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Mineral composition of pigments and plasters from the Hatshepsut Temple in Deir el Bahari. Upper Egypt.

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Introduction

Pigments and paints used for decoration of Egyptian temples and tombs were the objects of interests of numerous scientists (Gazda 1997, 1998, 200 a, b, 2001, Barwik 1998, 200 2001, Pawlicki 2000, Szafrański 2001). This work consists of two parts: first is devoted to mineralogy of colorful minerals occurring in the shale of Esna in the region of Deir el Bahari. The second presents the results of examinations of mineral paints covering sculptures and decoration parts in the Chapel of the Queen Hatshepsut. Sampled were only completely destructed elements). An explanation of its history was kindly provided by dr Mirosław Barwik from the Institute of Archaeology of the Warsaw University. The authors would like to express their gratitude to him.

General geology of the area

The region of Deir el Bahari is located on the platform structures of the Upper Egypt (Said 1965, Yehia 1987, Pawlikowski 1994). Esna shale was deposited on a 15 m thick lower part of light Theban limestones. The Shale was divided into the following beds:

1. A lower part - 15 m thick green-grayish shale containing small iron nodules.
2. A central part of the sequence composed of marly limestones with iron and gypsum mineralization
3. An upper part built of marls interbedded with shale containing iron nodules as well as gypsum mineralization.

All sequences described above are overlayered by a thick complex of Eocene limestones, the so called Theban Formation.

Detailed field observation of geological profiles in the vicinity of the Hatshepsut Temple allowed us to notice that ferrous concretions from the Esna shale, when weathered, alter to colorful minerals resembling the ones that cover the decorations in the interior of the Temple as well as the ones in the Valley of Kings. That is why, samples of the nodules, in various stages of weathering were collected (Photo 1, Photo 2) and submitted to research.

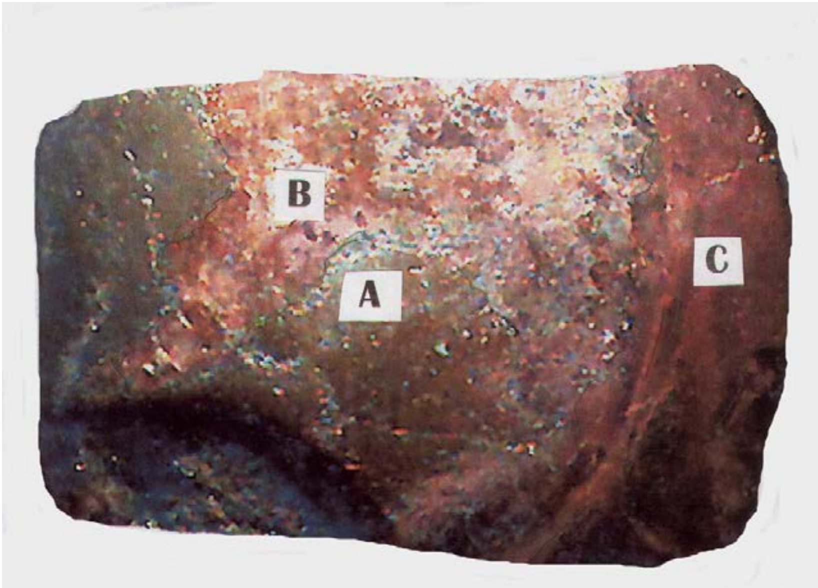


Photo 1. Cross section of a fragment of weathered pyrite nodule from Esna shale. A – relicts of pyrite, B – zone of natrojarosite, C – zone composed of hematite. Magnification 4 x.

Photo 2. Concretions from Esna shale composed of various secondary minerals formed after sulphides and used at the past as base for some mineral pigments.

Samples of paints that decorate the Chapel of Hatshepsut were collected from tiny architectonic fragments from the debris on the floor or directly from paintings. A detailed description is presented in the second part of the work.

Methods of research

During the examination both the natural colorful minerals and mineral paints from the Hatshepsut Chapel, the following methods were employed:

1. polarizing light microscopy in reflected light
2. polarizing light microscopy in transmitted light
3. X-ray diffractometric analysis
4. scanning microscopy with EDS microanalyses
5. Fourier infrared spectroscopy

Part I

Mineralogical characterization of colorful minerals present at the Esna shale at area near Hatshepsut Temple

Microscopic examination in polarized reflected light

It was established that a primary mineral in natural nodules present at Esna shale was determined as pyrite. Along with pyrite, a numerous pieces of organic fragments are present here. It proves that the origin of nodules is, at least partially, biogenic.

The mineral phases as the product of weathering prove the morphological changes and creation of many colorful minerals. Description of the mentioned minerals is presented below.

Mineralogical description of natural colorful minerals

Brown minerals with red shade

X-ray diffractometric phase analysis proved the presence of many minerals, mainly hematite and goethite. Colorless minerals are anhydrite, bassanite and quartz (Fig. 1).

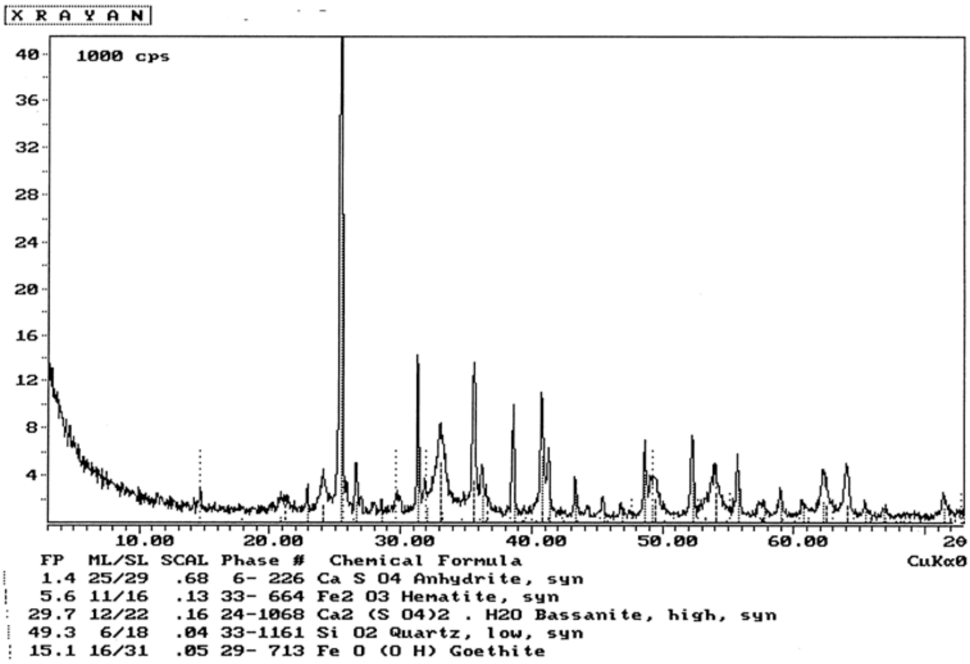


Fig. 1 X- ray pattern of brown minerals with red shade formed as secondary minerals in nodule from Esna shale.

Dark brown minerals

X-ray diffractometric phase analysis proved the presence of polymineral mixture (Fig. 2) with goethite prevailing over hematite. Bassanite, gypsum and barite were also recognized in the sample.

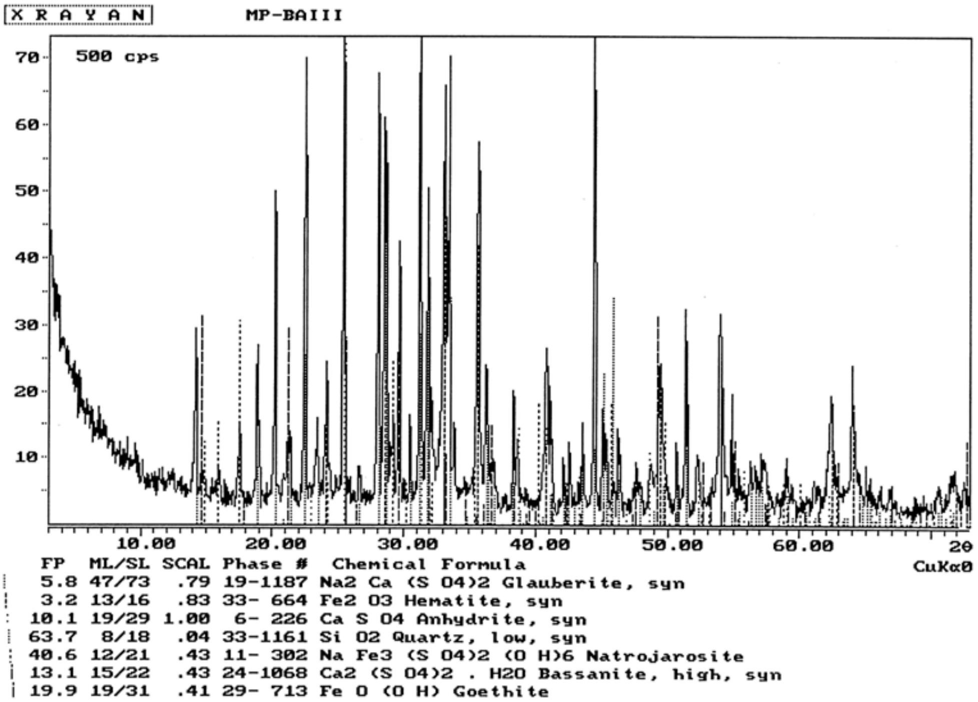


Fig. 2 X- ray pattern of dark brown minerals formed as secondary minerals in nodule from Esna shale.

