

# Characterization of Some Inorganic Pigments and Plasters Used in Old Kingdom, Saqqara Area, Egypt

Adel I. M. AKARISH\*, Ahmed S. SHOEIB\*\* and Hiroshi SUITA\*\*\*

## [Abstract]

This work presents the results of an investigation of the inorganic paintings used in the burial chamber at Idout tomb. This tomb was discovered in 1927 and dates back to the Old Kingdom, Early 6th Dynasty (2420-2280 B.C.). Blue, red, dark red, brown yellow, white and black colors were used in the tomb in order to creating the painting, which kept their original hue of their brilliance color till now. The technical features of the painting were investigated using optical and digital microscope (VHX). The components of the substrate, paintings and preparatory layer of the painted areas were characterized using chemical analyses; optical microscopy, X-ray diffraction (XRD) and Scanning Electron Microscopy Equipped with Energy Dispersive X-ray Analysis System (SEM-EDS). The pigments either natural or semi-synthetic, or synthetic were utilized to produce pure colors (blue, red, yellow, white, black and brown). SEM-EDS and XRD highlighted that the painting was made on a preparatory layer of gypsum, applied onto coarser layer built up mainly of gypsum admixed with limestone fragments and sand.

## 1 Introduction

The Mastaba of Idout lies at the middle of Saqqara archaeological site, alongside the south enclosure of the Step Pyramid of Djoser. Saqqara is one of the largest areas of ancient monuments and it is well known for housing various monuments, extending from the First Dynasty to the early Christian era, main ones being pyramids and mastabas of the Old Kingdom. The Mastaba of Idout dates back to 2360 B.C. and it is one of the well-known and beautiful in Saqqara area and also in Egypt. It was discovered in 1927 by Firth<sup>1</sup> and later published in 1935 by Macramallah<sup>2</sup>. When it was excavated, the mastaba became known well for its beautiful relief preserved in original brilliance. The burial chamber was hewn in calcareous rocks (mainly limestone and marl), several meters under the mastaba and connected to the mastaba through a vertical shaft. The rock surface was smoothed and covered by a reinforcing rough mortar layer, formed of coarse gypsum in which thin limestone flakes or powder together with fine sand was added as filler materials. The thickness of the mortar layer vary from 1 mm up to 10 cm. Over this coarse layer a fine layer composed mainly of gypsum was applied (0.035 - 0.050 mm). Therefore, the plaster layer was used to treat the irregularities and smoothen the surface of the bed rock (Nicholson and Shaw, 2003)<sup>3</sup>. On the fine plaster layer, a variety of foods and offering lists were depicted to secure the happy life of the deceased. The walls of the tomb and its burial chambers were decorated with brilliant colors (Fig. 1). The colors are mainly blue, red, yellow, brown and white in addition to black and faint green (Fig. 2). On the walls (South

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\* Department of Geological Sciences, National Research Centre, Egypt.

\*\* Department of Conservation and Restoration, Faculty of Archaeology, Cairo University, Egypt.

\*\*\* Faculty of Letters, Kansai University, Japan.

wall), the colors appear to be as fresh as they were applied. The pigments adhered to the surface of plaster gypsum substrate by using a binding medium of plant or animal origin without remoistening of plaster surface. This is Tempera technique.

Pigments vary in their chemical properties, because they composed of a broad variety of chemical compounds. The shade (hue) and clarity of the colors are mainly related to color absorption, the size, shape, and texture of pigment particles<sup>4</sup> as well as the presence or absence of impurities.

The main aim of this article is to perform detailed study to categorize some of the inorganic painting materials used in the creation of painted plaster belonging to the Old Kingdom at Saqqara area in Egypt. The studies performed in the current work include application of optical microscopy (OM), and Scanning Electron Microscopy Equipped with an Energy Dispersive X-ray Spectrometer (SEM-EDS), XRD and VHX-100 Series Digital Microscope.

## 2 Material and Methods

The painting in the burial chamber has suffered from severe deterioration that let large areas of plaster together with painted layer fall down from its wall support and fragmented. Therefore, the studied samples of pigments and preparatory layer were collected from the fallen fragments on the ground of the burial chamber (Fig. 3). The size of the selected samples was as large as necessary but as minute as possible.

