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**FACULTY OF NATURAL AND  
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# NATURAL RESOURCES AND TECHNOLOGY

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## PRELIMINARY RESULTS ON THE INFLUENCE OF LICHENS ON THE MONUMENTS AT THE STOBI ARCHEOLOGICAL SITE

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### Abstract

This paper provides preliminary data about the influence of gray and yellow lichens on the monuments in the Stobi archeological site. The origin of the minerals which adhere to the rhizine/hyphae was also determined. According to the SEM results, small grains of minerals are found in lichens which originated from parent rocks or weathering. In the lichens on marble the presence of the following minerals was determined: calcite, dolomite, Fe carbonate, Ca silicate, Ca, Fe, Al silicate and Fe, Al silicate. Carbonate minerals come from marble while silicates are the result of weathering.

In lichens on sandstone the following minerals were determined: K, Al silicate, Ca carbonate quartz, Fe, Mg silicate, Fe-oxide, zircon, and Na, Ca, Al silicate. Carbonate minerals are the result of weathering while other determined minerals originate from sandstone. Clay minerals are the result of the decomposition of feldspars.

**Key words:** lichens, marbles, sandstone, Stobi.

### INTRODUCTION

Stobi archeological site is an ancient city located at the confluence of the Crna River and the Vardar River near the village of Gradsko, about 80km south of Skopje. The earliest written evidence of Stobi is found in Livy's *Ab Urbe Condita*. It refers to the triumph of Phillip V against the Dardanians. Livy says that the battle happened near Stobi in 197BC. The next line that refers to our town informs that the river Erigon (Crna) flows into Axios (Vardar) near the "old town" of Stobi. The third information about Stobi takes us to the Roman occupation of Macedonia and the year 167BC, when Stobi became the main trade center of salt in the third meris. Written documents mentioning the Stobi site were recorded in the 19th century by [1-4], as well as Studies in the antiquities of Stobi by [5-7].

Lichens are considered the result of a symbiotic association of a fungus and an alga. In this association, the alga is the part that is occupied with the formation of nutrients, since it contains chlorophyll (Chl), while the fungus supplies the alga with water and minerals. Lichens are symbiotic organisms with an extraordinary capability to colonize areas of extreme climate and heavily contaminated sites, such as metal-rich habitats. Lichens have developed several mechanisms to overcome the toxicity of metals, including the ability to bind metal cations to extracellular sites of symbiotic partners and to subsequently form oxalates [8].

The effects of lichens on their mineral substrates can be attributed to both physical and chemical processes.

The physical effects are reflected by the mechanical disruption of rocks caused by hyphal penetration, expansion and contraction of lichen thallus, swelling action of the organic and inorganic salts originating from lichen activity. Lichens also have significant impact in the chemical weathering of rocks by the excretion of various organic acids, particularly oxalic acid, which can effectively dissolve minerals and chelate metallic cations.

The biodeterioration of the rock materials achieved by lichens results from physical and chemical processes [9-10]. As a result of weathering induced by lichens, many rock-forming minerals exhibit extensive surface corrosion. The precipitation of iron oxides and amorphous alumino-silica gels,

crystalline metal oxalates and secondary clay minerals have been frequently identified in a variety of rocks colonized by lichens in nature.

Lichens can provide bioprotection for stone surfaces, acting as a barrier against weathering, retaining moisture, increasing waterproofing, reducing thermal stress and erosion, and absorbing pollutants [11]. For the same species and lithologies, the balance between biodeterioration and bioprotection may change depending on (micro)-environmental conditions [12].

Some authors suggested that lichens are of significance in weathering and pedogenesis [13], while others argued that the importance of lichens in this context has been exaggerated [14].

Early investigations of lichen weathering of mineral substrates concentrated largely on mechanical aspects, leading to the conclusion that the effects of lichens might be mainly ascribed to physical causes [15].

