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MINERALOGICAL INVESTIGATION OF DESERT PATINA ON FLINT ARTIFACTS: A CASE STUDY

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ABSTRACT

The paper presents results of mineralogical analyses of patina covering pieces of flint from Deir el-Bahari in Egypt. Mineral composition and different kinds of patina are described. Forming of patina in desert conditions is connected with removal of iron, manganese, silicon, calcium and other metals from chemical structure of flint, as well as, crystallisation of minerals – derivative of these metals, both on the surface of flint and below surface. Composite patina covers of varying chemical composition and thickness are described, and the potential dating of flints from patination is discussed.

KEYWORDS: weathering, mineralogy, Egypt, Palaeolithic, flint, patination

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INTRODUCTION

Habitation in Nile Valley, as well as, Deir el-Bahari was for thousands years ago (Mond and Meyers 1937; Kaiser 1958; Drobniewicz and Ginter 1976; Ginter *et al.*, 1979; 1985; 1987; 1988; Heflik & Kozlowski 1977). Many Palaeolithic archaeological sites were discovered in this area. Flint artefacts and natural flint nodules are very common in this place. Most of them is covered with patinas of various colours and thickness. The colour of patina as well as thickness vary according to the age of flint and procedures in which patina was formed.

In region under the consideration flints in situ occur in light Eocene limestone, also called Theban Limestone Formation (TLF). Many horizons of flints of different size, shape and mineral composition can be seen in the limestone. Flint forms residual slope sediments, which cover the plateau and hills surrounding Nile Valley. They represent deposits which were formed as a result of weathering and concentration of flints of TLF. Those flints were used as a material for producing tools during Palaeolithic and Neolithic periods.

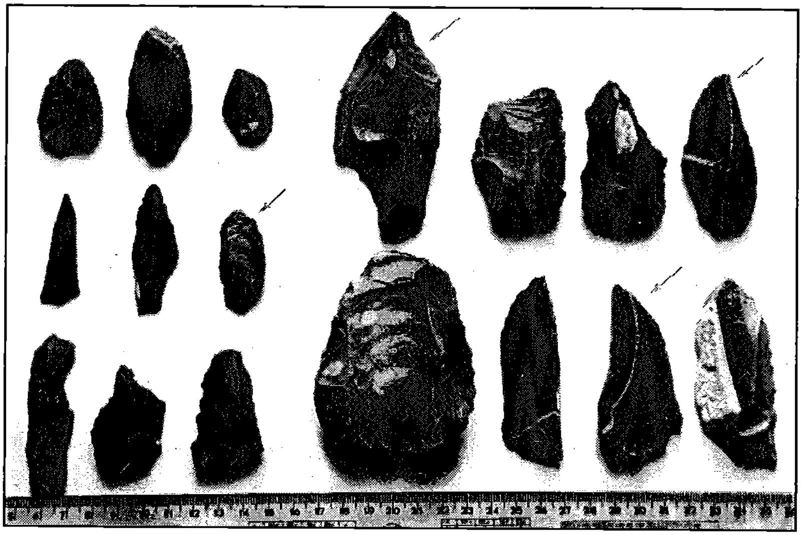

Fig.1: Flint artifacts from near Hatzepsut temple in Deir el-Bahari. Arrows indicate analysed artifacts.

The aim of the project is to recognise the structure and mineral composition of desert patina and determination of physical-chemical process of its formation. These investigations contribute towards possible relative dating of archaeological artefacts based on patina layers, which develop as a function of time, as explained below.

SAMPLES AND METHODS OF ANALYSES

About seventeen flint artefacts (core, flakes, blades, etc.) (Fig.1) and twenty pieces of unworked flint were collected from the area near Hatshepsut temple in Deir el-Bahari. We have distinguished six sorts of flint:

- beige with light brown, thin patina
- beige with brown, thick patina (Fig.2A)
- dark beige with black/dark brown and white thick patina (Fig.2B)
- milk-coffee with thin brown or without patina
- milk-coffee with multicolour thick patina (Fig.2C)
- black with black patina (Fig.2D)

The samples were cut with a diamond saw. The surfaces of investigated pieces and weathered layers were examined. The pieces of flint covered with the thickest and differential in structure layer of patina were selected for further research i.e. transparent polarised light microscopy. The observed phenomena were documented with microphotographs.

Next, samples were analysed using scanning electron microscope. Samples were coated with carbon and examined under the electron scanning microscope (SEM) Geol 540, coupled with an EDX-Ray analyser. This way the chemical composition of patina layers was determined.

