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## **Examination of the patina coating of natural Theban limestones as well as blocks of Hatshepsut Temple, Upper Egypt.**

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### **Abstract**

A mineralogical investigation was performed on the patina coating of natural walls of Theban limestone at Deir El Bahari Valley as well as of the patina coating of limestone blocks used for construction of the Temple of Queen Hatshepsut. The aim of the investigation conducted was to determine the speed of patination. Moreover the possibility of the use of patina for dating of objects was discussed.

**Key words:** patina, limestones, datation

### **Abstrakt**

Przeprowadzono badania mineralogiczne patyn pokrywających naturalne ściany wapieni tebańskich w dolinie Deir El-Bahari oraz patyn pokrywających bloki wapienne świątyni królowej Hatshepsut. Celem przeprowadzonych badań było określenie tempa powstawania patyny. Przedyskutowano także możliwość wykorzystywania patyny do datowania obiektów.

**Słowa kluczowe:** patyna, wapienie, datowanie

## Introduction

The processes of various rocks' patina have not been extensively examined mineralogically. Publications document that patina formed on the surface of various flints, obsidian (materials for chipping used in the Stone Age) was most frequently tested due to problem of reconstruction of paleoenvironment, climate changes and other factors (Pawlikowski M., Wasilewski M., 2004). The Queen Hatshepsut temple (Barwik 1998, 2001, Pawlicki 2000, Szafranski 2000,) and the surrounding area was selected for investigation of patina during the restoration and conservation of temple.

The occurrence of patina on limestones is interesting and mineralogically is seen as a kind of weathering of these rocks. Looking at the natural walls of the Hatshepsut Temple built of limestones, one can see various colors on the natural surfaces. Dark surfaces are older and generally darker than newer ones.

## Materials and methods

Based on the above mentioned questions for the investigation of patina, the following samples were collected :

**Sample K0** - a fragment of patined Butehamon signature done about 3100 B.C. executed in naturally patinated Theban limestone. Sample were collected from the surface of a natural big limestone block present in the valley – West of Deir el Bahari

**Samples K1-K11** - surface patina from various blocks of the old primary foundation of the Hatshepsut Temple. Places of collecting of selected samples are shown in fig. 1.

