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# Decaying of the marble and limestone monuments in the urban environment. Case studies from Saint Petersburg, Russia

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**ABSTRACT.** The results of a long-lasting research of sulphation process, which causes an essential deterioration of marble and limestone monuments in Saint Petersburg are reported. Based on a variety of field and analytical methods we can show that the decay process forming a gypsum-rich patina depends mainly on the local environment, the moisture accumulation, and is connected with the fissuring and porosity of the rock and the relief of a monument. Three main stages of gypsum-rich patina formation in the presence of microorganisms were revealed.

**Key words:** marble, limestone, travertine, stone decay, gypsum-rich patina, biodeterioration, Saint Petersburg, Russia.

## INTRODUCTION

The sculptures and constructions made of marble and limestone have a special position among the unique architecture ensemble of Saint Petersburg (Russia). Many of the famous monuments are intensively decaying under the influence of the natural and anthropogenic factors such as atmospheric humidity and temperature changes, air pollution, salts, aggressive microbial communities (Bulakh, 2005; Vlasov and Frank-Kamenetskaya, 2006). The complex monitoring of the Saint Petersburg stone monuments was carried out for many years (Frank-Kamenetskaya et al., 2003, 2005; Lepeshkina et al., 2005). The results allowed to understand the weathering mechanisms of some carbonate rocks and offered solutions for stone monuments protection (Vlasov and Frank-Kamenetskaya, 2005; Marugin et al., 2005; Vlasov et al., 2008). Various types of monuments damages were identified: surface erosion and forming of thick black crusts, the presence of biological films, stone detachment, microkarst, alveolar weathering and others. This paper is focused on the gypsum-rich patina (black crust) formation. Sulphation has been recognized to be one of the main causes responsible for the carbonatic rocks deterioration processes in urban environments (Camuffo et al., 1983; Garcia-Vallès et al., 1998; Feely et al., 2000; Maravelaki-Kalaitzaki, 2005; Gross et al., 2006; Siegesmund et al., 2007; Kramar and Mirtič, 2008). This “stone disease” is extended on the surface of unique Saint Petersburg monuments and results often in irreplaceable losses (Timasheva et al., 2007).

The aim of this paper is to study the origin and the growth mechanisms of the sulphated crusts formed on the Saint Petersburg monuments and in particular to investigate: (a) the morphology and the peculiarities of gypsum crystals, (b) the variations of chemical composition of the gypsum crusts, and (c) the role of micro-organisms in the gypsum crust formation.

## MATERIALS AND METHODS

The research was carried out on the Necropolis monuments of the “Museum of Urban Sculpture” located in the centre of Saint Petersburg (Russia). The museum contains an unique collection of monuments made of various types of marbles and limestones. The carbonate rocks samples differ in mineral composition, homogeneity and porosity (Table 1). Small rock slices naturally exfoliated from the monument surface were used as samples. Both, monuments with plain and complicated forms, were observed in order to estimate the influence of the monument surface relief on the degree of decay. The mineral composition and the petrographic characteristics were determined by polarized light microscopy (LOMO Min 5 microscope) on thin-sections. Additionally, few grams from each sample were milled in an agate mortar and analyzed by X-Ray diffraction (XRD), at room temperature, with a Dron-2 diffractometer operating at 35 kV and 20 mA, at a scan speed of $2^o\theta$/min, from 3 to $75^o$ $2\theta$, using $CuK\alpha_1$ radiation with $\lambda = 1.54051$ Å.

More detailed investigations on the surface layers were carried by scanning electron microscopy (SEM) using an MV 2300 (CamScan) and ABT-55 (Akashi) microscopes provided by A.P. Karpinsky Russian Geological Research

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Institute and the Institute of Precambrian Geology of RAS (analyst engineers: M. Tolkachev and M. Pavlov, Saint Petersburg). The study of morphological features of gypsum crystals and biological components of the patina was carried out on Au coated samples (at 15 and 25 kV with MV 2300 and ABT-55 microscopes, respectively). The electron microprobe (EMP) analyses were carried out on polished thin sections coated with carbon using the ABT-55 microscope, equipped with an X-Ray energy microanalyzer (LINK AN 10000/85S), at 25 kV acceleration voltage and 2 µm electron beam diameter. As standards, SEM Calibration Specimens (registrated standard number 1413) of MICRO-ANALYSIS CONSULTANTS LTD (wollastonite for Ca and Si, pyrite for Fe and S, corundum for Al, orthoclase for K, albite for Na) were used.

The EMP measurements were done across the whole thickness of the crusts on the surface of Kosikovskii monument (samples 2-5, Table 2). For each sample, three directions (profiles) and 4 to 6 fields/profile, respectively were measured (Fig. 1a, b).