RESULTS OF INVESTIGATION

The results were juxtaposed starting from artefacts and pieces of flint covered with a simple, monolayer patina, to pieces with multilayered, composite patina.

a) monolayer patina

This can be observed on flint containing significant admixture of fine-crystalline calcite. In patina, ore minerals under polarised light microscope are well seen (Fig. 3). The quantity of mentioned minerals rises from the central parts of flint towards the subsurface layer. The most intensive mineralisation can be noticed on the surface of flint and occasionally on the flint - patina contact. At the same time the organic debris near this surface is significantly more mineralised (Fig. 4). The patina layer is irregular and of thickness varying between 0.1 to 0.5 mm.

b) bi- and multilayer patina

Multilayer patina is the most frequent kind. In this case the following sequence of patina layers can be observed (in order from the surface):

A) the surface layer – Fe and Mn oxides and hydroxides on the flint surface (Fig. 4)
B) the silica layer – mostly fine-grained chalcedony under the A layer (Fig. 5, Fig.6)
C) the inner part of flint – consists of chalcedony with calcite admixture (Fig. 6)
D) the secondary opaque minerals zone-near the lower part of the B layer (Fig. 6)

Sometimes B layer could be differential and one can observe in it:

- layers of secondary silica (Fig. 7)
- one or more calcite layers (Fig. 8)
- layers of opaque minerals.

CHEMICAL CHARACTERISTICS OF THE EXAMINED PATINA LAYERS

SEM analyses, especially EDX, showed several interesting regularities due to distribution of elements (Fig. 9). The patina is rich in silica but generally does not contain calcite. It means that calcium, occurring in flint in the form of calcite is relatively easy dissolved and removed away. Therefore, silica is gathered in the outer part of flint. The concentration is however connected with decrease of calcite quantity and it is not affected by increase of chalcedony quantity (Fig. 10). In addition, the concentration of sulphur can be noticed just under the patina. Rather, the sulphur comes from oxidation of iron sulphides occurring in the flint. Iron originating from this process takes the form of oxides and hydroxides which form a dark glazing on the surface of the flint. Sulphur, mainly in the form of calcium sulphate (gypsum), remains under the patina. The chemical reaction is as follows:

$FeS_2 + 2H_2O + CaCO_3 + nO_2 = FeOOH + CaSO_4 \times 2H_2O + SO_2 + CO_2 + H^+ + S$

As it can be seen in the patina forming zone the chemical environment is aggressive with excess of protons. The acid environment leads to dissolution of endogenic calcite and could favour the corrosion of chalcedony occurring in the flint. There are many corrosion pits and voids in chalcedony, where, at the same time secondary concentration of flint silica originating from the areas of solution can be observed.

During patination another significant process can be observed. It is uneven distribution of organic phosphorus on the surface and subsurface of flint layer (patina zone). In the inner part of flint phosphorus it is distributed rather evenly.

The problem of elemental distribution in multilayers patinas is much more complicated (Purdy and Clark 1987). Scanning microscope analyses of patina cross-sections (Fig. 11) (especially elemental distribution) shows that patina could be formed in several different processes or in only one complex process. The latter possibility gives a very characteristic sequence of elemental distribution as a result of the dissolution and crystallisation succession of minerals. It is obviously connected with solubility of different minerals. In multilayers patinas the decrease of silica near the surface of flint can be observed. The surface itself can be enriched in Mn, Ti and sometimes P and Al (Fig. 12).

In monolayer patinas Fe– Mn oxides and hydroxides crystalline from the flint environment as well as from the flint itself. The process of withdrawing Ca is not advanced, however it may be that in the case of deficiency of Fe– Mn oxides and hydroxides monolayer patina is composed mainly of silica. Thus, the number of weathering rinds (patina layers) should not be directly connected with the age of patina. It seems that monolayer patinas are the indicators of stability of the flint weathering environment, whereas diversity of patina layers depends on changes of weathering conditions.

GEOLOGICAL CONDITIONS IN THE FORMATION OF FLINT ACCUMULATION

The procedure of flint accumulation on the surface of limestone under desert condition should be taken into consideration when searching for causes of patina. This natural process is similar to anthropogenic flint concentration (i.e. in archaeological sites). The formation of the natural flint residues is conditioned by karst of the limestone with primary origin flints (so called flint nodules).

Karstification is stimulated by rainfalls, especially by dissolution of limestone by slightly acid rainwater. Carbonates as the main components of limestone are usually replaced with red argillaceous sediment, called in the Mediterranean terra rossa. The flint nodules, exceptionally resistant from chemical corrosion, concentrate in these argillaceous sediments.

Under desert conditions the *terra rossa* and flint undergo further weathering. The intensity of this process depends on aeolian weathering activity. Desert winds blow out the fine-grained residuum in which flints are found. As a result of this process nodules gather on the eroded surface of TLF forming rubbles (Fig.13).