The components of the substrate and preparatory layer of the painted areas were characterized using confidential chemical analyses<sup>5</sup>. The obtained data was expressed in terms of acid insoluble residue (AIR), CaO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, SO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> as weight %. Moreover, water loss at 230°C was detected for mortar and plaster samples.

The morphology of the pigment particles, including homogeneity, shape, size, surface character, and crystal form, as well as the sequence of paint layers, color and texture of those layers and layer thickness, was examined using Digital Microscope, VHX-100 Series, Keyence.

The morphology and composition of pigments were, more accurately, investigated using SEM-EDS analysis. This analysis was performed using Environmental Scanning Electron Microscope (ESEM) coupled with EDAX (Energy Dispersive Analysis by X-ray), FEI Company Quanta 200, at the Center of Research and Conservation of Antiquities. This kind of microscope is non-destructive, as the samples are used as there are, without any treatment (coating). Semi-quantitative micro-chemical analysis was carried out using Energy Dispersive X-ray spectrometer (EDS), and the resulting analytical totals were automatically normalized to 100%.

X-ray diffraction was used to determine their mineralogical composition. The powder diffraction patterns of the samples were gained through Cu K $\alpha$  radiation. Spectra were collected from 2–60 2  $\theta$ ; the scanning speed was 2 $\theta$  = 1 degree/min. at constant voltage 40 kV, and 25mA using PW 1840 X-ray diffraction.

## 3 Results

The results of the analyzed inorganic pigments, plaster layer of the selected samples as well as the rock substrate are given hereunder.

### 3.1 Rock Substrate

The rock substrate (bed rock) was formed mainly of limestone (argillaceous in some parts) and marlstone. Its chemical analysis (Table 1) implied that they were formed mainly of calcite, judging from the high content of CaO with little quartz and clays, as can be indicated by the acid insoluble (AIR) content. This was confirmed by the mineralogical and petrographical studies; details of these are given by Akarish and Shoeib<sup>6</sup>.

### 3.2 Plaster Layer

Using Digital Microscopic investigations, we distinguished two main layers of the plaster (Fig. 4) used to overcome the faults in poor stone and to produce a flat and smooth surface for painting. The base coarse layer mainly consisted of gypsum, calcite and quartz (XRD analyses), while the top fine coat layer was mainly based on gypsum with or without very fine sand. Chemical analyses of the coarser layer (Table 2) revealed high content of acid insoluble materials, AIR, (37% in average), reflecting the high amount of sand. It contained relatively lower amount of combined water (average 4.5%). The average contents of CaO and  $\text{SO}_3^-$  were 26.5% and 9.5%, respectively. Moreover,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{Cl}^-$  concentrations were low. However,  $\text{Na}_2\text{O}$  and  $\text{Cl}^-$  showed relatively higher amounts in some samples, implying the presence of salts, a feature that was not indicated through X-ray analysis. The sulphate ( $\text{SO}_3^-$ ) content was too small to match with the content of carbonate, reflecting that much of CaO was present as carbonate (calcite), confirmed by less content of combined water. This suggested that thin limestone flakes or powder together with fine sand were added as filler materials during the preparation of the mortar. Presence of calcite was confirmed by XRD analysis. Absence of carbonate in the finer layer and plaster sample corroborated such interpretation. On the other hand, the finer layer was characterized by (1) low content of AIR, (2) high content of combined water, indicating higher percentage of gypsum, and low contents of  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Cl}^-$  (Table 2). The CaO concentration matches very well with sulphate  $\text{SO}_3^-$  content and also corroborates with the amount of water content, which reflect that CaO was present only in a form of calcium sulphate minerals; it is evident that the higher the water contents were the higher the percentage of gypsum was. This is in accordance with the results obtained from the mineralogical analyses.

### 3.3 Pigments

We started by characterizing the inorganic components of the illustrative layers. The color interpretation can be done by understanding the character of the pigments, their features such as morphology and thickness and the sequence of the colored layers.

