
RESEARCH OF FLINT PATINA FROM THE EASTERN DESERT OF EGYPT

Badania pustynnej patyny z krzemieni z Wschodniej Pustyni Egiptu

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Abstract

The subject of patination of flint has been discussed in many scientific publications. The majority of research concentrates on the applicability of the criterion of patina thickness on determining the age of flint artefacts, as well as for studying the correlation of archaeological profiles.

Detailed knowledge of the mechanisms of patination, both in terms of physical and chemical, as well as mineralogical processes, is necessary for the correct interpretation carried out for each archaeological site. The large number of factors affecting patination greatly complicates any analysis of these conditions. This publication presents the research results of desert patina developed on flint artefacts in the conditions of the Eastern Desert of Egypt. Studies indicate mineralogical and chemical variability of patina in different types of flint.

Keywords: patina, flints, desert, Egypt, SEM, EDS.

Introduction

Flints are siliceous rocks of various origin (Pawlikowski, 1980, 1989, 1990 a, b, 1993 a, b, 2001, 2002, 2008). Most often, they are recrystallized concretions formed from sponges with skeleton made of silica needles (spicules). This mechanism leads to the formation of 'primary' nodular flints with regular shapes.

The silicates may also be formed by chemical processes leading to the crystallisation of silica in crystallisation areas. This process usually leads to the

creation of 'secondary' flints, which typically have irregular, complex shapes (Ginter et al., 1996).

Two different types of patina can be distinguished in flints. Their occurrence is determined by many physical and chemical (environmental) factors occurring in two extremely different climates – polar and desert.

Bright patina is linked mainly to the physicochemical processes occurring in cold climates. White in colour, it is formed on silicates by the disintegration of subsurface zones exposed to moisture. During seasonal temperature changes, repeated sequences of freezing and thawing of moisture occurs in the flint, and especially on its surface. This results in the systematic destruction of flint structure, in turn loosening the chalcedony crystals in the surface areas of the flint, and causing the surface to crack in many places.

As a result of this process, not only the crystals edges become damaged, but are also 'split' from one another by microscopic cracks. This causes a phenomenon of surface light scattering – the specific absorption and refraction of light. The outcome of these processes is observed as a bright patina.

Dark patina is characteristic in flints present in warm climates (hot and dry). Its character and the patination process will be further discussed.

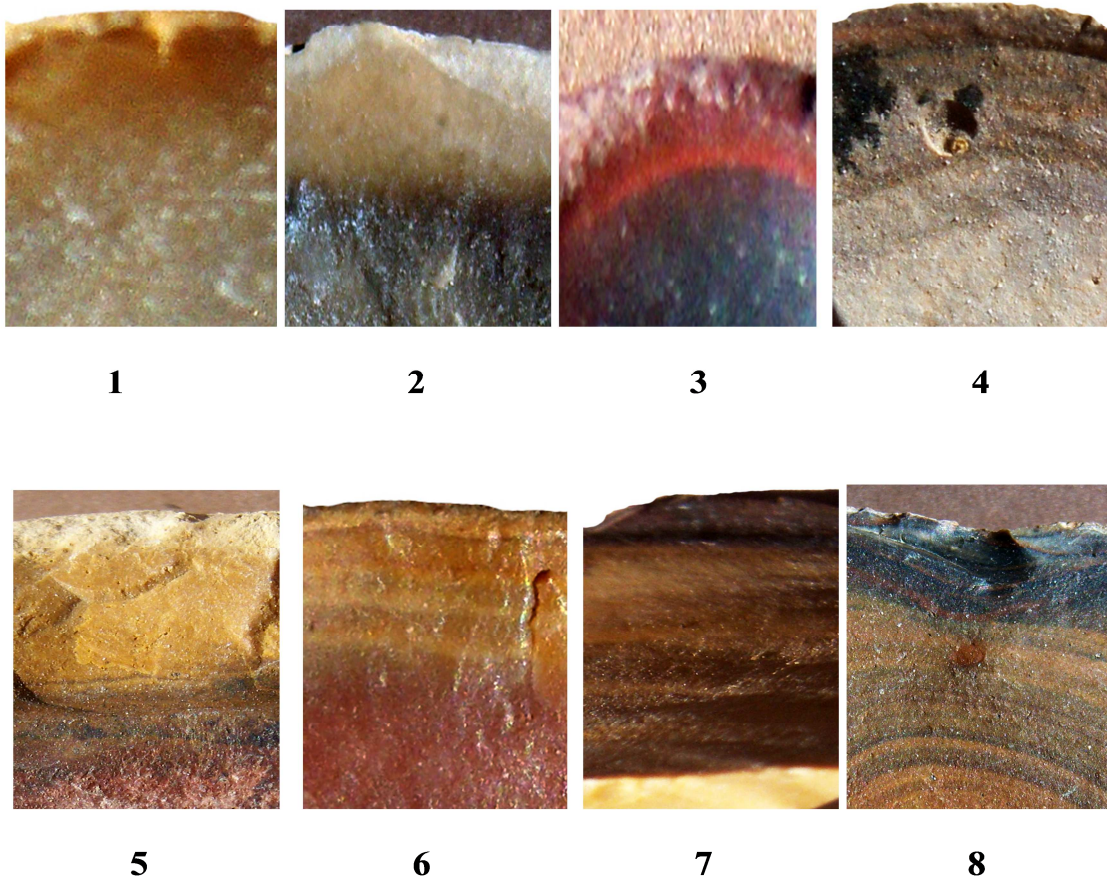
The patination of flint in warm climates is related to the phenomenon of migration (leaking) of various elements, mainly iron and manganese, from the core of flints to their surface, and their accumulation in the oxidised form in the superficial areas of flint.