Red minerals

Two samples of red shade were designated for X-ray analyses (Fig. 3). One of them was a pseudomorphs after pyrite nodule. The second one was powdery. Their mineral composition is different. Sample no 3 consists of hematite, goethite and jarosite as well as gypsum, anhydrite and glauberite (sulphate of natrium and calcite). The second red sample is composed of the same colorful minerals but in different proportions. There is no glauberite here.

Orange minerals

Orange sample (Fig. 4) is a mixture of hematite, goethite and natrojarosite. They are accompanied by colorless barite and bassanite. An orange color results from the mixture of red and dark-red ferric (hematite, goethite) minerals with yellow natrojarosite. The intensity of the red or yellow shade depends on the ratio of natrojarosite and other ferric minerals.

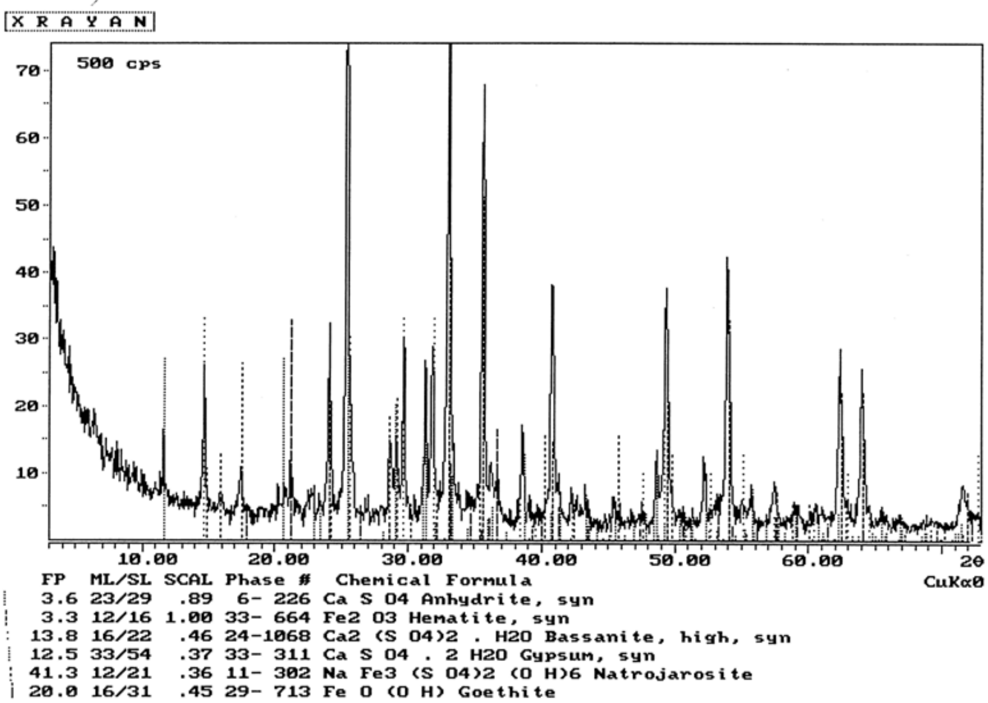


Fig. 3. X - ray patterns of red minerals formed as secondary minerals in nodule from Esna shale.

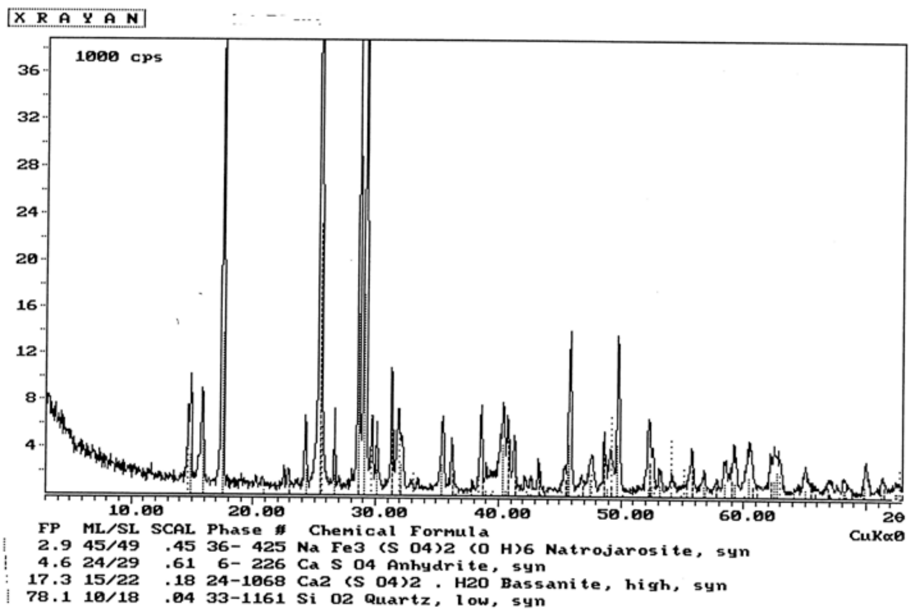


Fig. 4 X- ray pattern of the orange minerals formed as secondary minerals in nodules from Esna shale.

Yellow minerals

Yellow samples (Fig. 5) are composed mainly of natrojarosite and colorless minerals: anhydrite, bassanite and quartz. The intensity of the yellow hue depends on the ratio of the amount of natrojarosite and colorless minerals.

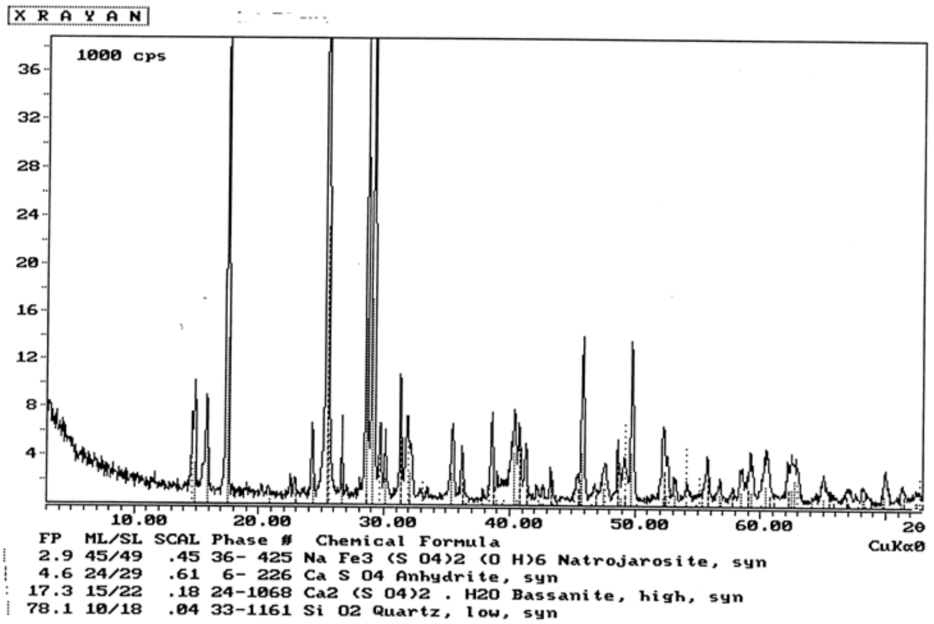


Fig. 5 X - ray pattern yellow minerals formed as secondary minerals in nodule from Esna shale