The result of continuation of the described above process is accumulation of uncovering consecutive flint nodules in residuum (concentration of nodules *in situ*). In this way successive flint nodules appear on the morphological surface. They are exposed to the erosive factors like wind, sun, water, temperature. Those of flint nodules which appeared on the surface earlier are the subject of longer patination process than nodules coming out later (fig. 13). Significant time differences in flint patination lead to formation of different kinds of patina. The process itself can change in any of the stages of forming the flint desert pavement. The intensive process of blowing out the material from spaces between the flint nodules may cause the situation in which the nodules accumulate on the limestone surface. Consequently the nodules of different age, degree of patination and often various type of patina may occur in the same horizon.

Variations of mineral composition and structure of the flint nodules interfere with the described processes. These influence the process of patination causing significant changes even in one flint concentration. As the result of all the processes described above the flint nodules and/or flint artefacts of differential patination can be observed both in natural and athropogenic accumulations.

MINERALOGICAL AND CHEMICAL PROCESSES IN FLINT AND FLINT PATINAS

Patination is mainly caused by withdrawing colloidal silica from chalcedony skeleton of flint and its crystallisation near the surface, the diffusion of H^+ ions and absorption of Fe-Mn oxides on and under the surface as well as their crystallisation from solution removed from the flint.

As mentioned above, the secondary mineral stages (phases) developed on flint's surfaces come up as a result of several simultaneous processes. The insolation, which means alternative heating and cooling of flint. This phenomenon repeating itself many times causes not only changes in capacity and loosing intergranular space but, what is especially important, changeable moistening of flint. Flint nodules dry during the day, while at night, when the temperature drops down, absorb only a small quantity of moist. This leads to dissolution of minerals in the flint (especially sulphides as piryte, markasite, which usually occur in form of isolated grains).

The decay (putrefaction) of sponge (natural, biological silica material which built flint) is not only the source of silica but also, in reduction conditions, causes the presence of post organic sulphides. Iron sulphides during oxidation become iron oxides and iron hydroxides. This process increase the acidity of environment. The formation of light carbonic as well as sulphuric acids is possible. Both acids present in the external (oxidized) part of flint may dissolve carbonates (calcite). This is the cause of absence of calcite in patination zone. Iron, manganese, phosphorus, calcium, silica dissolved in the inner (deeper) part of flint, go together with the water towards flint's surface. On the surface water evaporates. Fluid gets dense and some minerals crystallise forming dark glazing – patina.

The process described above causes the reflexive positive interlock. This means that the darker and thicker patina warms up faster. The rise of temperature together with other weathering agents like humidity, chemical composition of environment accelerates the process of patina formation. Obviously the longer these conditions last the thicker patina becomes.

DISCUSSION

Some authors (Rottländer 1997; Wagner 1998) question the possibility of working out the reliable system of dating flint, considering patina's characterisation only as a representation of sedimentary environment's dynamics. Estimation of the age of certain flint artefact or flint nodules is based on analysis of thickness and number of patina layers, as well as, differences between different kinds of patinas (for instance differences in colour and chemical composition).

But the environmental changeability (i.e physical and chemical conditions of weathering) is a significant factor which may disguise direct dependence between the thickness and character of patina and the time of its formation.

Thus, in our opinion the critic of datation based on patterns seems to overestimate an influence of unregistered environmental changes on the process of patina formation.

The time range of the method lies between 1000 and 500 000 years (Wagner 1998). This time span is outlined by the facts that patina layers less than 1000 years old are very thin that makes dating impossible or problematic, while, more than 500,000 years of patina, layers are so thick that all weathering processes cease. Unfortunately the datation based on weathering rinds (e.g. patinas) needs a very complex study on paleoclimate, environmental chemistry, weathering factors and mineralogy of rocks.

CONCLUSIONS

The mineralogical processes taking place on the surface of the flint depend on many factors, therefore working out clear and precise methods of dating is problematic. Differences in composition of flint artefacts, changes in environment humidity , pH, redox potential, but also temperature and presence of various dissolved substances, coming from geological surrounding, affect the chemical composition and thickness of patina layer. It should, also, be noticed that weathering processes (i.e. aeolic erosion or dissolution) can influence the character of patina.

Nevertheless, it seems that under certain conditions, such as the petrographic uniformity of investigated material, and the stability of some climatic and weathering factors (Purdy and Clark 1987) the estimation of the artefact's age on the base of patina's thickness may be possible. Only precise explanation of patina forming processes may help in working out useful methods of dating archaeological artefacts and young rock formation.

It must be emphasized that due to the complex processes the use of this method would be restrained to particular territories.