**Table 1.** *List and characteristic of the samples collected in Saint Petersburg Necropolis.*

| № | Monument | Sampling point | Phases of patina identified by X-ray diffraction | Characteristic of carbonate rock | | |
|---|---|---|---|---|---|---|
| | | | | Description | Mineral[1] composition | Assumed deposits[2,3] |
| 1 | A.I. Kosikovskii | Leg of sarcophagus (west side of monument) | Main phase: calcite<br>Significant amount: gypsum | White homogeneous, fine to medium grained marble | Calcite, quartz | Cretaceous marble (Carrara, Italy) |
| 2 | | Sarcophagus (south side) | Main phase: calcite.<br>Significant amount: gypsum | | | |
| 3 | | Sarcophagus (eastern side) | Main phase: calcite<br>Significant amount: gypsum<br>Traces of quartz | | | |
| 4 | | Sarcophagus (north side) | Main phase: calcite<br>Significant amount: gypsum<br>Traces of quartz | | | |
| 5 | | Sarcophagus (north side) | Main phase: calcite<br>Significant amount: gypsum<br>Traces of quartz | | | |
| 6 | V.B. Golizin | Top of gravestone | Main phase: calcite<br>Traces of gypsum, quartz, feldspar | | Calcite, quartz (traces) | |
| 7 | E.A. Rummel | Wall, inside of arch (west side) | Main phase: gypsum<br>Traces of calcite, dolomite, mica, talc, feldspar, chlorite | Grey-white banded, heterogeneous, heterogranular marble with different stages of gypsum-rich patina formation | Calcite dolomite, amphibole, talc, mica | Early Proterozoic marble (Ruskeala, Karelia-Sortovala region, Russia) |
| 8 | Unknown | Vertical flag of the semi-column (west side) | Main phase: gypsum<br>Minor amounts: calcite, dolomite<br>Trace amounts: gypsum | | Calcite, dolomite | |
| 9 | S.I. Lavrov | Vertical flag of the pedestal (eastern side) | Calcite, dolomite, quartz. | Grey-yellow, stratified limestone (*Putilovskaya plita*) | Dolomite, calcite, quartz, feldspars (trace amount) | Ordovician limestone (Putilovskoe, Leningrad region, Russia) |
| 10 | | | Main phase: gypsum<br>Traces of calcite, quartz, feldspar | | | |
| 11 | P.A. Golizina | Upper part of the grotto (south side) | Main phase: gypsum<br>Traces of dolomite, quartz | Grey, porous travertine (*Pudostskii stone*) | Calcite, dolomite, quartz | Quaternary travertine (Pudostskoe, Leningrad region, Russia) |

**Notes:**
[1]Mineralogical composition of the bedrocks was determined by polarized light microscopy on thin-sections and by X-Ray diffraction.
[2]Deposits have been assumed on the basis of the preliminary mineralogical-petrographic research (Lepeshkina et al., 2003).
[3]Geological ages of rock is indicated according to Ziskind (1989).

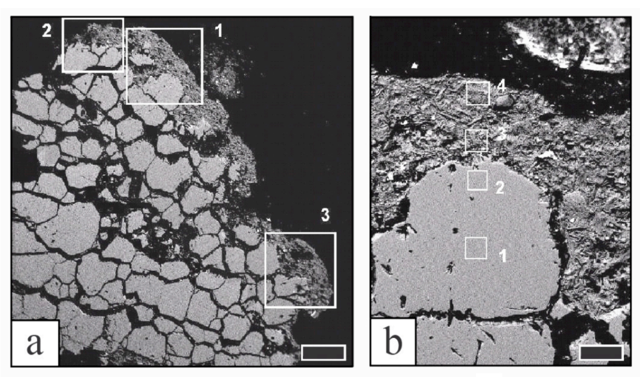



**Fig. 1.** *Back-scattered electrons images of sample 2. a) The measured areas marked by large squares (1 to 3); scale bar = 415 µm. b) The EMP analyzed profiles for the area no. 1, marked by small squares (1 to 4); scale bar = 85 µm.*

The samples for biological analyses were collected from the same stone objects as for mineralogical analyses. A variety of non-destructive techniques were applied for isolation of micro-organisms from deteriorated parts of monuments. In the laboratory, fragments of stone materials were set on different artificial nutrient media (agar Chapek, potato-dextrose medium, oat extract medium) surface, in Petri dishes.

The specific micro-colonial fungi were isolated from the stone samples by picking with sterile needles (under the stereomicroscope) and were transferred to nutrient media. The slide cultures were prepared according to de Hoog and Guarro (1995) method.

The microscopic fungi were identified using diagnostic keys (Ellis, 1971, 1976; von Arx, 1975; de Hoog and Guarro, 1995).