Each lichen species may have a different impact on physical-mechanical properties of sandstones, as measured by surface hardness, a proxy for durability [16-18].

Lichen colonization on limestone has been associated with counterposed patterns of surface hardening and porosity increase, with their balance depending on the limestone and the species involved [19].

## **MATERIAL AND METHODS**

The SEM/EDS method was used to examine the taken samples. SEM/EDS possesses adequate accuracy to obtain stoichiometric mineral from atomic ratios of constituent elements and identify analyzed mineral phases. The results of SEM/EDS analyses of mineral phases demonstrated the usefulness of this method for identification and characterization of mineral phases whose size is often below the resolution of an optical microscope.

**SEM-EDS-** Scanning electron microscopy VEGA3LMU, W-wire, voltage up 200 V to 20 kV, infrared camera, maximum sample size 81 mm height, 30 mm width. The standards used are as follows: O: SiO<sub>2</sub>; Na: albite; Mg: MgO; Al: Al<sub>2</sub>O<sub>3</sub>; Si: SiO<sub>2</sub>; P: GaP; Ca: wollastonite; Ti: Ti; Fe: Fe; Br: KBr.

## **RESULTS AND DISCUSSION**

There are three main types of lichens. 'Crustose' lichens grow as a thin crust that cannot be removed from the substrate without damage. 'Foliose' lichens have a lobed, almost leafy structure and can be removed readily from the surface on which they grow. 'Fruticose' lichens are branched and shrubby. They are attached to the surface by a small plate called a holdfast.

Lichens from Stobi are crustose type. Crustose lichens in particular grow extremely slowly. Many grow less than 0.5mm a year.

Crustose lichens grow radially from a small propagule to form a more or less circular patch or thallus. The circular shape is often lost over time as parts of the lichen are eaten by invertebrates, meet up with a neighboring lichen or encounter an unsuitable area of habitat.

Samples of yellow and gray lichens were taken for analysis as follows: lichens on marble from Proteichism at the Heraclea Gate; lichens on sandstone from Synagogue Basilica; lichens on sandstone on the eastern wall of the Episcopal Basilica.

Macroscopic views on gray and yellow lichens from Stobi are given (Fig.1, 2).