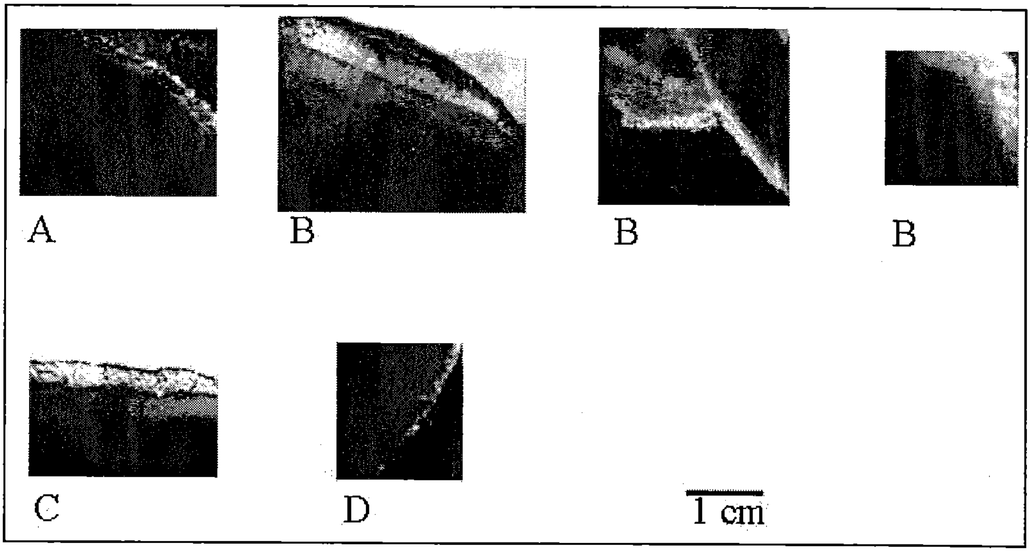

Fig. 2: Different flint patinas. A – beige with brown thick patina, B – dark beige with black/dark brown and white thick patina, C – milk-coffee with multicolour thick patina, D – black with black patina.

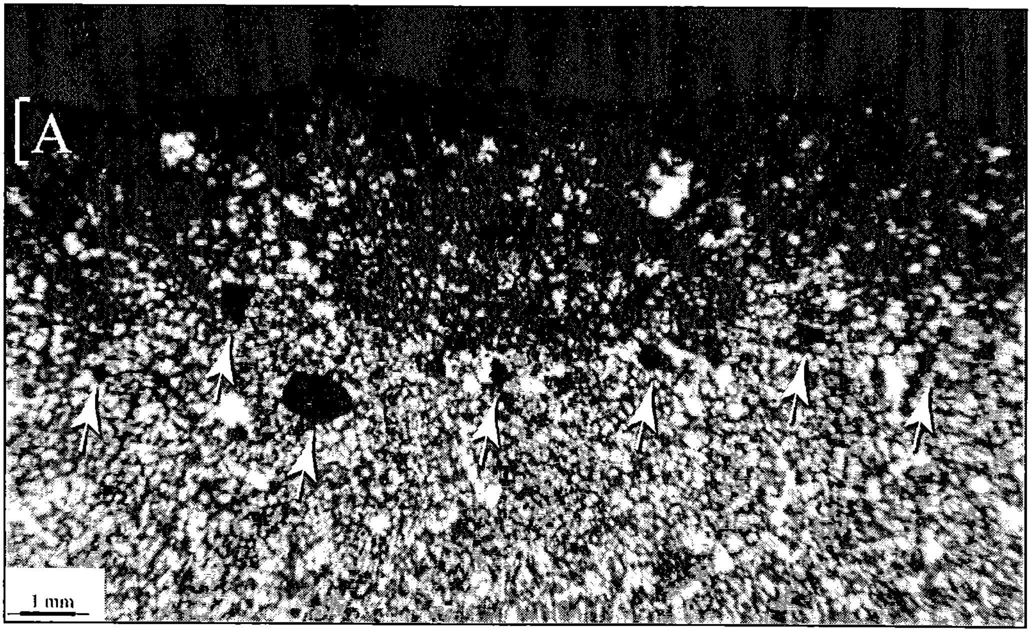

Fig. 3: Monolayer patina. Fe-Mn oxides (arrows) concentration under patina (under A layer). Polarised microscope, polaroids partially X, multiplication 80x.