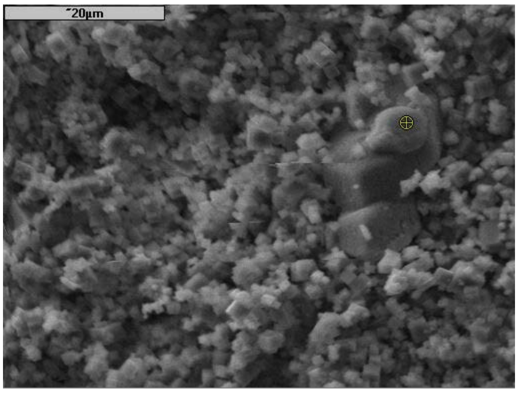
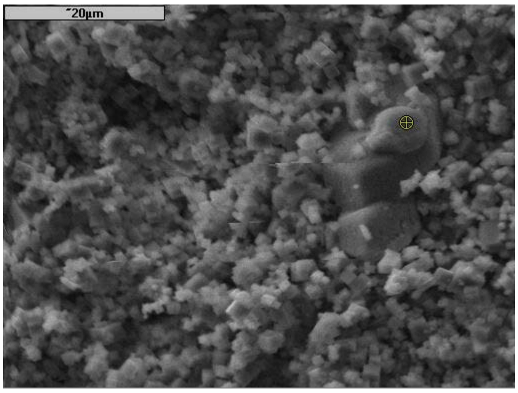
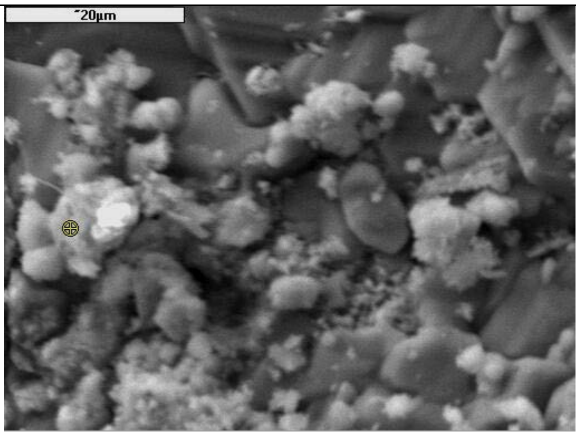
SEM/EDS examinations

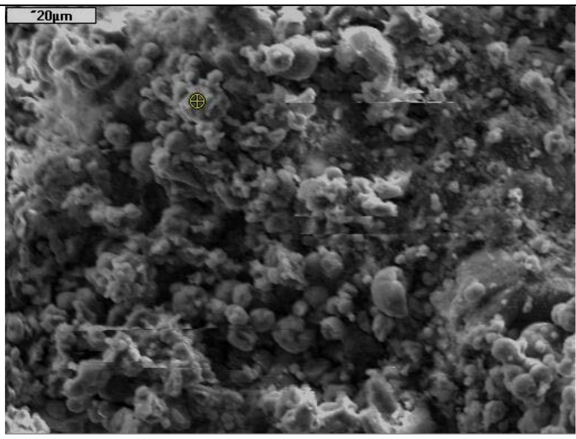
Five samples were subjected to SEM/EDS investigations: yellow, two dark red and brown samples. The results are summarized in the Table below.

Table 1

SEM/EDS analyses of yellow, red and dark red minerals of the Esna shale. The elements are listed according to intensity: from the highest to the lowest one.

Sample	EDS results Comments	SEM image

Yellow I	Pseudomorphoses of natrojarosite after pyrite are clearly visible here. 4) Fe, S, ..., K, Ca 2) S, Ca, ..., Fe, K 3) S, Fe, …, K, Ca, Na 4) S, Fe, ..., K, Na, Ca	 Magnification 2000x
Yellow II	Pseudomorphoses of natrojarosite after pyrite are clearly visible here. 1) Fe, S, ..., K, Ca 2) S, Ca, ..., Fe, K 3) S, Fe, …, K, Ca, Na 4) S, Fe, ..., K, Na, Ca	 Magnification 2000 x
Dark red I	1) Fe, ..., K, S, Al., Ca 2) Fe, …, K, Ca, Al, S 3) Fe, …, Si, Cl, Al, Na, S, K, Ca 4) Ca, S, ..., Fe, K	 Magnification 2000 x

Brown	1) Fe, ..., Ca, S, K 2) Fe, ..., S, K, Ca 3) S, Ca, ..., Si, Al., Fe, K	 Magnification 1000 x
Red	1) Fe, …., Ca, S, Si, P, Mg 2) Fe, Ca, ..., S, ...P, Mg, Al., Si 3) Fe, …, Ca, …S, Si, P, Mg, K High amount of calcium is important here	Flaky, irregular occurrences
Dark red II	1) Fe, ... Si, ...Al., Ca, S, Cu, Zn 2) Fe, ... Si, ...Ca, S, Mg, Cu, Zn 3) Ca, S, ...Fe, Si, Al., Cu, Zn 4) Fe, Ca, ...C, S, Al., Cu, Zn, Si 5) Fe, Ca, ...C, S, Al., Cu, Zn, Si Sample was not covered by graphite. It means that biogenic substances are present within it.	Oxides or Fe-oxides are concentrated in flower-like structures.

Natural minerals present in nodules of Esna shale were used for preparation of pigments. Variability of obtained colors is showed at fig. 7A.

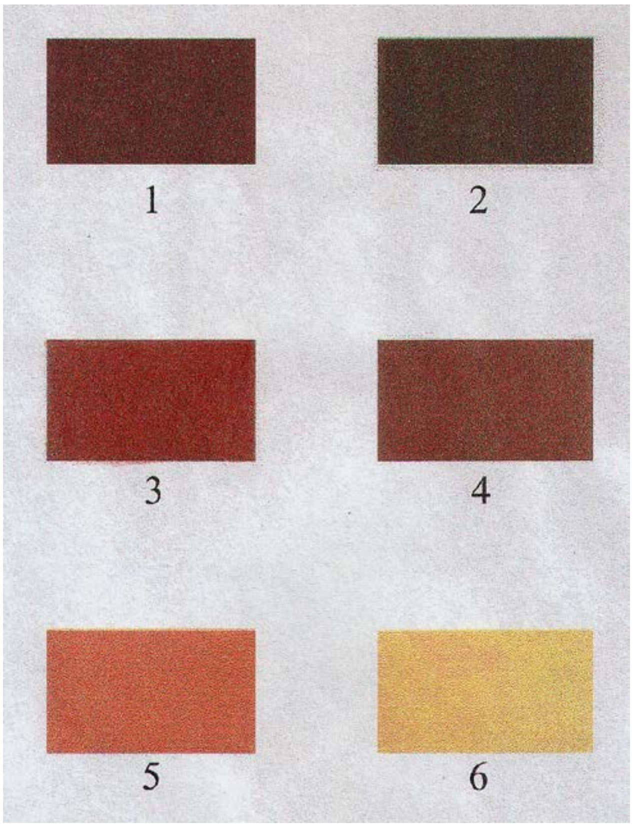


Photo 7A. Pigments obtained with the use of natural minerals from nodules present in Esna shale. Area of Hatshepsut Temple.

1- goethite, 2-goethite , 3-hematite 4 - hematite(50 %) - goethite 50 %, 5 – goethite (80 %) – calcite (20 %), 6 – natrojarosite.

Summary of the Part I

The examinations proved that the pyrite nodules present in the Esna shale weather into following minerals:

Fe_2O_3 - hematite - red
FeOOH - goethite - brown-red
$CaSO_4$ - anhydrite - white
$CaSO_4$ x H_2O - bassanite - white
$CaSO_4$ x $2H_2O$ - gypsum – translucent or white
$BaSO_4$ - barite - white
$Na_2Ca(SO_4)_2$ - glauberite - yellowish
$NaF_2(SO_4)_2$ - natrojarosite - yellow
SiO_2 - quartz – translucent or white

1. Brown color with a red (cherry) shade results from the presence of goethite accompanied by hematite. The intensity of hue depends on the admixture of white minerals

2. Red color results mainly from the presence of hematite and the brown shade is the consequence of the presence of goethite. The hue depends on the admixture of white minerals
3. Orange color results from mixing of cherry hematite and yellow natrojarosite.
4. Yellow color is of natrojarosite.
5. Only the dark red substance is characterized by the presence of low amount of Cu and Zn.
6. Characteristic features of morphology (e.g. cubes) obviously disappear after grinding, during the preparation of a pigment. Thus they can not serve as a guide in discerning a pigment origin.

Part II

Pigments and paints covering the decoration parts in the Chapel of Hatshepsut, Deir el Bahari

Description and localization of samples of mineral pigments

Sample 1

Painting on yellow limestone (Photo 3). Lime whitewash (II), (Photo 4, 5). and a blue painting layer on a white plaster (I) - (Photo 6, 7).

Place of sampling: northern part of a vault of the Chapel, III hour of night, a silhouette of the king. Sample was taken from the probable Coptic layer. Preserved fragments occur on surfaces of walls in almost all the Chapel, covering an original decoration and the reconstructions from the break of the 18^{th} and 19^{th} Dynasty (Tutmosis period?) and post-Amarna. The white layer (whitewash) was almost totally removed during conservation at the beginning of the 20th century.

Photo 3. Sample 1. Blue pigment on white plaster made on yellow limestone.

Sample 2

Painting layer – greyish blue (II) (Phot. 6) and a blue painting layer on a white plaster (I).