**Blue color:** The Egyptians developed a wide range of pigment variety including what is now known as "Egyptian Blue," which was the first of its color at the time of its development. The first recorded use of Egyptian Blue as color name in English was in 1809<sup>7</sup>. The earliest evidence for the use of Egyptian Blue is in the 4th Dynasty (ca 2575 - 2467 B.C.). It continued to be used as pigment for the decoration of tombs, wall paintings, furnishings and statues. Its use continued throughout the Late Period and Greco-Roman Period, only dying out in the 4th century A.D., when the secret of its manufacture was lost<sup>8</sup>. Egyptian Blue is a synthetic blue pigment; its color is due to a calcium-copper tetrasilicate  $\text{CaCuSi}_4\text{O}_{10}$  of the exact same composition as natural mineral, cuprorivaite. It was produced by mixing silica, lime, copper compound

and alkali flux (natron or plantash) to reduce the required temperature<sup>9</sup>. This mixture was heated to a temperature between 850 and 1000 °C (basing on the amount of alkali used) to produce a colored glass or frit and later ground to powder for use. The result is cuprorivaite or Egyptian Blue, carbon dioxide and water vapor:  $\text{Cu}_2\text{CO}_3(\text{OH})_2 + 8\text{SiO}_2 + 2\text{CaCO}_3 \rightarrow 2\text{CaCuSi}_4\text{O}_{10} + 3\text{CO}_2 + \text{H}_2\text{O}$ .

Two types of blue pigments used in Idout burial chamber were distinguished, dark blue (Fig. 5) and light blue (Fig. 6). Both microscopic and SEM observation showed that the dark blue color consisted of very coarse to coarse rectangular layers of coarse sized blue crystals (Fig. 7), cluster together formed of cuprorivaite. It was thickly applied with coarse particles up to 0.04 mm across (Fig. 8), giving the dark blue-hued appearance. In contrast, the light blue color has fine tabular crystals about 15 µm to 30 µm that are uniformly distributed with some unreacted quartz (Fig. 9). The light blue color containing white color may be of gypsum. But, it is not certain if it is an additive to the blue or appears as contamination from plaster layer.

The shade of blue, as revealed in our study, was related to the coarseness and fineness of Egyptian Blue as it was determined by the degree of aggregation of its particles. Coarse Egyptian Blue, had a thick in form, due to the large clusters of crystals, which adhere to the unreacted quartz. This clustering resulted in a dark blue color that was the appearance of coarse Egyptian Blue. Alternatively, fine-textured Egyptian Blue consisted of smaller clusters that were uniformly interspersed between the unreacted quartz grains and tended to be light blue in color<sup>10</sup>. The hue of the colors also depended on the level of alkali added to the mixture and, therefore the more the alkali, thus the more glass-formed, the more the diluted appearance was gained<sup>8</sup>.

The major components of the studied blue pigments are cuprorivaite and quartz (unreacted), as indicated by mineralogical analyses (XRD), and is confirmed by micro-chemical analysis (Fig. 10). The later revealed that the main constituents are SiO<sub>2</sub> (62.12 – 63.83%), CaO (12.63 - 13.54 %) and CuO (13.48 - 15.83%), which fall in the ranges given by Tite et al. 1987 for Egyptian Blue in Egyptian antiquities and elsewhere; their data indicated ranges of SiO<sub>2</sub>, CaO and CuO are 60 - 70%, 7 - 15% and 10 - 20%, respectively. SEM-EDS semi-quantitative analyses are shown in Table 3.

The total alkali content in analyzed samples was greater than 1%, suggesting that the alkali was introduced into the mixture and not as an impurity from other components. The sources of alkali may be natron as evident from the absence of phosphorous and low content of magnesia. It may be from Wadi el-Natron. The presence of some metals (e.g. titanium) in the studied samples could be a result of the presence Ti-bearing minerals found in desert sand. Its presence in Egyptian Blue indicates that quartz sand present in the area of manufacture was used as silica source.