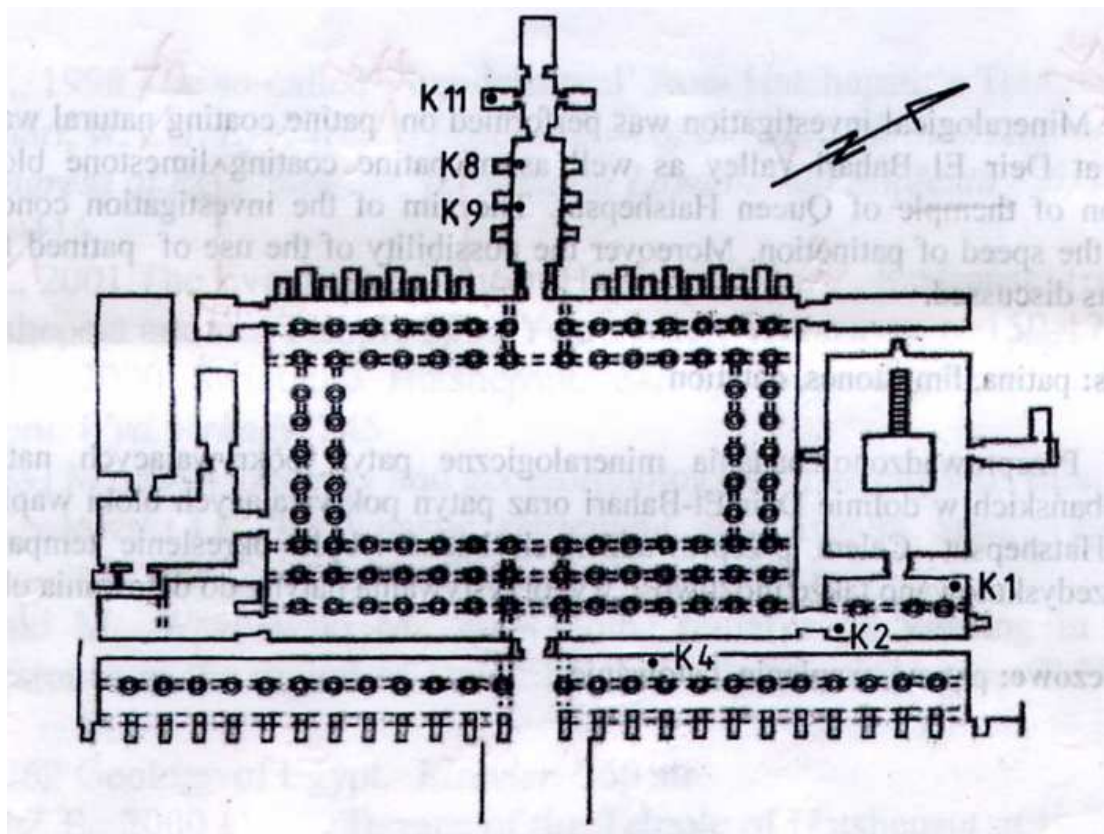


Fig. 1 Scheme of the upper terrace of Hatshepsut Temple (by Pawlicki 2000) K1- etc. – places of sampling of blocks coated with patina (only fragments which had naturally fallen down from the wall)

All samples collected were prepared in the form of thin sections for microscopic observation. Special attention was paid to the determination of the composition and thickness of the patinated layer.

The investigations of patina were done with the use of a polarizing light microscope Polmi A (Carl Zeiss-Jena) and recorded on microphotographs. In addition XRD analyses using a Philips diffractometer were performed..

## Results of the investigations

**Sample K0** –patina of a natural limestone block with the signature of Butehamon

A thin groove of a signature of Butehamon cut on a natural surface of limestone is primary old and thick patina (Fig. 2A, 2B). This groove cut about 3100 years B.P. has been secondarily patinated. This fact documents that the patina over the groove was formed about 3100 years B.P. i.e. is 3100 years old.



Fig 2 A – A fragment of groved lines of signature of Butehamon. Digital microscope, magnification 5 x. B – single patinated line of signature of Butehamon. Digital microscope, magnification 50 x.

The thickness of this relatively young layer of patina changes at various parts of the groove and ranges between 80 and 100  $\mu\text{m}$  (Fig. 3 - But. 1, But. 2). This means that, if the speed of formation of patina was constant, about 0,02-0,03  $\mu\text{m}$  of younger, patina was formed above the groove of Butehamon each year.

Taking under consideration the data obtained it is easy to calculate the time of the formation of natural patina present on the natural surface of a limestone block near the place where signature of Butehamon was found. A medium thickness of this old and natural patina is about 600  $\mu\text{m}$  (Fig. 3 - But 3, But 4). This means that this old patina was formed about six times longer than the patina above the groove of Butehamon. If the speed of patination during all time was constant, one can calculate that the natural patina on the limestone block was formed about 18 - 19 000 years B.P. This suggests that the tested wall block started to be patinated at the end phase of the maximum period of the last glaciation.

The structure of the natural old patina examined is mineralogically and structurally not homogeneous (Fig. 3 – But 3, But 4). Under the microscope, one can see in the patina layers of various mineral and chemical composition. This suggests that the thick layer of natural patina was formed during alternating climatic conditions.

