up to the second century BC.

The iron oxide pigments, such as haematite, goethite or the mixture of both, were widely used during this period as red and yellow coloring materials. Cinnabar (HgS) was also used as a red pigment (identified by the authors on the wall-paintings of the neighbouring Vergina tombs [6]).

The most widely known synthetic pigment in antiquity, Egyptian blue, continued to be the source of blue coloring material during the Pella period.

Pure calcite was the only white pigment used, while black and grey were probably, as usual, a mixture of a carbon black with calcite.

The interesting point of this work was the identification of a ferrous silicate celadonite and/or glauconite as green pigment. The mixture of these two silicates is known as green earth [7]. In all our previous analyses no green pigment was identified, the green surfaces being made by the artist as a mixture of Egyptian blue with ochre.

A special feature of this wall-painting was the presence of a pink pigment applied with true fresco technique in contrast to the other pigments which were applied with a brush as a thin layer. With the techniques used here it was not possible to identify the pink pigment, the XRD and XRF patterns being identical to that of the plaster.

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Résumé—Des échantillons de pigments provenant d'une maison pompéinne Première Epoque (400-168 avant notre ère) trouvés à Pella en Grèce, ont été analysés par des méthodes non-destructives telles que la fluorescence X et la diffraction X. Les pigments rouges ont été identifiés comme étant constitués de cinabre et d'oxyde de fer (hématite et goethite). Le bleu est le bleu égyptien bien connu, et le jaune de la goethite. Une charactéristique de ces peintures murales est la présence de terre verte, c'est à dire de celadonite et clauconite, rencontrée pour la première fois dans ces séries.

Auszug—Es wurden Proben von Pigmenten einer Wandbemalung eines Hauses des ersten pompeischen Stils (400 v.Chr. — 168 v.Chr.), die in Pella, Griechenland, gefunden wurde, durch die zerstörungsfreien Methoden der Röntgenstrahlenfluoreszenz und Röntgenstrahlenbeugung analysiert. Rote Pigmente wurden als Zinnober und Eisenoxydpigmente (Hämatit und Goethit) identifiziert. Blau war das bekannte Ägyptischblau, und Gelb wurde als Goethit identifiziert. Ein charakteristisches Merkmal der Wandbemalung war das Vorhandensein von Veroneser Grünerde, d.h. Seladonit und Glaukonit, die zum ersten Male in dieser Untersuchungsreihe vorgefunden wurde.