**Red Colors:** Red pigments show that massive granular aggregate particles appears to be uniform (Fig. 11). The results obtained from the XRD analysis indicated that the red color was formed mainly of hematite (red iron oxide, Fe<sub>2</sub>O<sub>3</sub>). The EDX analysis (Fig. 12) confirmed the presence of iron oxide by the presence of the iron peak (~37%). Presence of aluminium and silicon detected by EDS analysis suggested the existence of aluminosilicate materials (clay minerals etc.), together with the presence of traces of minerals (Ti, V, Co) (Fig. 12), judging that the red ochre was used as red pigments in Idout tomb. Red ochre is natural mineral pigment colored by the presence of the anhydrous, iron oxide, hematite. Ochre forms a very wide class of natural inorganic pigments. Ochre is characterized by having wide color range that can differ from deep red or brownish to orange and finally to bright yellow. Red ochre was used in Egypt from 5th Dynasty till the Roman times. Lucas (1962)<sup>11</sup> recorded the Dakhla Oasis, Western Desert as provenance for good ochre.

Yellow color: Yellow layer was compact and homogeneous. Its chemical constituent confirmed that yellow ochre, where the yellow was given by goethite, had been mixed with gypsum. Inclusion of red which, when confirmed by analysis, showed that its major component was iron.

Brown Color: It was formed mainly of brown ochre as hematite mineral ( $\text{Fe}_2\text{O}_3$ ) was the main component identified, plus aluminum and silicon detected by EDS analysis, suggesting that the brown ochre used as brown color.

Grey color: Grey pigment was produced by applying black (carbon black) over white gypsum layer or mixing of black with white gypsum (Fig. 13), while dark grey pigment may be applied over an unprepared surface as we can see that the painting layer shows irregular line with different thickness.

White color: White pigment produced by spreading a film of gypsum plaster (hemihydrate,  $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ ), which was the same as the one used for preparatory layer but was less thick and had a compact surface.

Black color: The black pigment layer is uniform and contained fibrous particles and sometimes might be applied directly on the coarse irregular plaster layer. The presence of fibrous particles suggested that black color was produced using carbon black, deriving from wood charcoal (Pallecchi et al.)<sup>12</sup>. Pallecchi et al. indicated that the anatomical structure of wood was one of the first characteristic elements that stood out in the fibrous particles. Black charcoal was found to be mixed with white or applied over white in grey samples.

#### 4 Conclusions

The paintings of the inorganic pigments from Old Kingdom were performed, signifying extensive usage of pigments frequently used in ancient Egyptian wall paintings.

The paintings in Idout burial chamber was produced with a palette formed of four basic colors: white, red, blue, yellow and black that were produced using various hues.

Red, yellow and brown ochres were used for the creation of red, brown and yellow pigments; hematite in the first and second case, and goethite in the third, are the iron minerals that provide the colors.

White pigments produced by spreading a thin film of gypsum, which was the same as the one used for preparatory layer.

Blue appears to be produced from pigment taken from Egyptian Blue, based on the presence of mineral cuprorivaite. Two types of blue pigments (dark and light blues) were distinguished. Natron was the alkali used and might come from Wadi el-Natron. Quartz sand present in the area of manufacture was used as silica source.

Two layers of plaster were noticed: the coarse one with higher thickness, consisting mainly of quartz, calcite and gypsum: the fine white wash thin irregular layer consisting mainly of gypsum with little or without quartz.

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Fig. 1 Wall at the burial chamber decorated with brilliance colors