**Table 2.** *Selected microprobe analyses (in wt.%) of black crust: the variation of the chemical composition across the thickness of the black crusts developed on the surface of the Carrara marble (sample 2, Fig. 1).*

| Profile | Field | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | FeO | MgO | CaO | $Na_2O$ | $K_2O$ | $SO_3$ | Σ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 0.26 | 0.20 | - | - | 0.76 | 53.86 | - | - | - | 55.09 |
| | 2 | 0.18 | - | - | - | 0.63 | 54.20 | - | - | - | 55.01 |
| | 3 | 5.26 | - | 2.80 | 0.81 | 0.53 | 27.94 | 0.71 | 0.58 | 28.56 | 67.19 |
| | 4 | 2.62 | - | 1.56 | 0.56 | 0.24 | 30.07 | 0.19 | 0.25 | 41.99 | 77.47 |
| 2 | 5 | 0.15 | - | - | - | 0.78 | 54.47 | - | - | - | 55.40 |
| | 6 | 0.15 | - | - | - | 0.78 | 54.50 | - | - | - | 55.42 |
| | 7 | 4.19 | - | 1.48 | 0.76 | 0.33 | 32.30 | 0.34 | 0.25 | 28.76 | 68.43 |
| | 8 | 6.04 | 0.34 | 1.87 | 0.70 | 0.20 | 27.14 | 0.54 | 0.41 | 37.95 | 75.19 |
| | 9 | 3.83 | | 3.86 | 0.94 | 0.14 | 24.25 | 0.27 | 0.56 | 33.93 | 67.78 |
| 3 | 10 | - | - | - | - | 0.68 | 54.80 | 0.27 | - | - | 55.74 |
| | 11 | 0.24 | - | 0.84 | - | 0.69 | 54.61 | - | 0.12 | 0.23 | 56.72 |
| | 12 | 5.47 | 0.29 | 2.59 | 1.06 | 0.53 | 26.19 | 0.55 | 0.65 | 33.43 | 70.75 |
| | 13 | 11.14 | - | 1.85 | 0.83 | 0.43 | 29.78 | 0.36 | 0.81 | 43.55 | 88.73 |
| | 14 | 4.56 | - | 1.22 | 0.56 | - | 28.11 | 0.14 | 0.34 | 38.90 | 73.83 |

## RESULTS AND DISCUSSION

The study results demonstrate that a gypsum-rich patina (Fig. 2) develops on various marble and limestone monuments, as black crusts of various thickness and extention.

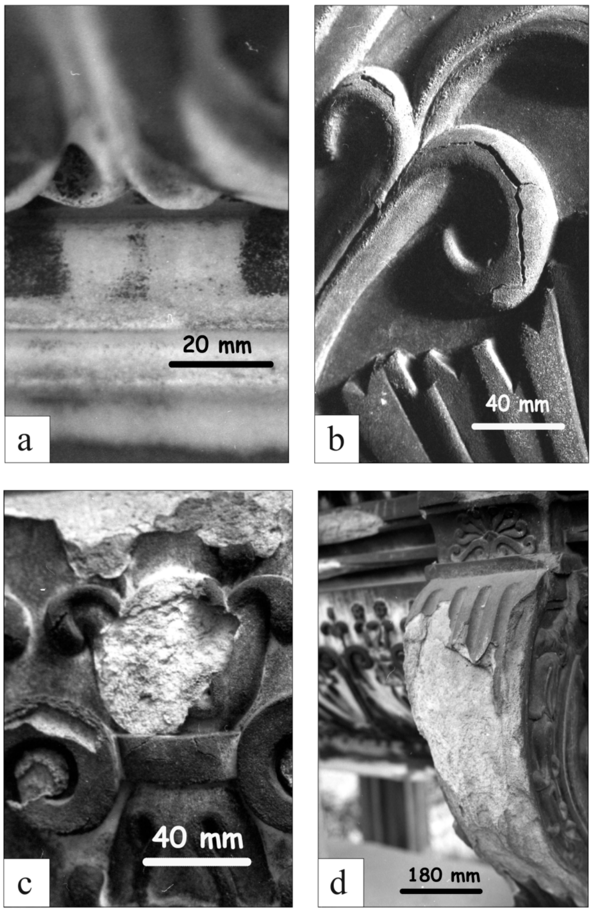



**Fig. 2.** *The main stages of sulphation on the surface of the Carrara marble (A.I. Kosikovskii monument): a) beginning of the primary black crust formation; b - primary black crust with the cracks; c – the fresh and rough surface of marble after the gypsum crust exfoliation; d - beginning of secondary black crust formation.*

The process starts with the formation of gypsum crust due to the reaction between tiny amounts of sulphuric acid from polluted air and carbonate minerals (Figs. 2a, b). Mostly due to physical factors such as freezing, insolation and moisture, the gypsum crust begins to exfoliate together with a thin layer of the bedrock (Fig. 2c). A new gypsum-rich patina begins to form on the fresh rock surface. The primary and secondary crusts differ already at macroscopic scale. The secondary is usually thinner and develops on fresh rock surface exposed after the exfoliation of the primary crusts (Fig. 2d).