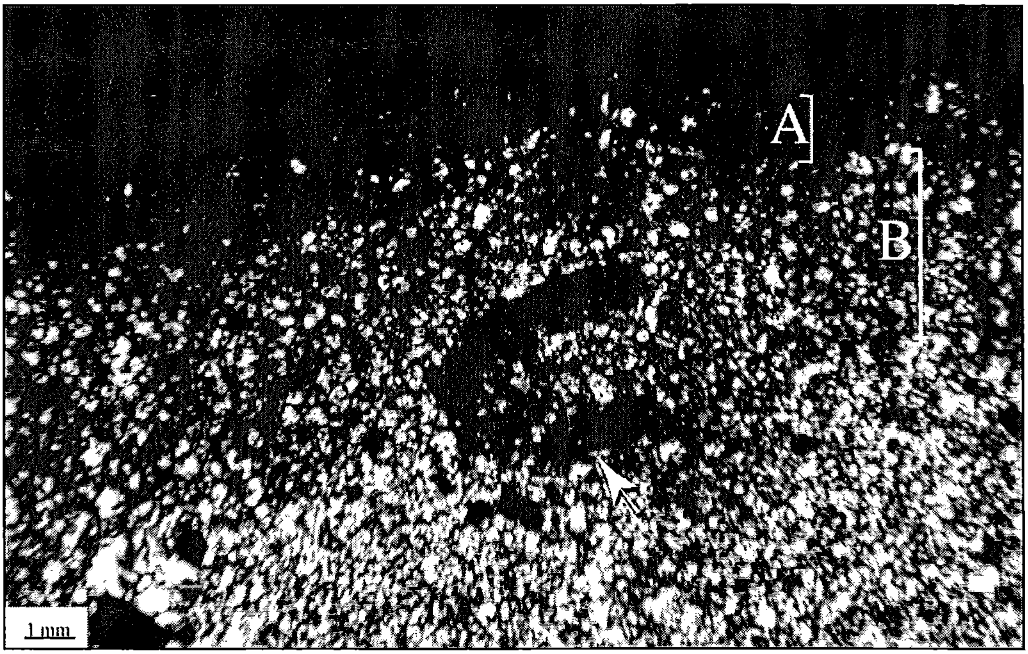

Fig. 4: Bilayer patina. Dark concentration of Fe-Mn oxides and hydroxides in A layer. Minerilised organic debris is well visible (arrow). Polarized microscope, polaroids partially X, multiplication 80x.

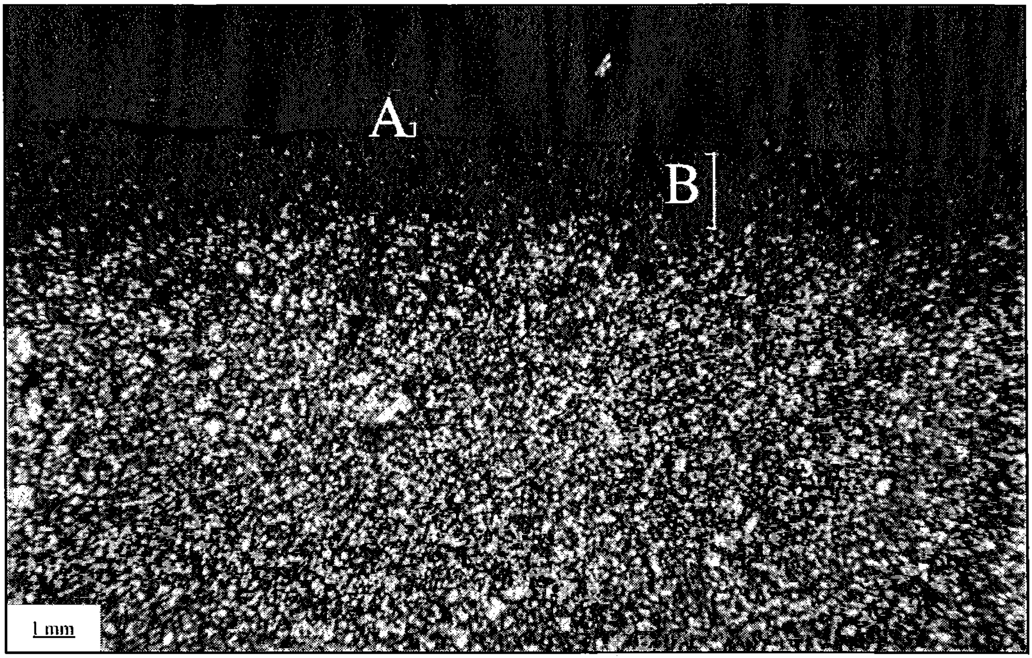

Fig. 5: Bilayer patina. Layer B is composed mostly of chalcedony, without calcite. Polarized microscope, polaroids partially X, multiplication 80x.