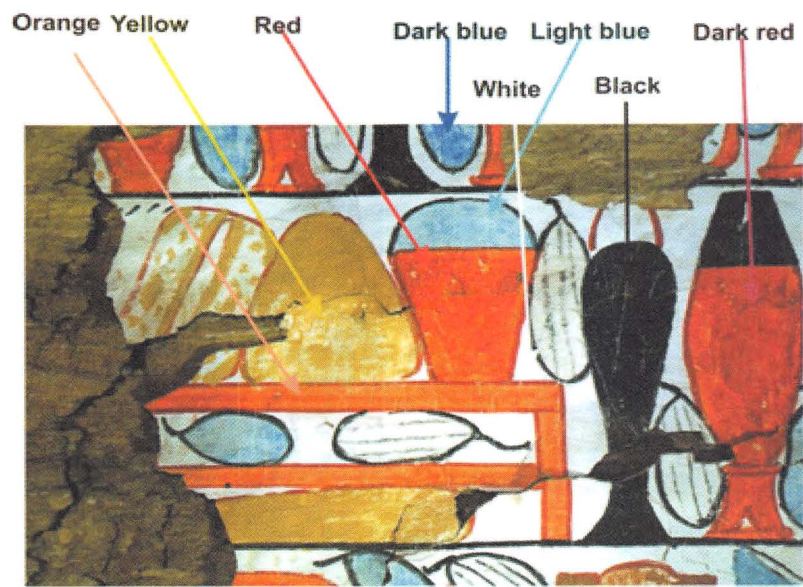


Fig. 2 Inorganic pigments used in Old Kingdom decoration of Idout burial chamber



Fig. 3 Fallen fragments

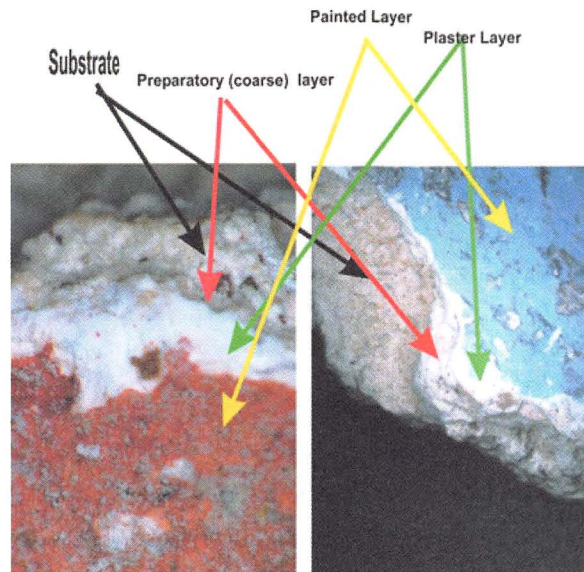


Fig. 4 Microscopic observation of the two plaster layers and the painted layer produced on the limestone substrate

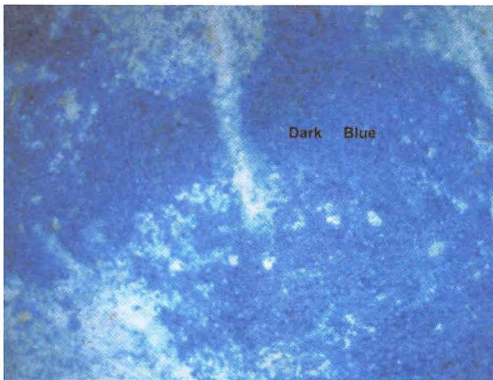


Fig. 5 Microscopic view for the dark blue colour formed of coarse particles of cuprorivaite (Egyptian Blue pigment)