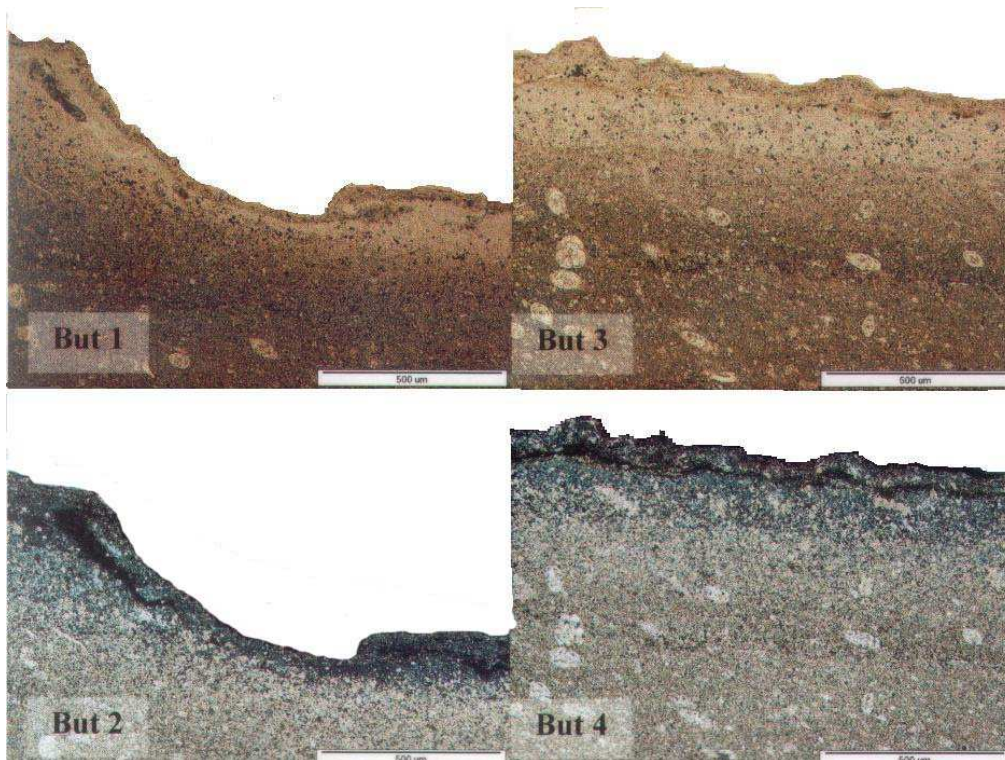


Fig. 3 Microscopic picture of thin sections of limestone perpendicularly to grooves of Butehamon signature (left pictures) and natural patina (right pictures)

But 1 – Perpendicular section of line of Butehamon signature. Polarizing light microscope, 1 polaroide.

But 2 - Perpendicular section of line of Butehamon signature. Polarizing light microscope, polaroides X.

But 3 - Cross-section of limestone at patinated surface. Polarizing light microscope, 1 polaroide.

But 4 - Cross-section of limestone at patinated surface. Polarizing light microscope, polaroide X.

Scale = 500  $\mu\text{m}$

A thin, up to 50  $\mu\text{m}$  thick, surface part of patina contains concentrations of clay minerals, as well as iron oxides, but the amount of calcite (kutnahorite) there is reduced (Fig. 4). This situation makes the patinated surface of the limestone yellowish.



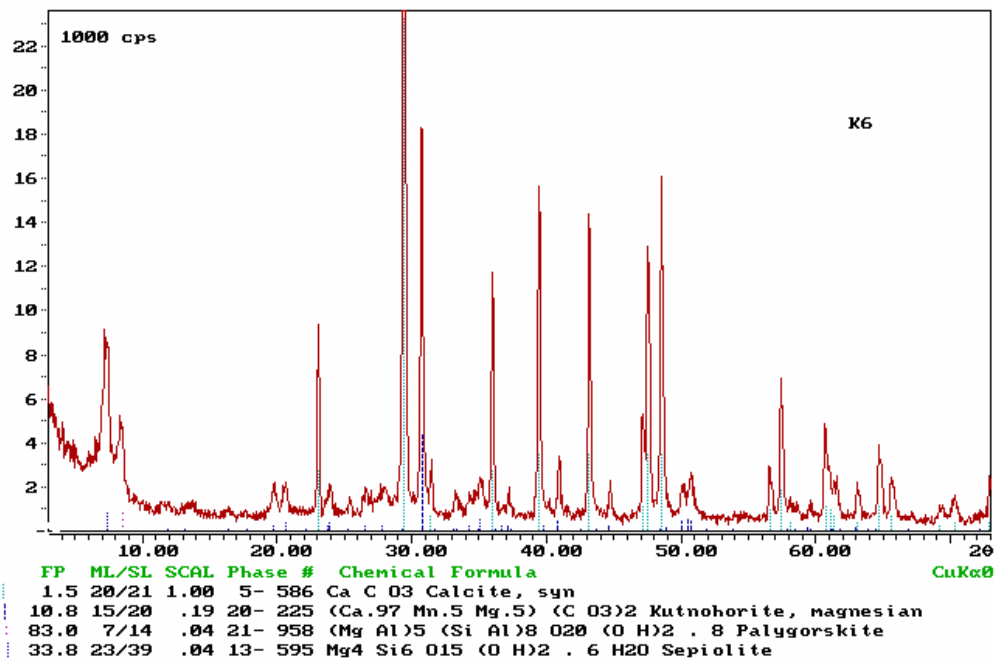


Fig. 4 X-ray pattern of the tested patinated coating surface of the limestones

The next, deeper part of patina is about 200 –250  $\mu\text{m}$  thick. The color of this part of patina is lighter because it contains mainly calcite but the amount of iron oxides is reduced.