In hot and dry climates large diurnal temperature changes occur, associated with strong insolation during the day and low temperatures at night. Night cooling causes the condensation of small amounts of water vapour. The resulting moisture is deposited on the surface, including artefacts and siliceous nodules. After its deposition on flints, moisture penetrates into their interior. As a result, the minerals contained in the flints, mainly iron and manganese, dissolve in the moisture. When exposed to sunlight, the 'soaked' flints begin to heat up, evaporating the moisture accumulated during the night. This process of evaporation leads to capillary action, i.e. the transfer of moisture (containing Fe and Mn) to the surface of the flint. Consequently, Fe and Mn elements transported from deeper layers of the flint to its subsurface (where moisture evaporates completely) become crystallised. This phenomenon – observed in the subsurface and surface parts of the flint – is referred to as dark patina.

Dark patina has the appearance of one or more dark lamina (patterned layers). The thickness of this lamina is determined by the length and intensity of the described process and the amounts of Fe, Mn and others elements present in the flint. The process of patination of flint in warm climates is cyclical, and may occur many times.

Sample collection and research methods

Flint samples collected in the Eastern Desert were studied. This paper discusses only a selection of the results obtained. The study was conducted using stereoscopic microscopy, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). The study focused on the mineral variation of patina in the collected samples. Figure 1 presents several of the studied samples.



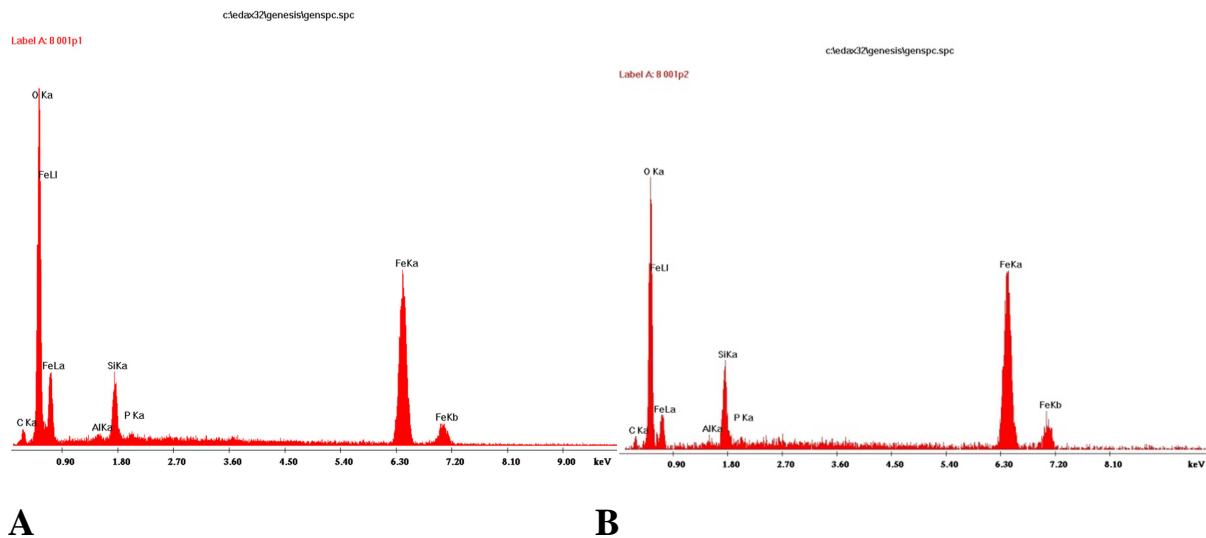
Fot.1, **1** - Young patina build of one layer of iron oxides, **2** – surface area of flint containing chalcedony, **3** – two layers patina build of chalcedony with various mixtures of iron oxides, **4** – many layers of patina of Mn and Fe oxides, **5** – multi-layered patina, Fe and Mn oxides, **6** – layered patina – layers with and without iron oxides, **7** – dark layered patina formed mostly of Mn oxides and containing admixture of iron, **8** – layers of patina containing Mn-Fe oxides at various depth under the flint surface.