Place of sampling: northern part of a vault of the Chapel, II hour of the night, a silhouette of the king. Most probably this is a secondary layer and occurs only in the places where Hatshepsut was imaged as a king. At the break of the 18^{th} and 19^{th} Dynasty it was painted with blue paint to unify it with the blue background of the original layer. The hue of the later layer is colder – greyish blue – when an original layer remains intensively blue.

Sample 3

Painting layer – a yellow (Photo 8) - very thin layer on a white plaster (I). and blue (II) (Photo 9 and 10).

Photo 8. Sample 3. Yellow pigment on hieroglyph at central part of photo.

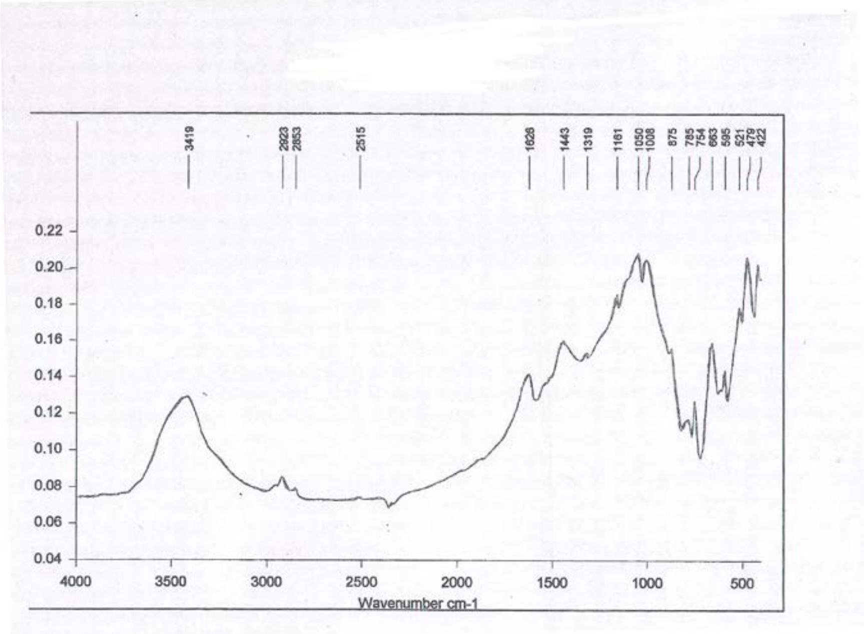


Fig. 6 Sample 3-II. FTIR spectrum of a layer under a painting layer. High amount of an organic compounds, probably a cereal glue is present here.

Place of sampling: northern part of a vault of the Chapel, II hour of the night. Blue paint sampled from the groundwork of a vault. The queen Hatshepsut period, 18th Dynasty. FTIR of this sample is showed at fig. 6

Sample 4

Pink plaster (II) (Photo 11 and 12) and multilayered paint (green, red, orange, blue) (I).

Place of sampling: northern part of a vault of the Chapel, a silhouette of a goddess, II hour of the night. Secondary plaster, pinkish, very soft.

In the Amarna period the silhouettes of gods were removed. At the end of the 18th or at the beginning of the 19th Dynasty a reconstruction was performed, and plaster was put on, on which again a relief was performed and covered with paints. FTIR of this sample is showed at fig. 7.

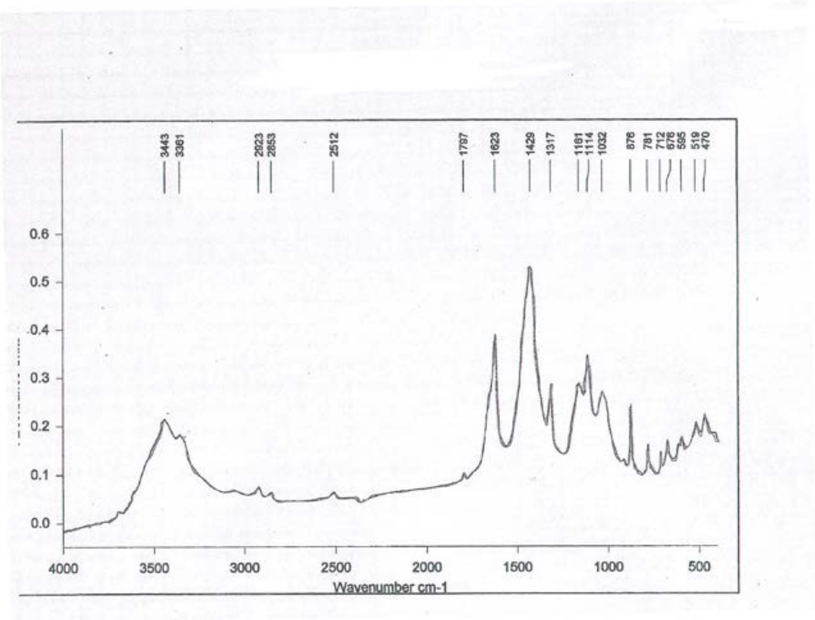


Fig. 7 Sample 4 –I. FTIR spectrum of a green painting layer with the underlayer (I). Calcite with a kaolinite-group mineral dominate and a copper chloride-type green pigment is probable here. An organic binder seems to be an oil type.

Sample 5

Painting layer – red (II) (Photo 13, 14 and 15) and grey (I).

Place of sampling: northern wall of the Chapel, a belt of a strip of Hekeron (from aprons of sacrificers). Original painting layer of the Hatshepsut period, 18th Dynasty.

Sample 6

Painting layer – green (II) (Photo 16) and orange-red (I).

Place of sampling: northern wall of the Chapel. A belt under Torus. Original painting layer, Hatshepsut period, 18th Dynasty. FTIR of this sample is documented at fig. 8.

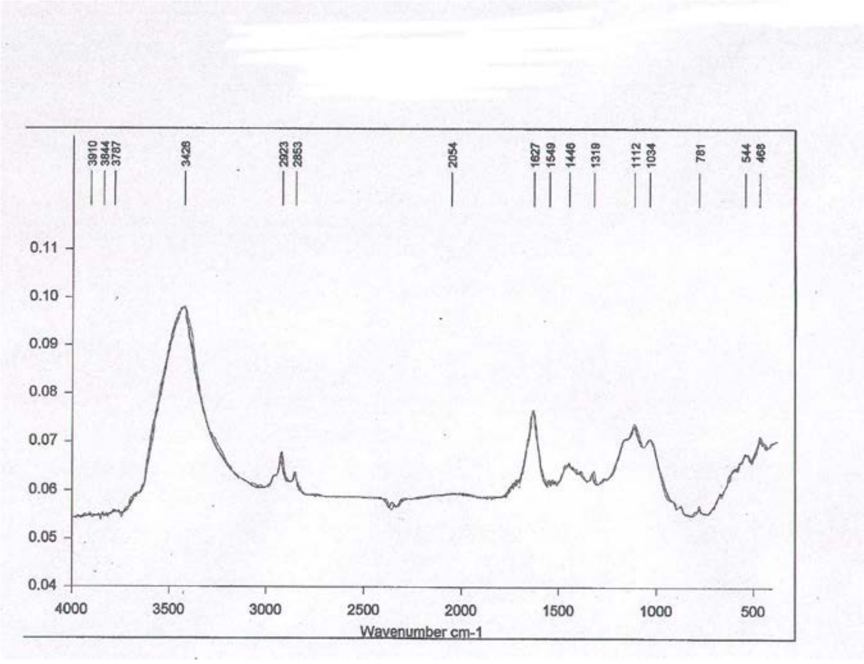


Fig. 8 FTIR spectrum of a orange-red (I) painting layer. Weakly thermally treated clay minerals with an organic substance.

Sample 7

White plaster (II) and a red, red-orange painting layer (Photo 17 and 18) (I).
Place of sampling: southern wall of the Chapel.
Plaster applied to filling and correcting defective blocks of a stone. On a surface of the plaster there is an imprinted relief with traces of polychromy.

Photo 17 Sample 7. Fragments of blocks coated with red painting

Sample 8

Plaster and a blue painting layer I - (Photo 19 and 20) and uderlayers (Photo 21,22).

Place of sampling: stele in the western wall of the Hatshepsut Chapel. The color of the plaster is brownish, the plaster is soft. It is dated to the Coptic period.

Sample 9

Underlayer (I- Photo 23) and blue (I) and white underlayer (II –Photo 24).

Place of sampling: southern wall of the Hatshepsut Chapel. Hatshepsut period, 18th Dynasty.

Sample 10

Painting layer – greyish-blue (II) (Photo 24).