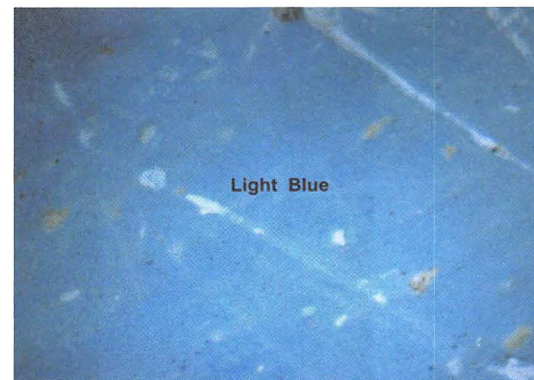


Fig. 6 Microscopic view for light blue formed of fine particles

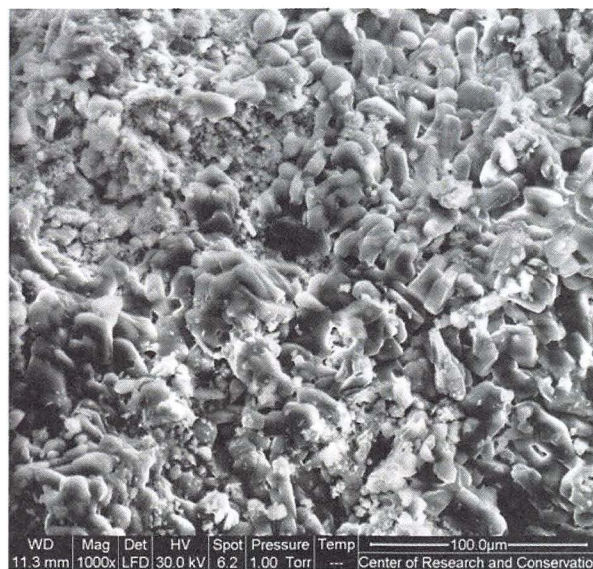


Fig. 7 SEM photomicrograph showing coarse tabular crystal of the dark blue color



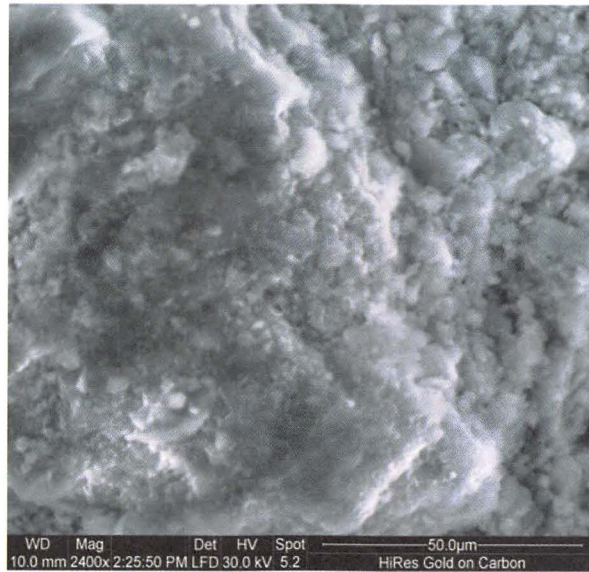


Fig. 8 SEM microphotograph showing thickly applied layers of coarse dark blue crystals

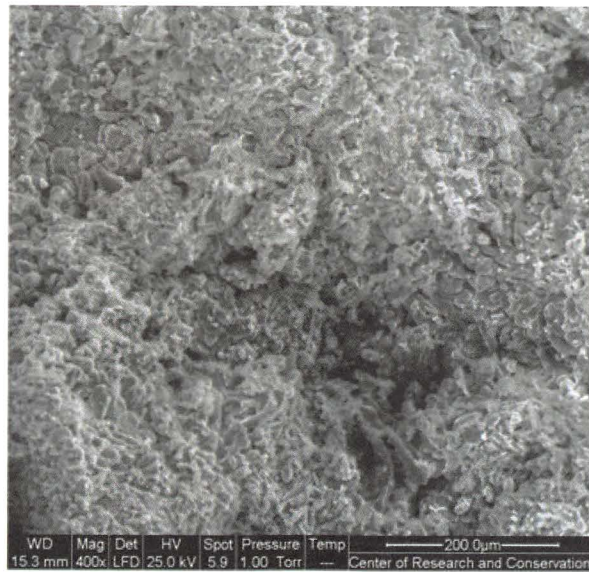


Fig. 9 SEM photomicrograph showing fine crystals of light blue colour

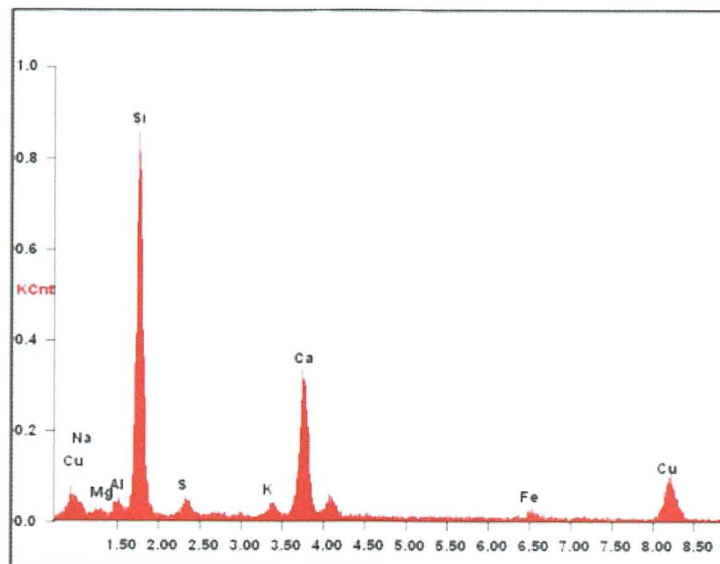


Fig. 10 Micro chemical analysis of blue pigment



Fig. 11 Microscopic view of red pigments (massive granular aggregate particles appear to be uniform)