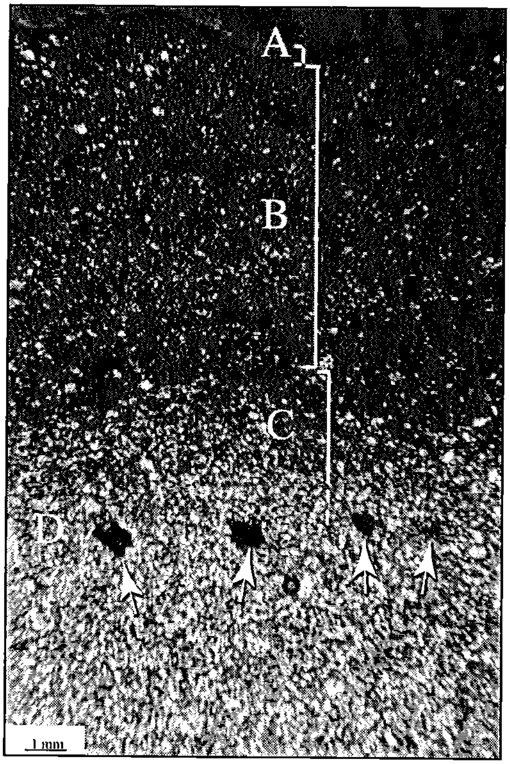

Fig. 6: Multilayer patina. Layers A-D – explanation in the text. In layer D idiomorphic ore minerals concentrations are well visible (arrows). Polarized microscope, polaroids partially X, multiplication 80x.

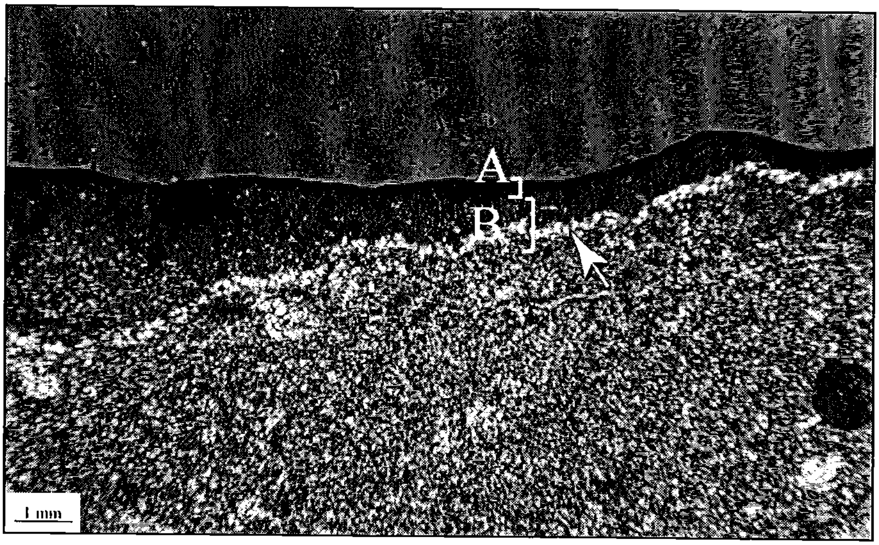

Fig. 7: Bilayer patina. Layers A-B – explanation in the text. Arrow shows secondary, fine crystalline quartz layer, on the 1B-layer contact. Polarized microscope, polaroids partially X, multiplication 80x.

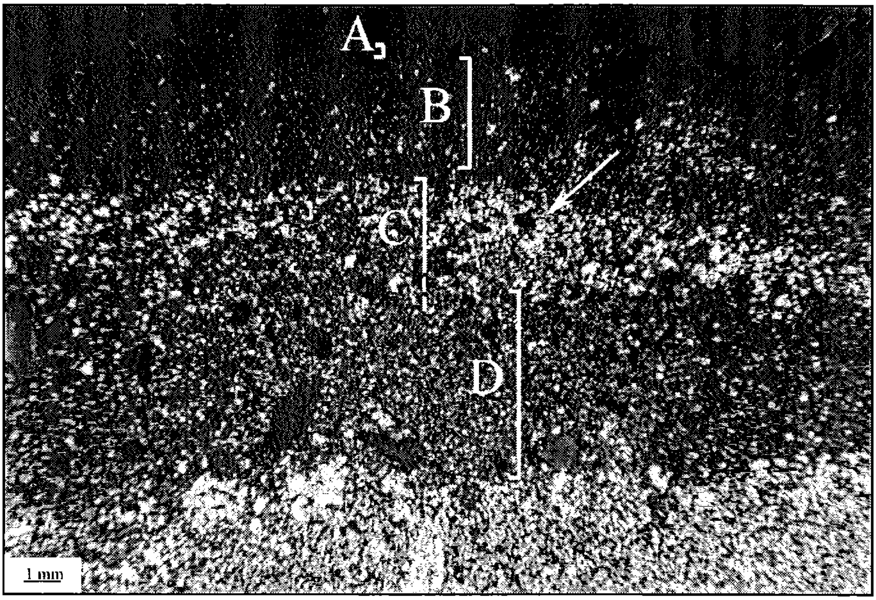

Fig. 8: Multilayer patina. Layers A-D – explanation in the text. Calcite enriched sublayer can be seen in the C layer (arrow). Polarized microscope, polaroids partially X, multiplication 80x.