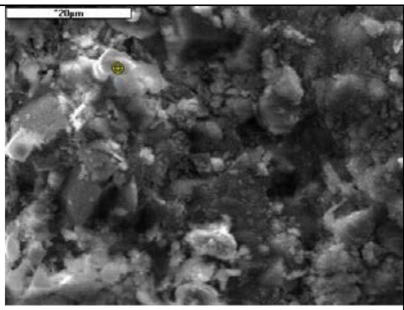
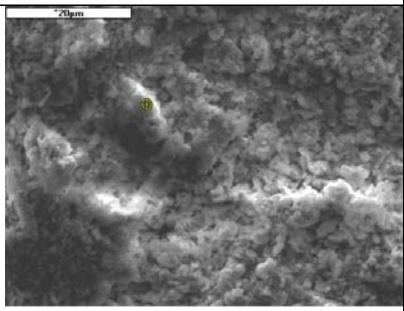
Place of sampling: southern part of the Hatshepsut Chapel, a background layer. It is an original layer of the Hatshepsut period.

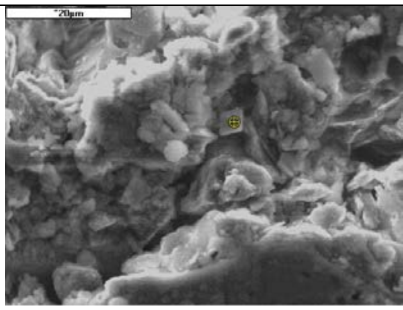
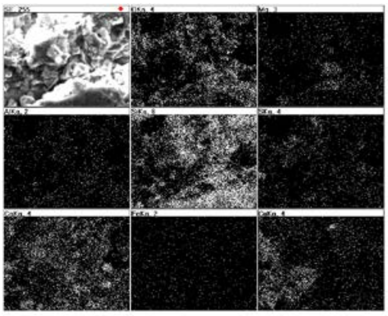
Table 2

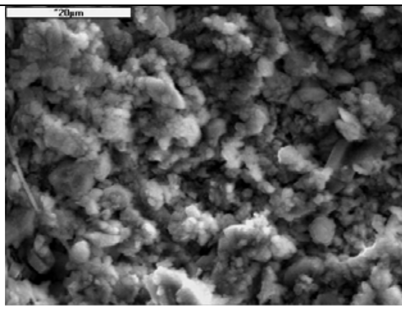
Results of pigment from Hatshepsut temple and their underlayers investigations.

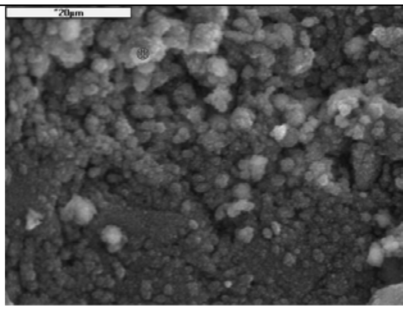
(The elements are presented in the order of their mount starting from high to low)

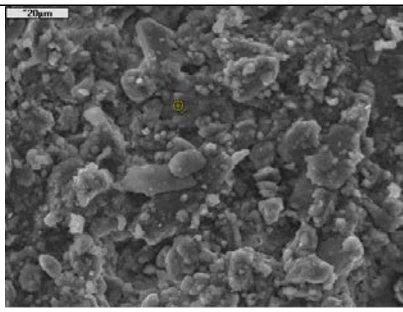
Sample	Macroscopic and microscopic (PLM) observations	EDS results	SEM results	Comments

1-II	Underlayer: white, uniform, with mineralised plant remains.	1) C, ..Si, Al., Fe, Ca, Mg, P, S, Cl, Ti, Cu 2) Ca, Mg, C, ...Si, Al., Ti	 Photo 4	The underlayer is very fine grained, dolomitic (or with Mg-calcite), with clays: either alumosilicates of Mg and Ca or kaolinite. Carbonate crystals, composed of equal amount of Ca and Mg, are automorphic. Organic compounds are detected. Low amount of P is present as well as very low concentration of Cu, probably connected with Fe.
1-II	nt.		 Photo 5	Tiny clay minerals
1-I	Painting layer:	**1) Ca, C, Mg, O, ...Si,**		Automorphic dolomite

	Grains of blue pigment are under microscope colourless to blue. They have crystalline habit, resembling an isometric one, apparent pleochroism and relief.	**..S, Al., Na, Cu** 2) Cu, C, O, ...Si, Ca, S, Cl, K 3) Si, ...Ca, Cu, C, O, ...Al., S, 4) O, C, Si,...Ca, Cu, Mg, Al., S, P, Cl, Fe	 Photo 6  Photo 7	crystals are present in the painting layer. It may have appeared after performing a painting. Two varieties of blue pigments are present here. One of them consists of Cu, Si and Ca, others are without Si (comp. mapping). Organic compounds co-occur with a pigment. Their compact, crusty structure, suggesting an application of a dense binder, is visible.
2-II	Painting layer: in a greyish matrix, blue grains of a	1) S, Ca, C, Si, Na, ...Mg, P, ...K, Cl 2) C, S, Na,		Blue pigment is represented by particles of flaky and

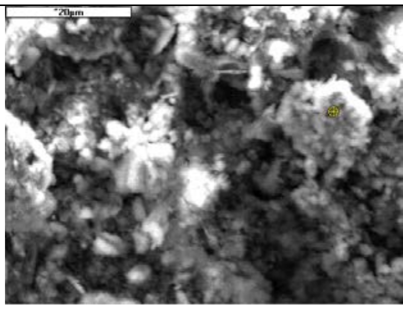
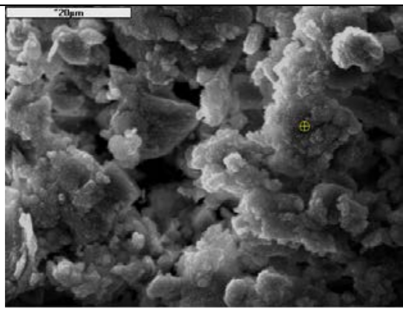
	pigment are present. Very tiny particles of red interference colour can be noticed as well as dark, irregular opaque (at plane polarized light) flakes. Crystals of blue absorption colours, elongated habit, low relief, weak pleochroism are present. Rhomboedric carbonate crystals occur here.	...Si, Ca, Al....Mg, Cl, Fe, K		grainy habit, from 5 to 20 μm. Greyish substance building the painting layer must be a sulphate of Ca or Ca-Na-Mg. Opaque flakes, seen under PLM, give a grey hue.
3-I	Underlayer: white, uniform, fine grained	1) S, Ca, O, ...Si, Al., Mg, P, Fe 3) Si, Al., ...Na, Mg, Cl, Ca, K, P 4) C, Si, Al., Ca, Mg, Na, S, Cl, P, Fe		Very fine grained underlayer, gypsum-clayey with kaolinite and alumosilicates of Ca and Mg.
3-I	Painting layer: yellow, very thin	2) Si, Ca, S, Al., Fe, K, Mg, O, C,	 Photo 9	Typical image of very fine grained Fe compounds (most probably ferrooxides).

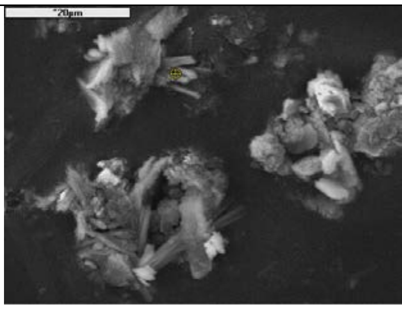
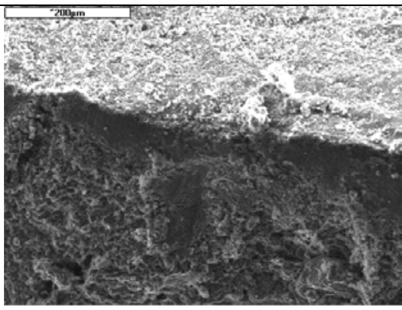
				Organic compounds are here very often associated with gypsum. The SEM image shows an uniform structure, not secondary crystals of gypsum.
3-II	Underlayer: white with single blue grains. PLM reveals the presence of micrite with microfauna. Surface of the underlayer is carefully smoothed.	1) C, Ca, S, Si, ...Al., Mg, Cl, K, Fe	 Photo 10	Very fine grains of rounded shape, crusts. The image suggests a high concentration of organic compounds (Trąbska 1998). Calcium, gypsum and alumosilicates are the mineral compounds. The amount of chlorine compounds is very low. FTIR analysis of a binder suggests the presence of a cereal glue