Macroscopic observation under low magnification focused on the presence of accumulated leached elements. These occur in the form of narrow, usually regular lamina.

A pattern was observed, consisting of thicker layers forming in disrupted sections of the samples, i.e. with a higher predisposition for water penetration. A less regular pattern was observed in some of the laminae, probably due to the internal heterogeneity of the samples. The migration of dissolved compounds

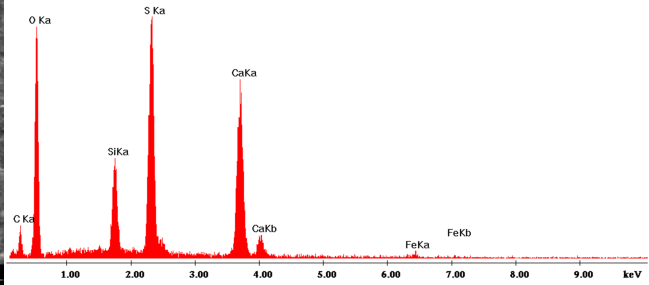
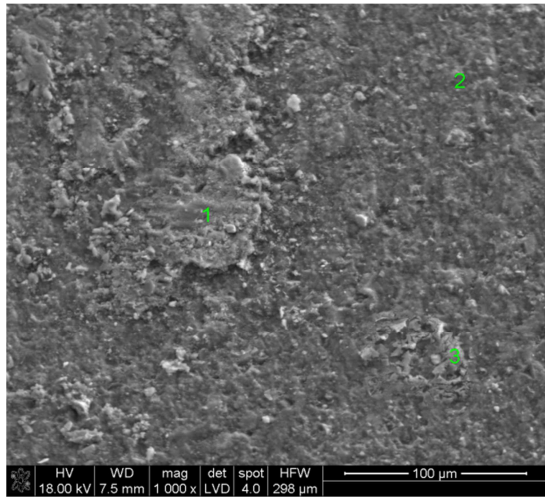
and the accumulation of oxidised elements is strongly affected by the defects in the flint structure.

The exact chemical composition of each sample was studied using energy-dispersive X-ray spectroscopy (EDS). Based on the results, it was found that the main elements affecting the coloration of the samples were oxidised iron and manganese compounds (Fig. 1, A, B).



A **B**
Fig. 1 A, B - Sample EDS spectrum of the Eastern Desert flint patina composed of iron and manganese minerals.

Particle analysis of flint structure using scanning electron microscopy reveal a polymineral character of the material. In addition to finely grained chalcedony, the flint samples contained automorphic crystals of gypsum, halite, and strontium (Fig. 2, 3). Within the samples used for this study, these crystals were usually larger than the 'background material' composed of chalcedony. The origin of strontium sulphate and gypsum in the samples is likely to be related to the phenomenon of iron sulphide oxidation resulting in the formation of iron oxides. Halite may occur in flint due to secondary crystallisation induced by moisture present in the sandy soils from which the samples were collected.