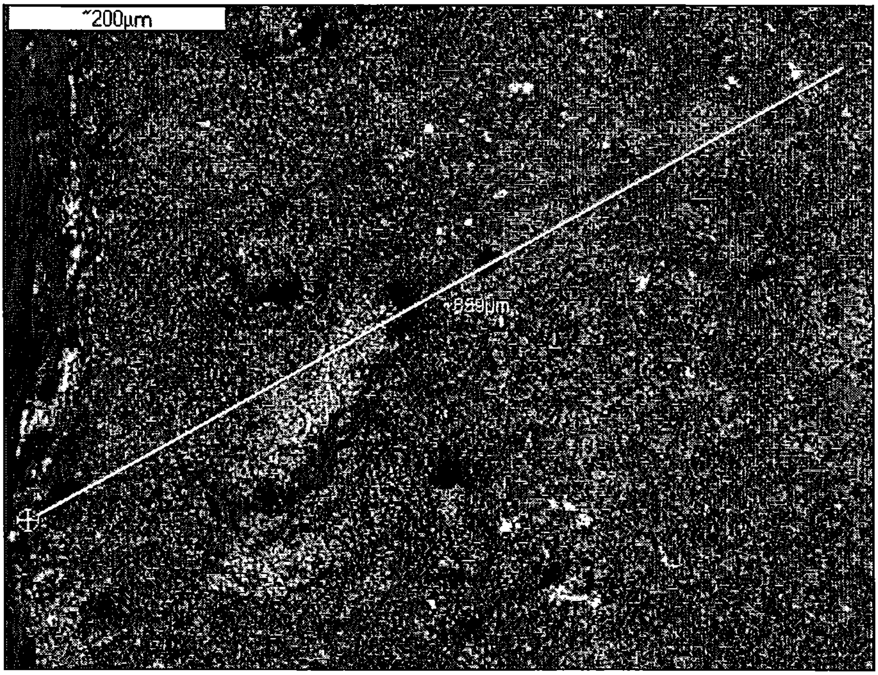

Fig. 9: Microscopic view of one multilayer patina on flint by scanning microscope. White line shows the most intresting direction of chemical analysis (EDX) mentioned on Fig. 10. Crossed circle shows the surface of the flint.

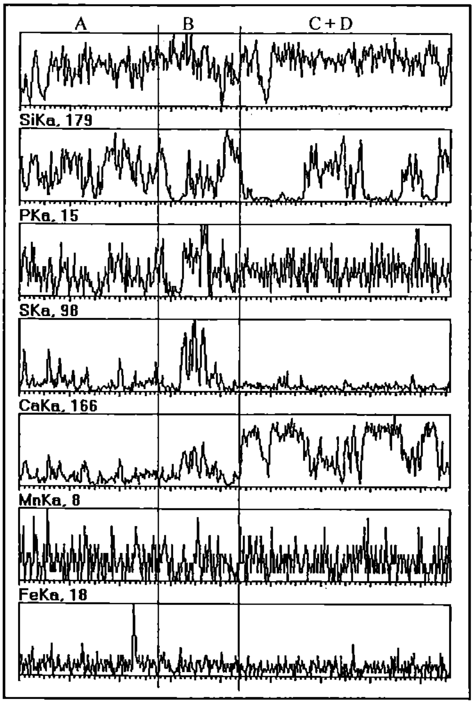

Fig. 10: Semiquantitive chemical analysis (kevex) of external, patinated part of flint. One layer patina.