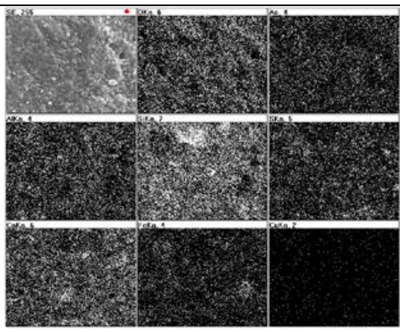
				(Fig. 8).
3-II	Painting layer: blue, consists of large grains. PLM shows that a painting layer is thick. Binder is translucent under plane polarisers. Pigments have an elongated habit, apparent parallel cleavage, pleochroism, high relief. Along with them, blue particles (under plane polarized light), crystalline, resembling isometric, with weak pleochroism, brownish, are present. Fine grains of gypsum are present also. Flakes of an organic binder: semi-translucent, irregular, of	Phot. II-3-1-1000 1) Si, ...Ca, Cu, ...C, K, Cl 2) Si, C, Ca, Cu,...K, Cl 3) C, Si, Ca, S, Cu...K, Cl 4) Si, ...Ca, Fe, Al.,Ti, Cu...S, K, Cl 5) Si, ...Ca, Cu, Al., S, Fe Yellow substance on a blue painting layer 1) Si, Ca, Mg, S, Al., Fe, Na 2) Si, ...Ca, Cu, S, Na, Al., Mg, Fe	 Photo	Fot. II-3-2-1000 presents grainy particles of a blue pigment. PLM image suggests a process of weathering of grains and creation of brownish rings around them. It may be connected with the presence of iron in a pigment particle. Phot. II-3-1-1000 presents another Cu-Si-Ca pigment of quite different morphology. This pigment is bound by higher amount of an organic binder than the former. It may be a pigment that under a PLM

	grainy surface, are present.			has an elongated habit. So there are at least two blue pigments of the same chemical composition here: both Si-Cu-Ca. But the ratio of Ca/Cu to Si/Cu (Tab. 3) is different. In grainy pigments it equals 0.2 and in another: 0.6. Pigments are accompanied by a low amount of gypsum. Yellowish, earthy occurrences on a painting layers are composed of clay minerals and sulphates.
4-I	Underlayer: yellowish, uniform, with red-pink and green painting layers. Over			Green painting layer consists of very fine grains, pleochroic,

	them there is a very thin whitewash with red-orange paint. PLM reveals an micritic structure of the underlayer. It is pinkish under plane polarized light, with abundant microfauna and fine quartz grains. Another fragment of the sample is composed of yellowish underlayer and slight traces of a blue painting layer.			with green absorption colours. FTIR of this layer reveals the presence of calcite and kaolinite. A pigment may be a kind of synthetic copper chloride one. A binder may be of oil type (Fig. 9). Red-orange painting layer in the PLM image seems to consist mainly of dark orange variety of orpiment (comp. West FitzHugh 1993, pp. 55-57). Pigments are mixed with an organic binder. Crystalline grains of blue absorption colours,

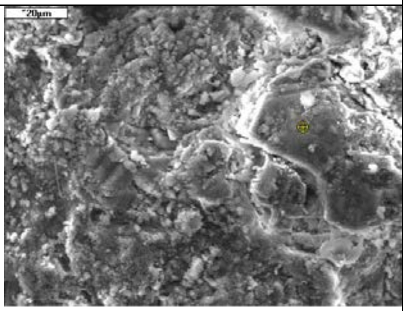
				weak pleochroism and medium relief construct a blue painting layer,
4-II	Underlayer: white with pinkish hue Single blue and black grains are present. PLM reveals the image of a weathered tuff. Along with clay minerals, feldspars and amphiboles are present.	1) Ca, C, ...Si, Al., Mg, S	 Photo 11	The underlayer was strongly impregnated with organic compounds. Gypsum and calcite are also present within it.
4-II	Very weak traces of a grey and blue painting layer.	2) Si, C, ..., Al., Ca, S, Mg, Cu, Fe, Cl, P 3) C, Si, Ca, S, ...Al., Mg, Cu, Fe, Cl	 Photo 12	Grainy occurrences represent organic compounds. They are very rich in carbon. It may be a black colourant. The amount of P is too low to tell that a bone black may have been applied. The blue pigment is a

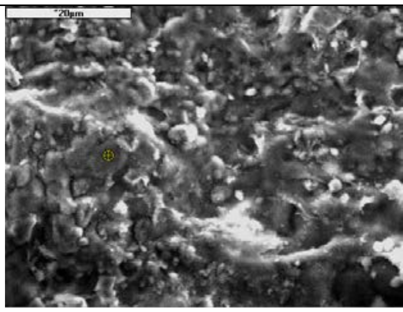
				Cu silicate, containing some iron. Due to a very low amount of a pigment, optical features under a PLM were impossible to establish.
5-I	Grey powder. Under PLM only irregular, bushy, opaque particles are visible.	1) C, S, Na, Ca, Si,...O, Al., Mg, K, Ti, Fe, P, Cu 2) Ca, S, C, Mg, Si, Na, Al., O...P, Cl, K, Ti, Fe 3) S, O, C, Na, Ca, ...Si, Mg, P, Fe, Ti 4) S, Si, Ca, Na, C, O, Al., ...Mg, P, Cl, K, Ti, Fe, 5) Si, Al., O, C, ...,S, Ca, Fe, K, Cl	 Photo 13	A sample consists of clay minerals, probably kaolinite and sulphates of Na and/or Ca. Elongated crystals, visible on a photography , are consisted of it. High amount of an organic substance (sooth?) is noted.
5-II	Underlayer: white with single grains of quartz, with a thin whitewash on it. PLM observations	1) C, Ca, ...Si, Al., Mg, P, ...Fe 2) Ca,....C, Si, K, Fe Slightly beneath the painting layer:	 Photo 14	Density of a binder, applied in a painting layer is very high and easy to observe on a SEM image.

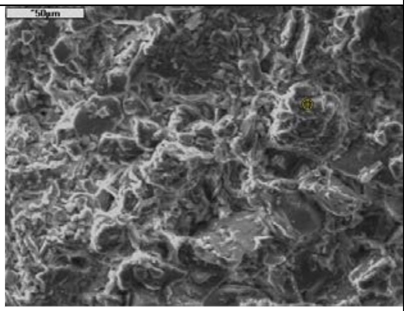
	prove the presence of micrite with single grains of quartz and rhomboedric crystals of carbonates, sometimes of rim structures. Locally, under a painting layer, the underlayer detaches. Painting layer is put on an even, well prepared surface.	3) Ca, ...Si, Al., Mg, S, Fe...K		Chemical composition of an underlayer is typical for carbonates.
5-II	Painting layer is red. Under PLM it is thin, almost opaque, with numerous breaks. Single grains of quartz, gypsum and rhomboedric carbonates are present within it. Binder does not penetrate inside the underlayer and this fact suggests the	1) C, Fe, Ca, As, S, Si, Al., Na, Cu 2) C, Fe, S, Al., Mg, Ca, K, Si, Na, ...Cl 3) C, Si, Ca, Al., S, Mg, Fe, Na, K 4) Ca, Si, Al., Fe, Mg...Cl 5) Si, Al., ...Ca, Fe, Mg, P, S, ...Cl, K	 Photo 15	Red painting layer is composed of Fe pigment of extremely tiny grains. Thus the description of it as an ocher would be risky. An extremely abundant organic substance is striking here. P is present only sporadically. The arsenic pigment of

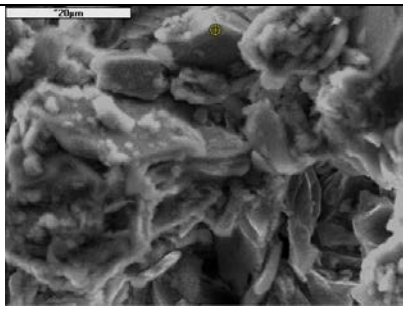
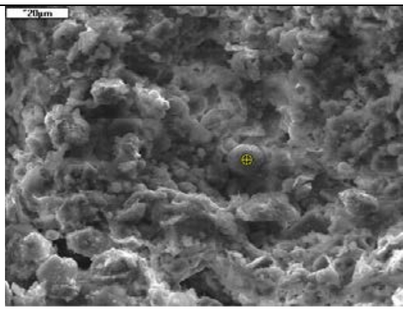
	application of *al secco* technique. Red pigment is a very fine grained powder of high relief and red absorption colours. Very tiny blue particles are also present.			very fine grain diameter may be a synthetic realgar. Then it would be applied with equally tiny haematite (probably synthetic). Gypsum and calcite are present also in the painting layer. Very high amount of Al suggests an application of alun here.
6-I	Underlayer is dark grey. In a plaster there are single shiny, black grains. A thin whitewash with a painting layer was put on it. PLM examinations give an image of pinkish micrite, heavily cracked, dark at plane			