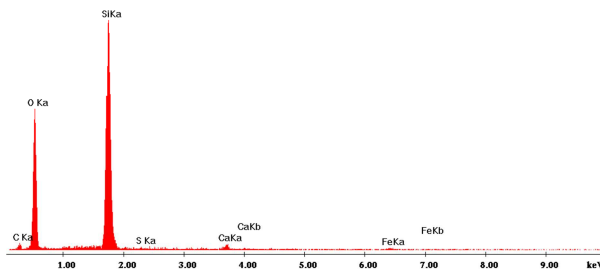


A

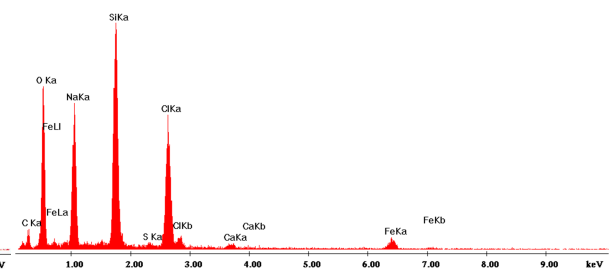
Label A: 10 001p2

B

Label A: 10 001p3

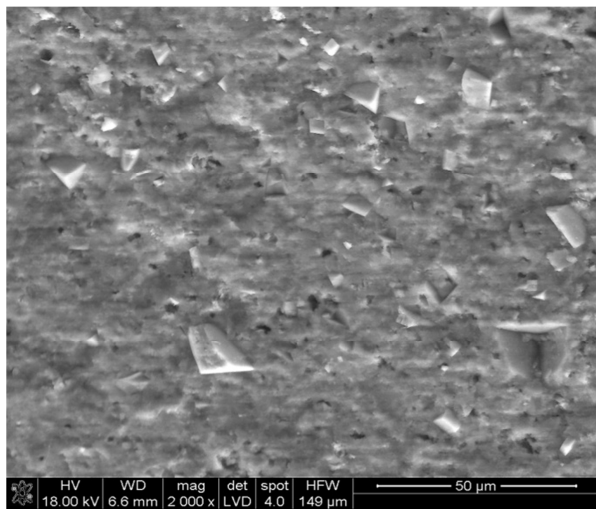


C

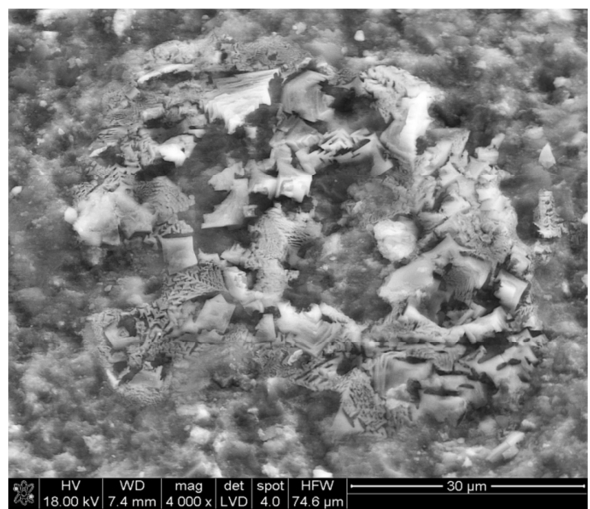


D

Fig 2 A - SEM micrograph of the flint surface with EDS microanalysis areas marked, B - EDS spectrum of point 1; the accumulation of elements characteristic for calcium sulphate (gypsum/anhydrite), C - EDS spectrum of point 2; silica; D - EDS spectrum of point 3; the accumulation of elements characteristic for sodium chloride and silica.



A



B

Fig. 2 A - flint structure with larger crystals of gypsum - No. 1.
 B - concentration of halite crystals in the flint subsurface zone (below patina). No. 3.
 SEM magnification by scale.