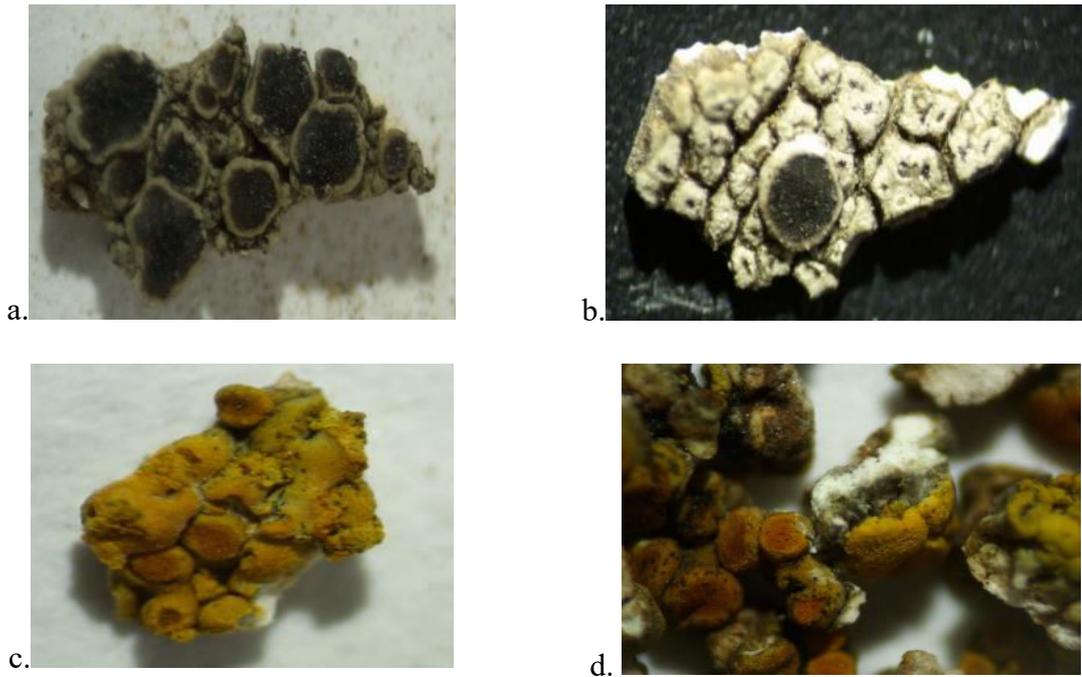


Figure 1. Macroscopic views on (a, b) gray lichens; (c, d) yellow lichens



a) lichens on marble of the Proteichism at the Heraclea Gate at Stobi



b) lichens on marble of the Proteichism at the Heraclea Gate at Stobi



c) lichens on sandstone from the Synagogue Basilica at Stobi



d) lichens on sandstone from the eastern wall of the Episcopal Basilica at Stobi

Figure 2. Places where the test samples were taken

The SEM microscopic images on gray lichens are given in Fig.3.