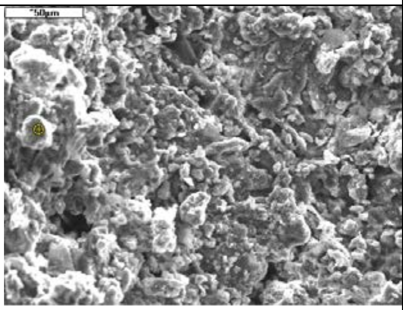
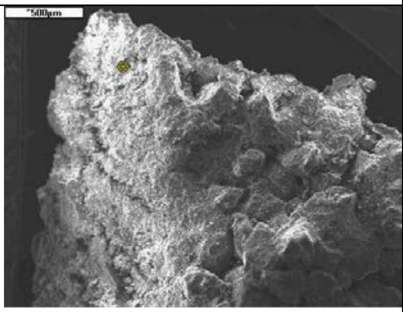
	polarised light. Single microfauna shells are present as well as rhomboedric rim carbonates.			
6-I	Painting layer is red-orange with irregular grey crusts.	1) Si, ...Mg, Ca, Al., C, O, Fe, K, Cl, S, 2) Ca, Si, C, Mg, Al., P, Cl, S		The amount of Fe is very low and it is irregularly distributed in the painting layer. FTIR analysis revealed a mixture of an organic compound (resembling cereal glue) and clay minerals (connected with an ocher?), weakly thermally processed (weak bands of 400-600 cm-1, lack of OH bands characteriscic for clay minerals) (Fig. 10).
6-II	On a very thin	1) Si, C, Ca, S, Cu, Mg,		Carbonates with clay

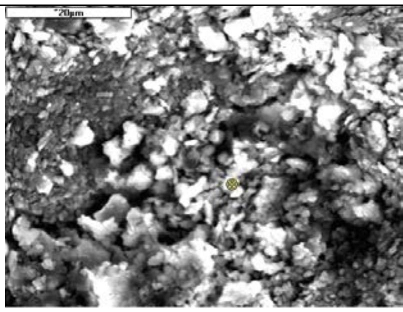
	whitewash a blue painting layer occur. Under microscope irregular flakes of calcite impregnated with organic substances are visible.	Cu, Al. 2) Si, C, Ca, Cu, Na, Al., Cl, S, Mg		minerals and organic compounds build an underlayer. Secondary gypsum is present.
6-II	Painting layer consists of very fine grains, with green absorption colours, apparent pleochroism and moderate relief. Along, grains of a pigment of blue absorption colours with very weak pleochroism are present.	1)S, Ca, ..Si, C, ...Al., Mg, Na, Cu, Fe, K...Ti 2)S, Ca, C, Si, ...Fe, Al., Mg, Ti, P, Cl, K 3) S, Si, Al., Ca, ...Mg, Na, Cu, K, 4) S, Ca, ...C, Si, Al., Mg, ...Ti, Fe, Cu, K, P 5) Si, S, Ca, C,...Al., Mg, Fe, Na...P, K	 Photo 16	Flaky occurrences suggest the presence of green earth pigment. As it is very tiny, it is difficult to establish whether it is glauconite or seladonite. High amount of gypsum is characteristi c for the sample. Grainy pigments are composed of Si, Ca and Cu. The ratio of Ca:Cu/Si:Cu is around 0.4. Crusty occurrences of organic substances

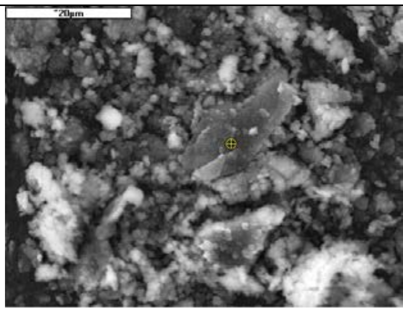
				are visible.
7-I	Underlayer: white, uniform	1) Ca, ...Si, 2) Si, ...C, Mg, Ca, Al., Fe, Cu 3) Si, …C, Mg, Ca, Al, P, K, Ti, Fe, Cu 4) Ca, C, …Si, Mg, Al, 5) Ca, Mg, C, ...Si, ...S		Underlayer is calcitic-dolomitic-clayey. Fe is accompanied by a low amount of Cu.
7-I	Painting layer: thick layer of red. Under PLM golden-red particles of high relief are noticeable. Dark flakes of organic compounds are also present.	1) Si, C, Ca, Fe, Al., Mg, S, K, Ti, Cl, 2) Si, Al., C, S, Ca, Fe, Mg, ...Cu, K 3) Ca, Fe, S, ...Si, ...Al., Cu 4) C, Si, Ca, Fe, Mg, S, Cl 5) C, Si, Ca, S, Fe, Al., Mg, Ti, ...Cu, K, P	 Photo 18	Very fine particles. An application of ocher (Fe with Ti and Cu here!) is possible. Gypsum is present here. Organic compounds are connected with an ocher but it was applied also without them. Organic substances are mixed with gypsum. The latter may have been used here intentionally.
7-II	Underlayer:	1) Si, O, C,		Clayey-

	white, powdery. Single grains of red and blue pigment in it.	Ca, Cu, ...Mg, S, Cl, Fe 2) Si, C, O, ...Ca, Fe, Cu, Al., S, Cl 3) Si, C, ...Ca, Fe, Cu, S, K		carbonate underlayer, impregnated with gypsum and sulphates of Na. Irregular crusts of organic compounds. Tabular crystals of rounded edges consist of Cu. The ratio of Ca:Cu/Si:Cu equals 0.17 and 0.15 and is typical for the examined population of the Chapel.
8-I	Underlayer: white, uniform			
8-I	Painting layer: blue, composed of very fine grains.	1) Si, Al., Ca, Mg, ...Cu, K, Fe, P, Cl, S 2) Si, ...Ca, Al., Mg, Fe, Cu, K, P, Cl, S 3) Cu, Si, Ca, O, Fe, ...K 4) Si, Cu, K, Ca, Fe, ...Cl,	 Photo 19	*Cu silicate with Ca. A mixture of unusual, tabular pigments and clay minerals. Organic compounds applied here.* Very dispersed

		Al., 5) Si, Ca, Cu, ...Fe, K, Al., S, Cl	 Photo 20	values of a Ca:Cu/Si:Cu ratio (from 0.32 to 1). It may be assumed that this is an Egyptian blue but not very typical.
8-II	Underlayer: brownish. A white layer on it, covered with a black layer.	Brownish layer 1)Ca, Si, Al., Mg, Na, Fe, S, K, Cl, ...P	 Photo 21	Clay minerals suggested by flaky morphology of occurrences. Also grainy crystals of carbonates are present. Organic compounds seen as crusts. In this part of an underlayer – quite a high amount of P, that may be derived from an organic substance.
	Whitewash	4) Ca, C, Si, Al., Mg, K, Fe, S, P, Cl 5) C, Si, Ca, ...Mg, Al., Fe, S, P, Cl, Cu		Clayey-dolomitic-organic underlayer. A rounded particle is a calcium

		6) C, Ca, S, Si, Mg, Al., P, Cl, K 7) Si, Ca, Na, Al., Cl, S, P, Mg, K, Fe		carbonate. Traces of Cu are noticeable here.
8-II	Dark-grey underlayer (or painting layer)	2) Ca, Si, Mg, Al., P, S, Cl, K, Na, Fe 3) Ca, Si, Mg, Al., P, S, Na, Cl, K, Fe	 Photo 22	Ca-Mg carbonates, alumosilicat es of Mg and K, gypsum, low amount of P and Cl.
9-I	Underlayer is composed of quartz and feldspars grains, well sorted, not rounded. Painting layer penetrates into it. Organic binder.		 Photo 23	
9-I	Painting layer is blue with abundant organic binder. A pigment of green-blue absorption colour, with strong pleochroism, high relief. A hue is distributed	1) C,....Al., Cu, Si, Mg 2) C, Si, Ca, Cu, Al., Fe, S		A Ca:Cu/Si:Cu ratio equals 0. It seems that the pigment is azurite

	unevenly in the grains. Hairy gypsum occurs also in the painting layer. A second variety of a pigment is characterized by weak pleochroism, elongated habit. Moreover, particles of pink-red absorption colour with weak relief, isotropic are present. Single quartz grains are noted.			
9-II	Underlayer: white, uniform.	1) Ca, ...C, Mg, Si, S, Al., Cl, P, Fe	 Photo 24	Mg calcite .
9-II	Painting layer: yellow, very thin, with single blue grains.			Tiny, flaky occurrences. It may be an ocher.

10-II	Black bushy, opaque (at plane polarised light) occurrences. Plant remnants. Elongated crystals of low relief, pleochroic, with green absorption colors.	1) C,...Mg, Si, Ca, Al., S, P,	 Photo 24	Flaky occurrences of an organic colourant. High amount of organic substances.

The EDS microanalyses of single grains of blue copper pigments were listed together and the ratio of Ca:Cu and Si:Cu, then Ca:Cu/Si:Cu was calculated on the basis of the intensity of peaks. The aim was to search for regularities in the concentration of Si and Ca in pigments, that should be mostly an Egyptian blue. It seems that certain rules of composition exist (comp. Riederer 1993, pp. 28-32) but they have never been traced in a very simple EDS analyses. After making a calculation, suspicious analyses were rejected (e.g. grains containing only copper and calcium). Then it appeared that, summarizing all the cases, the most abundant ratio centers around 0.2 (12 analyses). Contamination of single grains is obvious and has to be taken into account but it is an imminent feature of samples submitted for analysis.