Going deeper, one can see that the next layer of patina has thickness ranging between 100 and 200  $\mu\text{m}$ . This layer contains mostly calcite but is evidently enriched in darker iron oxides.

Samples K1-11 – patinated coating of various limestone blocks from the foundation of the Hatshepsut temple.

The location of some of the samples for the determination of patina is shown in fig. 1 (upper terrace of Hatshepsut Temple). Only patinated fragments that have fallen naturally from the wall of the temple were collected.

Microscopic observation of patinated surfaces of limestone blocks is shown in fig. 5.



Fig. 5. Various patinated coatings of four examples of limestone blocks from the Hatshepsut Temple. Digital microscope, magnification 5 x.

The general thickness of the patina is about 0.3-0.5 mm. The thickness of the patina of tested blocks is listed below:

Sample K1	- patina - 850 $\mu\text{m}$
Sample K2	- patina - 260 $\mu\text{m}$
Sample K3	- patina - 20 $\mu\text{m}$
Sample K4	- patina - 70 $\mu\text{m}$
Sample K5	- patina - 30 $\mu\text{m}$
Sample K6	- patina - 20 $\mu\text{m}$
Sample K7	- patina - 90 $\mu\text{m}$
Sample K8	- patina - 80 $\mu\text{m}$
Sample K9	- patina - 150 $\mu\text{m}$
Sample K10	- patina - 110 $\mu\text{m}$
Sample K11	- patina - 100 $\mu\text{m}$

The thickness (theoretical) of patina coating the limestone blocks of Hatshepsut Temple (on the base of natural patina on limestones) is as follows:

3500 years (age of temple - time of construction of Hatshepsut Temple)  
 X 0.02 - 0.03  $\mu\text{m}$  (rate of growth of patina per year - calculated from patina coating signature of Butehamon) =  
**70 - 105  $\mu\text{m}$**  (theoretical thickness of patina on blocks of temple).

After comparison of the value calculated above with the actual measured thickness of patina coating the limestone blocks of the temple, one can say that the theoretically calculated thickness is 3 times smaller on 8 times longer than that measured on the blocks.

There are a few reasons for this effect.

The diversification of the thickness of the patina on limestone blocks of the temple is a reason for the variability of the mineral composition of limestones. This feature may lead to faster or slower patination of limestones. The main reason for this phenomena is the relationship between calcite, clay minerals and iron minerals (sulphides) as well as the porosity of rock.

A second reason for the various rate of patination is the condition of the limestone blocks present. Blocks coated with sand and not exposed to sun light or exposed from time to time are protected against patination. Because of this, the patina is not fully developed and is thin.

The next reason for the various rate of patination is the difference in the local humidity of the place where the limestone blocks are present. Blocks located at the base of stone walls (foundations of temples) are often slightly more wet than blocks present above. The presence of wet and dry conditions plays an important role in the process of patination i.e. alternation of minerals.



## **CONCLUSIONS**

### **1. Genesis of patina**

The formation of patina on the surface of rock is a kind of weathering and depends on climatic condition i.e. humidity, temperature, mineral composition of rock, etc (Pawlikowski 1994, Pawlikowski and Wasilewski 2004). The phenomenon observed for the tested samples suggest that the patina under consideration is diversified. Old patina observed on the natural surface of limestone is composed of a few layers showing various mineral compositions. Younger patina is generally composed of one layer. This observation suggests that old and thick patinas were formed at various climatic condition while younger where formed at relatively constant climate (Said 1962).

### **2. Patina as a factor for stone objects dating**

Our investigation showed that the speed of formation of patina is not constant i.e. at some climatic conditions patination is faster and at others slower. Moreover, most probably even on the same block of stone, the rate of patination is some time reduced (Pawlikowski and Wasilewski 2004). This phenomenon cause the formation of patina to run slower at deeper parts of the ealier patinated surfaces.

Other problems concern the mineral composition of various limestones as well as their porosity and grain size composition. This means that even limestones from one Theban formation will be patinated at different rates the same time.

Taking under consideration mentioned phenomenon one can say that the thickness of patina is possible to us as factor for data of patinas developed at Egypt during desert climate and only on similar type of the stone. But this climate has been constant during the last 8-9 000 years generally only in Upper Egypt and farther to the South. Near the Mediterranean Sea, a hot and dry climate has not been formed even up to now.

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