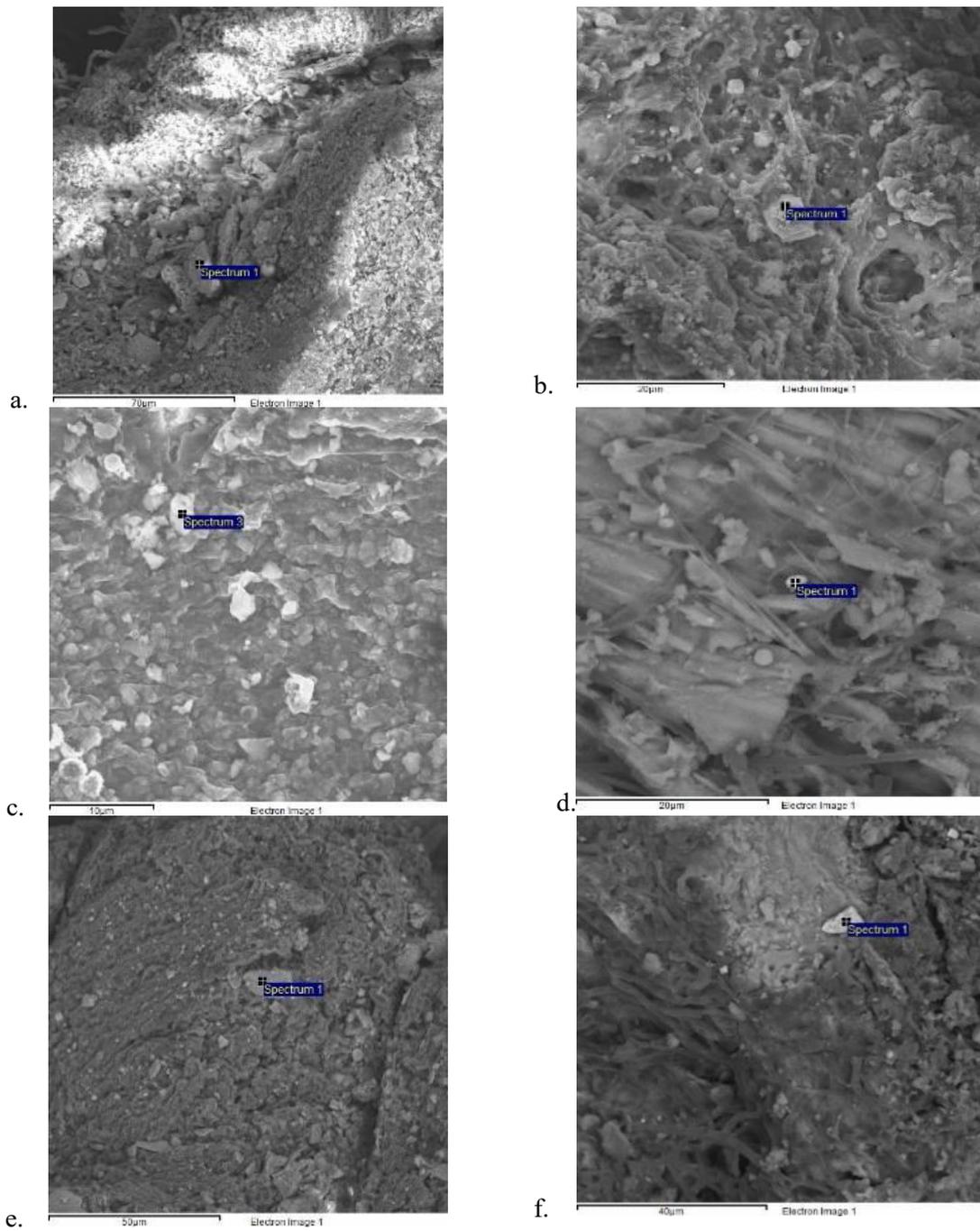


Figure 3. The SEM microscopic images on: a) Na, Al silicate; b) quartz; c) calcite; d) Fe, Mg silicate; e) Al silicate; f) Fe oxide

The presence of the following minerals was determined in the gray lichens: Na, Al silicate, quartz, calcite, Fe, Mg silicate, Al silicate-clay and Fe oxides.

The SEM microscopic images of yellow lichens are given in (Fig.4).