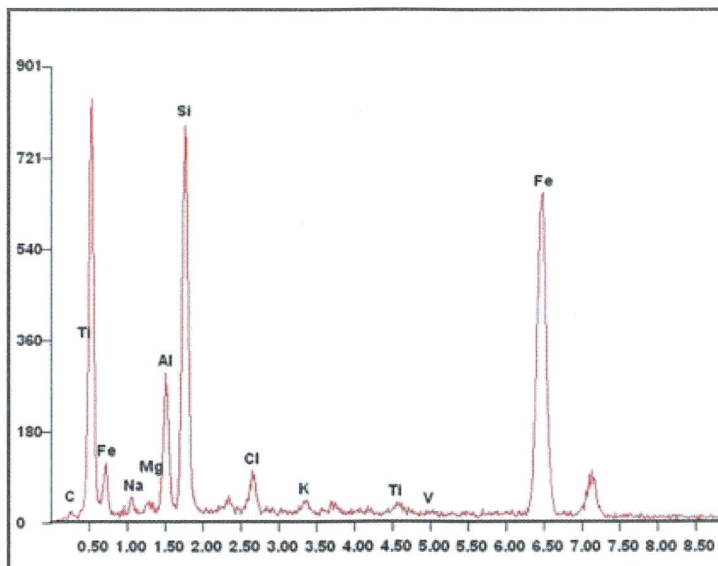


Fig. 12 EDX analysis of red pigments



Fig. 13 Microscopic view of grey pigments (black carbon applied over white plaster)



Fig. 14 Microscopic view of dark grey with fibers particles

Component%	Wall support samples	
	Limestone	Marlstone
	AIR*	18.58
CaO	44.39	20.08
MgO	Nil	Nil
Na <sub>2</sub> O	0.48	1.69
K <sub>2</sub> O	0.06	0.10
Cl <sup>-</sup>	0.62	1.77
SO <sub>3</sub> <sup>2-</sup>	0.24	1.08
LOI**	35.87	23.40

Table 1 Chemical analysis of the wall support substrate

Component%	Preparatory plaster layer			
	Rough coat		Finer coat	
	A	B	A	B
Insoluble Residue (AIR)	37.32	37.33	4.93	4.86
CaO	26.43	26.67	32.96	35.55
MgO	----	----	----	----
Na <sub>2</sub> O	1.13	0.48	0.07	0.06
K <sub>2</sub> O	0.16	0.10	0.06	0.05
Cl <sup>-</sup>	0.54	0.48	0.20	0.27
SO <sub>3</sub> <sup>2-</sup>	9.17	9.99	45.40	42.51
Water loss at 230°C	5.38	3.72	14.58	12.37

Table 2 Chemical analysis of preparatory plaster layer

Element %	Sp. 1	Sp. 2	Sp. 3	Tite et al. 1987*	Cuprorivaite composition
Na <sub>2</sub> O	01.87	01.99	01.96		
MgO	01.10	01.25	01.30		
Al <sub>2</sub> O <sub>3</sub>	02.25	02.40	02.44		
SiO <sub>2</sub>	63.83	62.12	62.47	60-70	64
SO <sub>3</sub>	3.95	03.09	4.56		
K <sub>2</sub> O	01.43	01.25	01.28		
CaO	12.76	12.63	13.54	7-15	15
Fe <sub>2</sub> O <sub>3</sub>	01.34	01.45	0.92		
CuO	11.48	13.83	11.55	10-20	21

Table 3 EDX analysis of the blue color compared with Tite et al., 1987, and Cuprorivaite composition