Table 3

Results of examination of pigments used in temple of Hatshepsut – summary.

Sample Color	Underlayer	Pigments	Technique
1-I blue	Fine grained, uniform, dolomitic (or with Mg-calcite)-clayey, organic compounds. Single grains of blue copper crystals – Egyptian blue. Mineralized plant remains – intentional	Egyptian blue – a variety with strong pleochroism and crystalline habit. Azurite Organic binder in the painting layer.	Natural pelitic sediment was used as a plaster. It was impregnated with an organic substance and then a painting layer was put on

	addition or accidental occurrence? Organic compound in the underlayer.	Secondary, yellowish layer over a painting layer, composed of sulphates and clay minerals.	it.
1-II Light yellow	White-bluish, clayey, with opaque grains (sooth?) Organic substance in the underlayer.	Calcite or aragonite, probably lime. Very low amount of gypsum Organic binder in the yellow layer.	Plaster is clayey here, not typical.
2-I Blue	Fine crystals of dolomite, clay minerals. Very low amount of Cu containing grains (added? natural?) Gypsum Organic substance in the underlayer	Egyptian blue - of calculated ratio 0.2 - of calculated ratio 0.6 Azurite Organic binder in the painting layer, a very dense one.	Plaster impregnated with an organic substance. Then a mixture of azurite and two varieties of Egyptian blue was prepared, mixed with an organic binder and put on a plaster. Rhomboedral carbonate crystals seem to be of secondary origin.
2-II Blue	Dark grey, with oolites (onkoides?), gypsum, glauberite, clay minerals. Not very much consistency. Organic substance in the underlayer.	Grey „matrix” of a painting layer consists of gypsum or sulphate of Ca-Na-Mg. Grey hue is a result of black particles added. Probably single particles of red ocher, Egyptian blue of weak pleochroism.	Painting layer here is very unique. Gypsum or other sulphate must have been mixed with some grains of Egyptian blue and with an organic binder.

		Organic binder in the painting	
3-I Light yellow	Very fine grained, gypsum-clayey, with kaolinite and possibly with alumosilicates of Mg and Ca. Organic substance in the underlayer	Yellow ocher Gypsum Organic substance in the painting layer, often mixed with gypsum, may be intentional.	Gypsum was either mixed intentionally with an organic binder or was a natural constituent of a yellow ocher.
3-II Blue	White, micritic with microfauna. Gypsum, clay minerals. Very even surface. A lot of an organic substance, probably cereal glue (Fig. 8).	Two varieties of Egyptian blue: grainy and tabular. Gypsum	Natural pelitic rock was applied as a plaster. Before painting it was soaked with cereal glue. Tabular Egyptian blue required more binder than another, grainy one. Low amount of secondary gypsum is present.
4-I Green Red Blue	Micritic with microfauna. Organic substance.	In a painting layer calcite occurs with kaolinite and the green seems to be of a copper chloride type. Organic binder of a green painting layer of an oil type (Fig. 9) Red-orange orpiment with an organic binder. Egyptian blue with	Painting layers are composed of very tiny pigments here. Calcite and kaolinite identified in the painting layer may come from the plaster.

		an organic binder.	
4-II	Weathered tuffite with feldspate and amphibole grains. Strong impregnation of an underlayer with an organic substances	*Black organic particles.* Egyptian blue (?) Rhomboedric carbonates are present in the painting layer.	
5-I Black		Organic black, kaolinite, natron. Kaolinit Natron with organic compounds.	Crystals of natron are intergrown with an organic compound.
5-II Red	Micritic, rhomboedric carbonates, sometimes with rims.	Synthetic haematite *Synthetic realgar* *Quartz, gypsum, alum?* Very strong organic binder in the painting layer.	Too much organic substance was used: either in a plaster or in a painting layer. Tension caused detachments of a layer of the plaster just beneath the painting layer.
6-I Dark red	Micrite with an organic substance and single shells of microfauna. *Rhomboedric carbonate crystals, clay minerals*.	An ocher, weakly thermally processed. Dense organic binder.	
6-II	Irregular flakes of calcite, some clay minerals. Most probably this is lime. Organic substances in the underlayer.	Green earth Egyptian blue Dense organic binder in the painting layer	
7-I Red	Calcitic-dolomitic-clayey. Organic substances in the underlayer	Ocher Gypsum mixed (intentionally?) with organic substances or a natural component of an	

		ocher. Organic binder in the painting layer	
7-II	Clayey-carbonate underlayer, impregnated with gypsum and sulphates of Na. Irregular crusts of organic compounds.	Egyptian blue of tabular (!) habit Organic binder in the painting layer	
8-I **Blue**	White, uniform	Egyptian blue – tabular habit (!) Clay minerals Organic binder in the painting layer	
8-II **Dark whitewash or painting layer**	Clayey-carbonate Gypsum Organic binder in the underlayer	Carbonates and clay minerals	
9-I **Blue**	Well sorted quartz and feldspars, not rounded. It resembles an aleuritic rock. The underlayer is not prepared carefully for a painting layer. Organic binder in the underlayer	Azurite Egyptian blue Hairy gypsum Orange-pink glassy pigment Organic binder in the painting layer	This is the only case when an underlayer is not prepared carefully. Painting layer penetrates in it.
9-II	Mg-calcite	Yellow ocher?	
10-II	Carbonate (calcite?)	Organic black Unidentified green pigment resembling malachite, but of low relief.	

Chronology

Blom-Bőer showed (1994) that in the time of the 18th and 19th Dynasty almost all pigments known in Egypt were applied, excluding malachite and Cu-glass pigment. The application of realgar is limited very narrowly only to this period (p. 76).

Early chemical analyses of Egyptian blue shows that on average the pigment is composed of 70% SiO_2, 8% CaO, to 3% Na_2O, 2-3% Al_2O_3 and Fe, 16% Cu_2O. French chemist Fouqué produced a variety with no alkalis. In the Chapel the Egyptian blue does not consist of potassium, rarely is composed of natrium. Usually these are Cu-Ca-Si pigments, but the ratio of Ca:Cu/Si:Cu varies (Table 3). There are some cases, where tabular crystals of Egyptian blue were observed (3-II, 7-II) and it must be mentioned that in general opinion it is a very rare phenomenon (Riederer 1997, p.34).

Azurite is a common pigment of a bit different hue than an Egyptian blue. That is why it may have been used as an admixture. In Egypt it was known from the time of the Fourth Dynasty (Gettens et al. 1993, p. 32). The same is true of malachite: it was used in pre-dynastic time, first, as an eye painting (Gettens et al. 1993, p. 184).

An occurrence of green earth was noted only once (6-II) and it was mixed with an Egyptian blue. Actually, it was not an extremely widespread pigment in ancient Egypt at all. In Cretan fresco paintings it was discovered in a mixture with Egyptian blue (Grissom 1982, p. 143).

Realgar was only identified once (5-II) and it is most probably of synthetic origin.

Hematite is known from Deir-el-Bahari as a dyer for a mummy wrapping, from around 1900 BC – it was a very little known technique and rare application of hematite in this way (Wouters et al. 1990). The mineral is generally confined to paintings. In the examined material it was identified only once, also in the sample 5-II and also it is probably synthetic.

Ochres must have been prepared very carefully: grains are uniform and tiny. Sometimes a thermal processing was applied to obtain a required color (6-I). Gypsum always occurs together with ochres. Either this is a result of natural conditions or gypsum was added intentionally. Ocher is rather a dull pigment – this is an organic binder that provides a deep, shiny surface of an ochre painting.

There are very many varieties of orpiment: both natural and synthetic (West Fitz Hugh 1997, pp. 47-81). Among the examine samples a red-orange variety was discovered (4-I).

Raw Materials

Examined raw materials from the Esna shale are, with one exception, very pure, if a concentration of accompanying elements, e.g. Cu, is taken into account. A set of secondary minerals is always similar in the Egyptian climate.
It was observed that in the samples of plasters and pigments there are quite often abundant low amount of copper, following Fe and not connected with blue pigments (samples 1-I, 2-I, 2-II, 5-I, 7-I, 8-II). Hence, it is supposed that a raw material generally might have been exploited from one source, but not necessarily from the Esna shale.

Corrosion processes

They were not observed in examined samples. Most probably, this is due to a very low amount of chloride in all the samples. Sulphate corrosion is slower than the chloride one (Trąbska 2001). This situation may be a result of a protective role of an organic binder applied.

Remarks on technique

Always, except one case, a variety of ***al secco*** technique was applied. Thus, a surface of a whitewash or plaster under a painting was treated with an organic substance (a cereal glue in the samples examined with FTIR) that was usually dense and made a surface soft, sticky and impermeable for a binder of a painting layer.

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