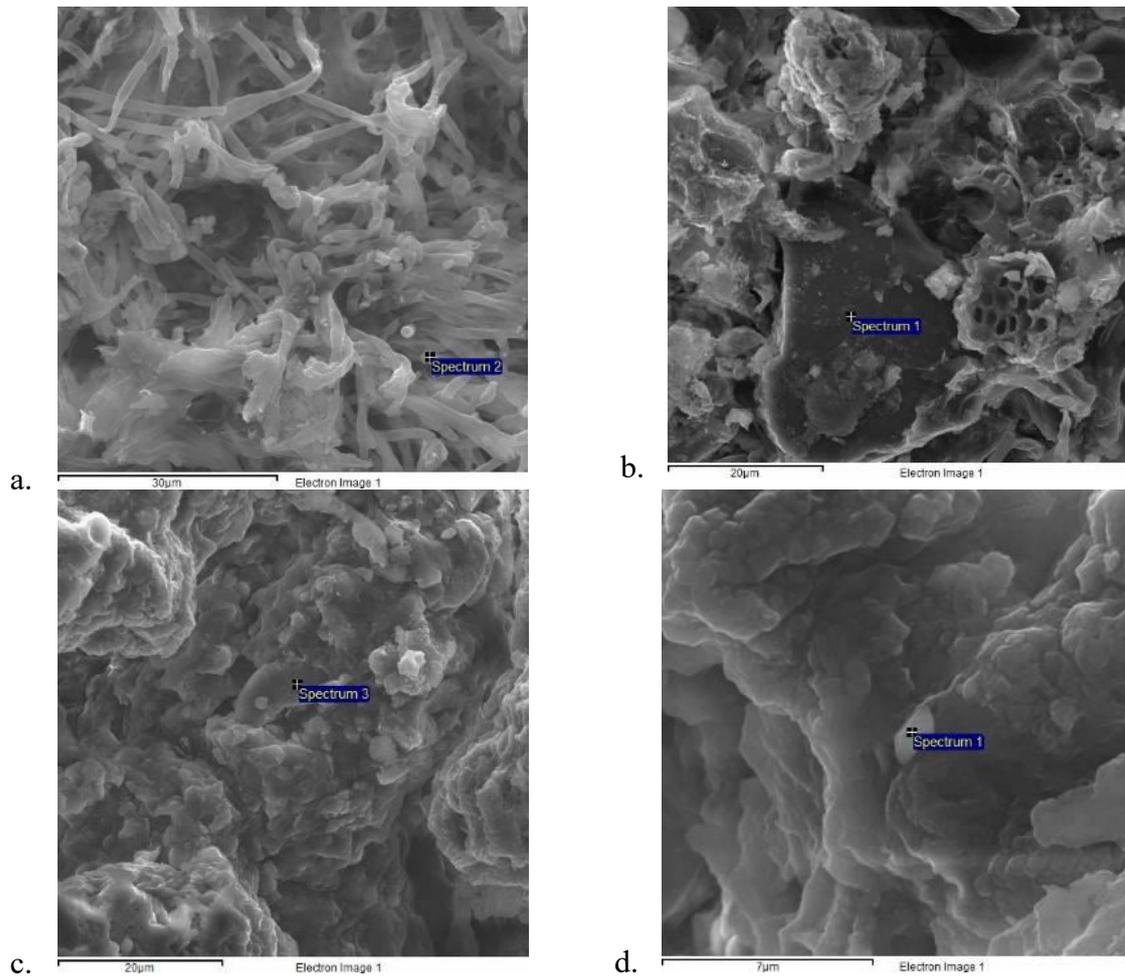
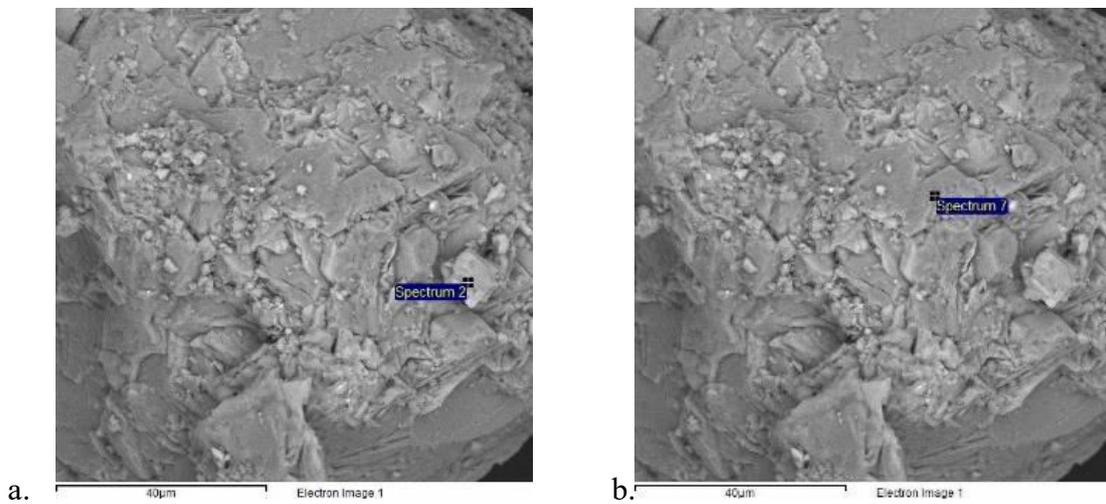


Figure 4. The SEM microscopic images of a) calcite; b) quartz; c) K, Al silicate; d) Ca, Al silicate

The presence of the following minerals was determined in the yellow lichens: calcite, quartz, K, Al silicate and Ca, Al silicate.

The SEM microscopic images of lichens found on the marble surfaces are given in Fig.5.