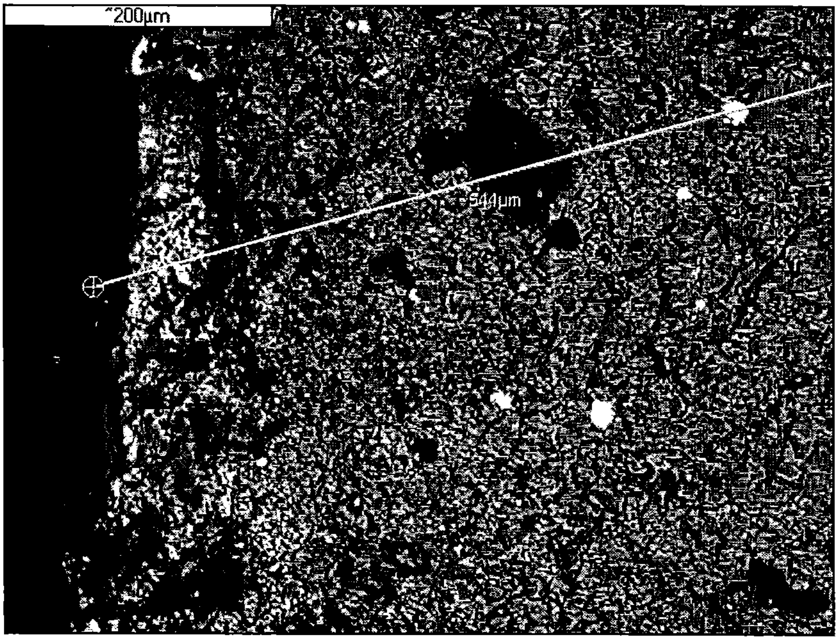

Fig. 11: Microscopic view of bilayer patina on flint by scanning microscope. White line shows the place of chemical analysis (EDX) mentioned in Fig. 12. Crossed circle is flint's surface.

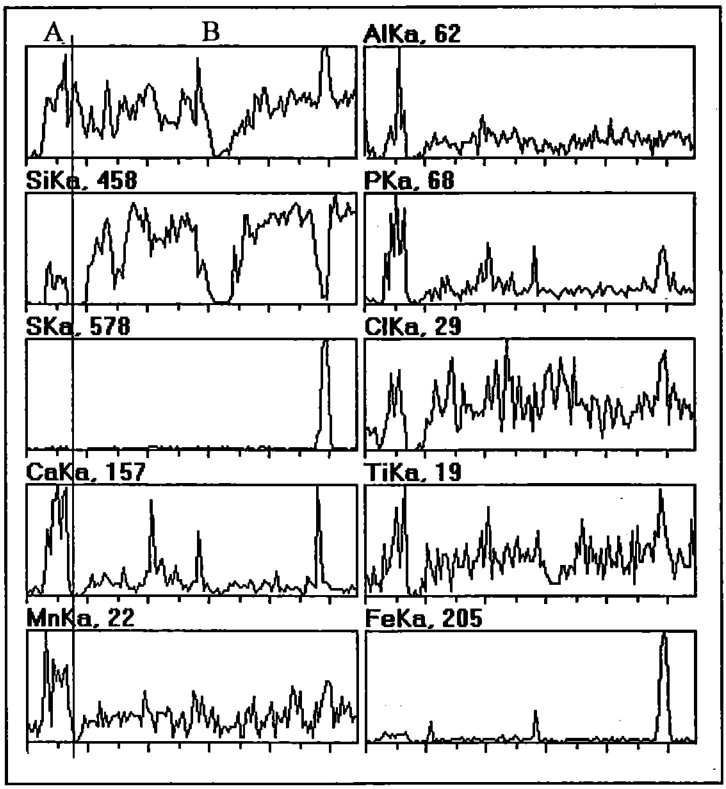

Fig. 12: Semiquantitive chemical analysis (kevex) of external, patinated part of flint. Two layers patina. Legth 544,3 µm, vertical scale: counts/sec. (Corresponds to fig. 11).

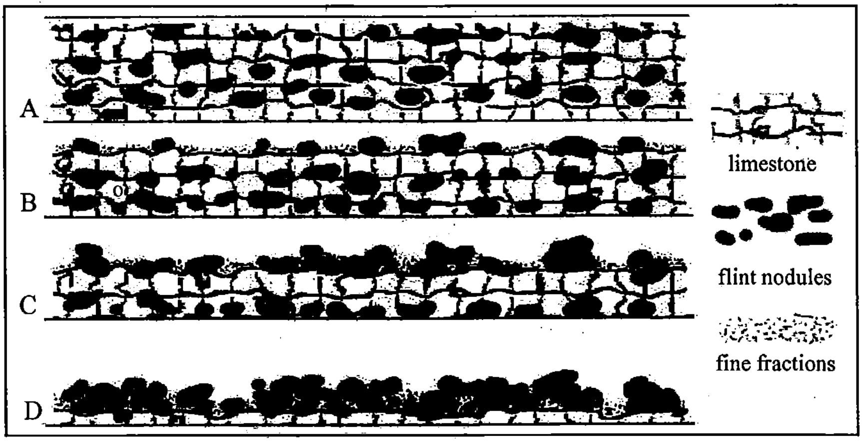

Fig. 13: Weathering of limestone causing different patination of flint. A, B, C, D show successive stages of weathering from intact limestone bed (A) to the present situation (D).

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