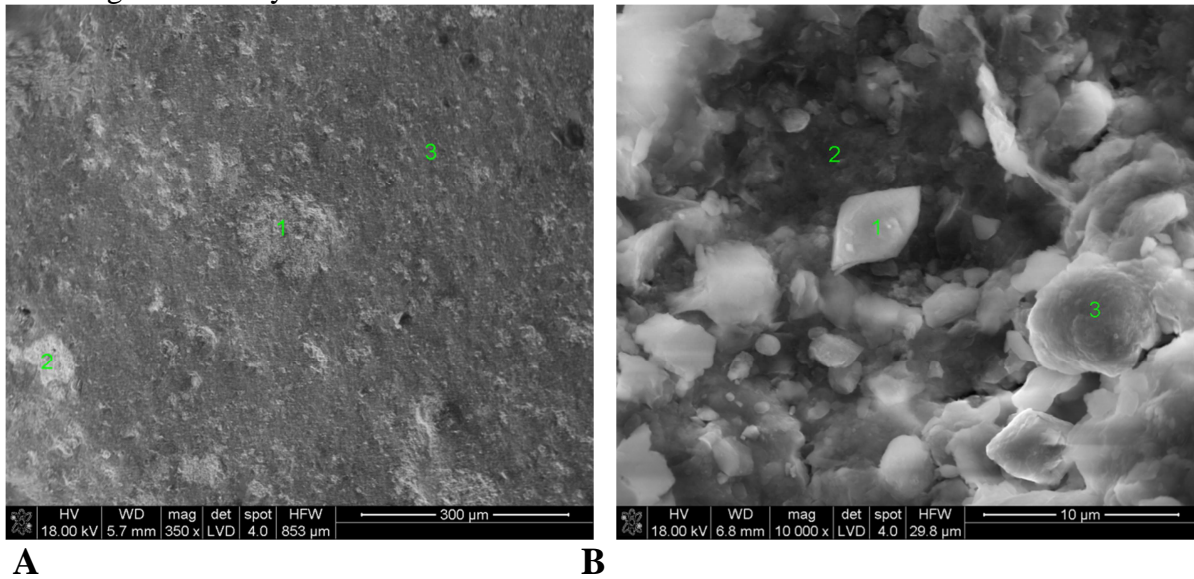


Fig. 3 A - flint fracture surface observed at low magnifications. 1, 2, 3 mineral concentration in larger crystals. B - microscopic image of coarser crystalline section of the flint, point 1 indicates the presence of strontium. SEM magnification by scale.

Label A: 6 003p1

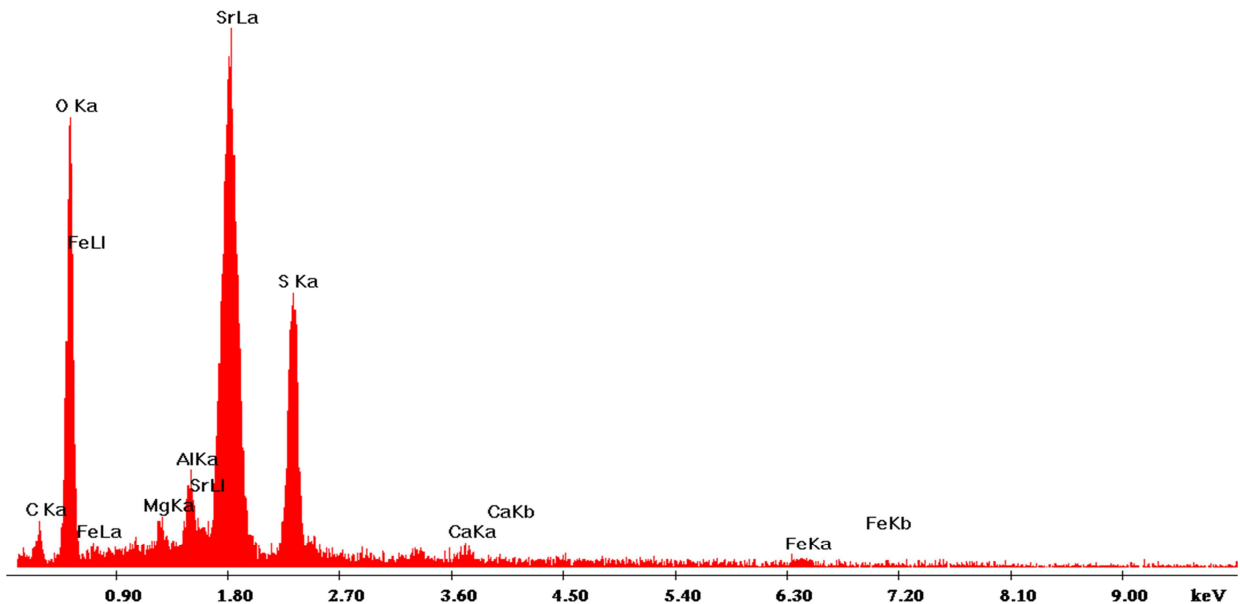


Fig 3. EDS chemical analysis of area in point 1 Fig. 3 B. Visible accumulation of strontium and sulfur.

Conclusions

The process of patination in warm and cold climates is always accompanied by the degradation of the flint structure. Flint patination can be described as a complex set of physical and chemical phenomena. For this reason it is important to determine the exact factors affecting the process.

Apart from the effect of moisture on the formation of dark patina, the process of patination of flint is affected by the exposure to UV radiation. It has been proven (Rottlander, 1975) that UV radiation has a destructive effect on the SiO₂ structure.

The effect of pH on the process of patination is visible in temperate environments, in which a significant effect on the disintegration of the structure is caused by humic acids (Glauberman & Thorson, 2012).

Based on the data obtained, it can be concluded that red patina contains more iron (Fe⁺³) elements than patina of darker shades, rich mainly in Mn. The study also shows that the correlation analysis and indirect dating of flint, based on the main criterion of patina thickness, should include additional factors, such as:

- Flint samples should be exposed to identical conditions (climate, exposure to UV radiation, pH of the environment),
- Flint samples should be of the same mineral and chemical structure.

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