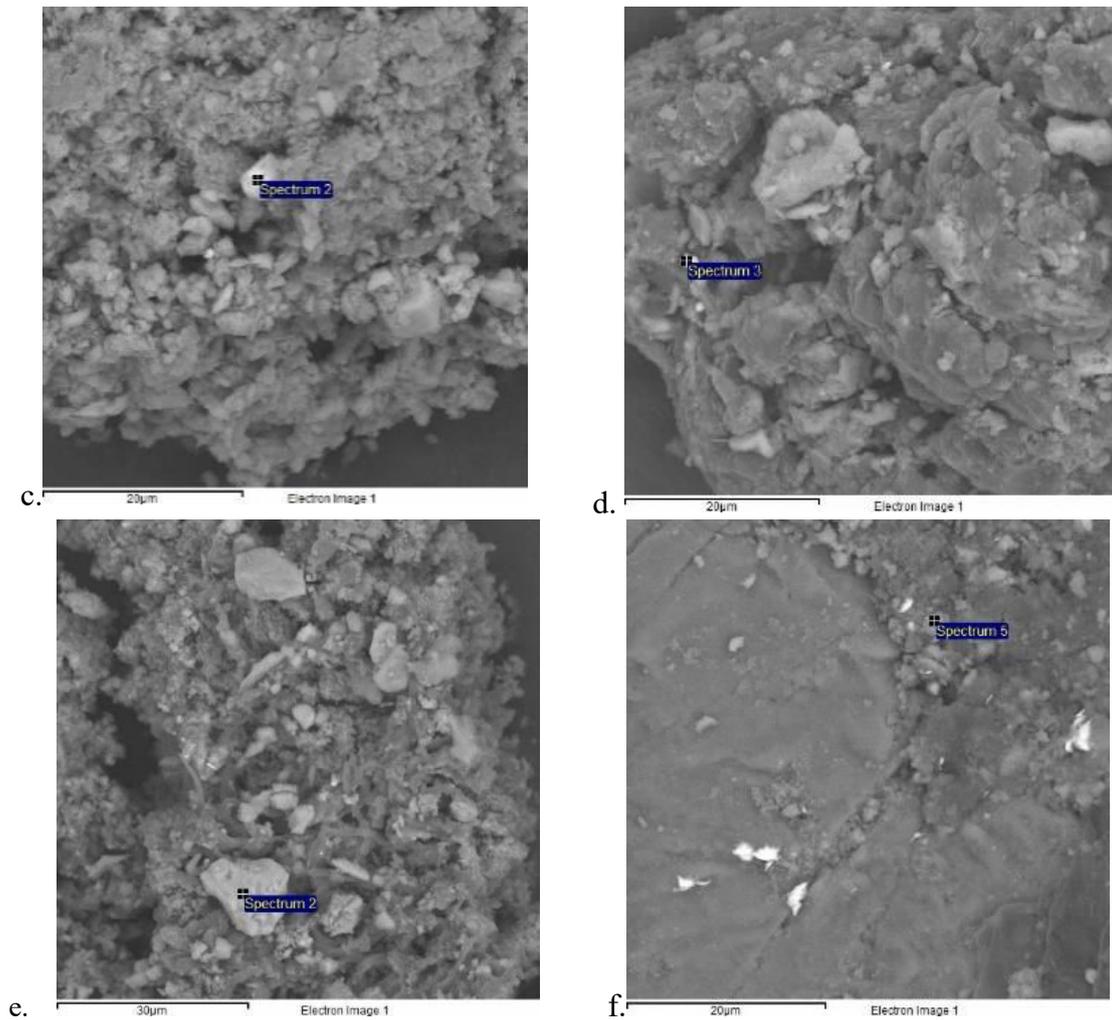


Figure 5. The SEM microscopic images of: a) calcite; b) dolomite; c) Fe, Al silicate; d) Fe carbonate; e) Ca, Fe, Al silicate; f) Ca silicate

The presence of the following minerals was determined in the lichens on marble: calcite, dolomite, Fe carbonate, Ca silicate, Ca, Fe, Al, silicate and Fe, Al silicate. Carbonate minerals come from marble while silicates are the result of weathering.

The SEM microscopic images of lichens found on sandstone surfaces are given in Fig.6.

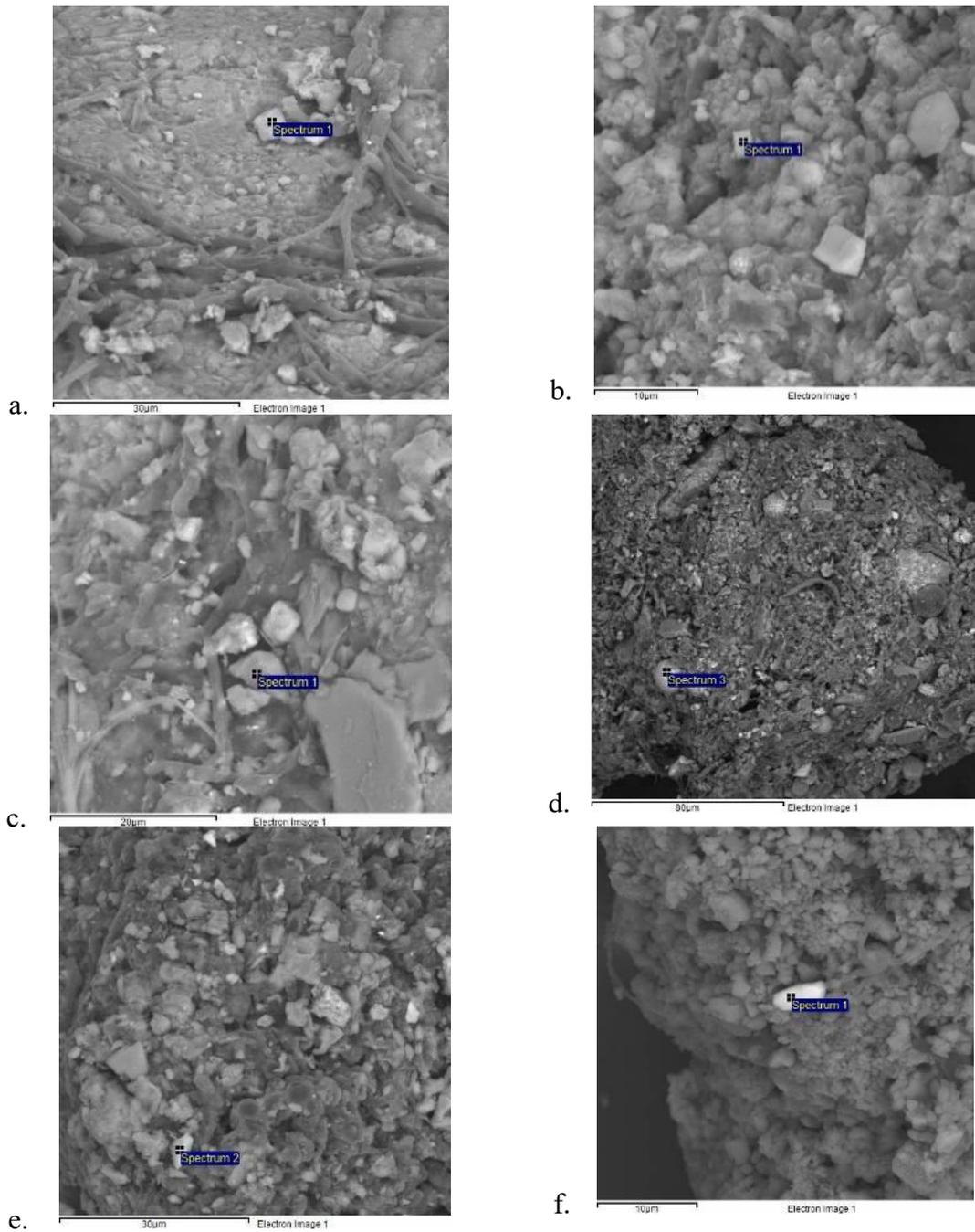


Figure 6. The SEM microscopic image of: a) feldspar; b) calcite; c) quartz; d) Fe, Mg silicate; e) Fe-oxides; f) zircon

The presence of the following minerals was determined in the lichen on sandstone: a) feldspar, calcite, quartz, Fe, Mg silicate, Fe-oxides and zircon. Silicate minerals originate from sandstone while carbonate and oxide minerals are the result of weathering.

## CONCLUSION

Summarizing available data from this study, we concluded that in the Stobi archeological site two types of lichens are present: grey and yellow. Lichens are found on marble and sandstone monuments. The presence of the following minerals was determined in the lichens on marble: calcite, dolomite, Fe carbonate, Ca silicate, Ca, Fe, Al, silicate and Fe, Al silicate. Carbonate minerals come from marble while silicates are the result of weathering.

In lichens on sandstone the following minerals were determined: K, Al silicate, Ca carbonate, quartz, Fe, Mg silicate, Fe-oxides, zircon, and Na, Ca, Al silicate. Carbonate minerals are the result of weathering while other determined minerals originate from sandstone. According to the SEM results, small grains of minerals are found in lichens which originated from parent rocks or weathering. Clay minerals are the result of the decomposition of feldspars.

Each lichen species may have a different impact on the physical - mechanical properties of marble and sandstones. Our analyses suggested that microscopy observations may be integrated with mineralogical investigations, to unveil the extension of the sphere of lichen interaction within the rock substrate beyond the limit of hyphal penetration. Such findings are also of relevance in the field of cultural heritage conservation, indicating that decisions on the preservation or removal of lichens, as agents of biodeterioration or bioprotection, cannot be generalized.

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## ПРЕЛИМИНАРНИ РЕЗУЛТАТИ ЗА ВЛИЈАНИЕТО НА ЛИШАИТЕ НА СПОМЕНИЦИТЕ ВО АРХЕОЛОШКИОТ ЛОКАЛИТЕТ СТОБИ

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### Резиме

Во овој труд се дадени прелиминарни податоци за влијанието на сивите и жолтите лишаи на археолошките споменици во Стоби. Исто така, беше утврдено потеклото на минералите кои се прилепуваат на ризинот/хифите.

Според резултатите добиени со SEM во лишаите од Стоби се пронајдени мали зрна на минерали кои потекнуваат од матичните карпи или атмосферските влијанија. Во лишаите кои се наоѓаат на спомениците од мермер е утврдено присуство на следните минерали: калцит, доломит, Fe карбонат, Ca силикат, Ca, Fe, Al, силикат и Fe, Al силикат. Карбонатните минерали доаѓаат од мермерот, додека силикатите се резултат на атмосферските влијанија.

Во лишаите кои се наоѓаат на спомениците од песочник се утврдени следните минерали: K,Al силикат, Ca карбонат, кварц, Fe,Mg силикат, Fe-оксид, циркон и Na,Ca,Al силикат. Карбонатните минерали се резултат на атмосферски влијанија додека другите детерминирани минерали потекнуваат од песочникот. Глинените минерали се резултат на распаѓањето на фелдспатите.

Секој вид лишаи може да има различно влијание врз физичко-механичките својства на мермерот и песочниците. Нашите анализи сугерираа дека микроскопските набљудувања може да се интегрираат со минералолошките испитувања, за да се открие проширувањето на сферата на интеракцијата на лишаите во рамките на карпестата подлога над границата на пенетрација на хифата. Ваквите наоди се исто така релевантни во областа на зачувувањето на културното наследство, што укажува дека одлуките за зачувување или отстранување на лишаите, како агенси на биоразградување или биозаштита, не можат да се генерализираат.

**Клучни зборови:** *лишаи, мермер, песочник, Стоби.*