In the areas of the gypsum-rich patina various micro-organisms such as bacteria, microfungi, algae and lichens are present. Their activity accelerates the dissolution of the carbonate rocks by the aggressive digestive products, accumulation of the moisture and by favoring the accumulation of aggressive salts and air pollutants in the external layer of the stone. The microfungi can be observed at different stages of sulphation of the carbonatic rock, as shown in Table 3. The number of their species present on the parts of Carrara marble showing different degrees of sulphation (A. I. Kosikovskii monument; Fig. 2), varies from 4 to 11. Some dominant species of biodestructors, e.g. Aureobasidium pullulans, Cladosporium sphaerospermum, are present in all stages of the crust development. They are characterized by strong resistance to unfavorable atmospheric influence. The cells of these fungi contain melanin pigments which protected them. They form small colonies and mycelia in the cracks and between gypsum crystals.

**Table 3.** *Micromycetes isolated from the damaged areas of the Carrara marble in different stages of the gypsum-rich patina formation (A.I. Kosikovskii monument).*

| Stages of the gypsum-rich patina (black crust) formation | Number of micromycetes species | Dominant micromycetes species |
|---|---|---|
| Beginning of the black crust formation | 4 | *Aureobasidium pullulans* *Cladosporium sphaerospermum* |
| Primary black crust, with cracks | 10 | *Alternaria alternata* *Aureobasidium pullulans* *Candida* sp. *Cladosporium cladosporioides* *Cladosporium sphaerospermum* |
| Marble surface after the exfoliation of the primary black crust | 11 | |
| Secondary black crust | 9 | |

The X-Ray diffraction shows that the patina consists of gypsum and bedrock minerals (Table 1). The quantity of gypsum considerably varies. According to the SEM data, the size and morphology of the gypsum crystals is also very variable. On the surface of A. I. Kosikovskii monument with a complicated surface relief and made of compact and homogeneous Carrara marble (samples 1-5), characteristic lamellar crystals of gypsum can be seen (Fig. 3a). The size of the individual crystals (on average) varies from 15 to 20 μm. They aggregate into rosettes, which indicate a high number of nucleation centers. Isolated, prismatic crystals up to 120 μm in length, with the strong development of the second pinacoid occur as well.

The rounded alga cells can be observed around the gypsum crystals (Fig. 3b), as well as thin hyphae of microfungi.

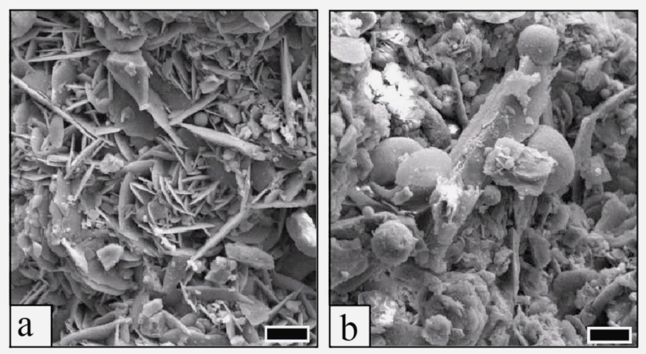


**Fig. 3.** *SEM images of the black crusts developed on the Carrara marble surface (sample 4): a) lamellar crystals of gypsum, aggregated into rosettes; b) elongated prismatic crystals of gypsum and spherical algae cells. Scale bar = 15 µm.*

On the SEM image of patina developed on the surface of the V.B. Golizina monument with a plain surface relief, manufactured from the same homogeneous Carrara marble (sample 6), a biofilm formed by micro-organism cells and their metabolic products is observed. Various precipitation products from the atmosphere are also part of the biofilm. A small quantity of gypsum crystals (Table 1) was only detected by XRD, possibly because they were covered by the biofilm.

The degree of sulphation depends not only on the rock properties (porosity, fissuring) but also on the monument relief. The complicated relief shape of the A. I. Kosikovskii monument promotes moisture accumulation, thus the decay of its marble is much more intense than the surface of the V. B. Golizina plain monument.

The patina on the surface of monuments made of Ruskeala marble (sample 7; E.A. Rummel monument; sample 8 from an unknown gravestone) and Putilovskii fine-bedded limestone (samples 9 and 10; S. I. Lavrov monument) is also heterogeneous. In sample 7 the quantity of gypsum is essentially larger than in sample 8. In hollows and cracks of the rock surface numerous lamellar crystals, up to 30-40 µm in size, are visible (Fig. 4). Colonies of micro-organisms such as fungi and algae form often clusters of microbial cells.

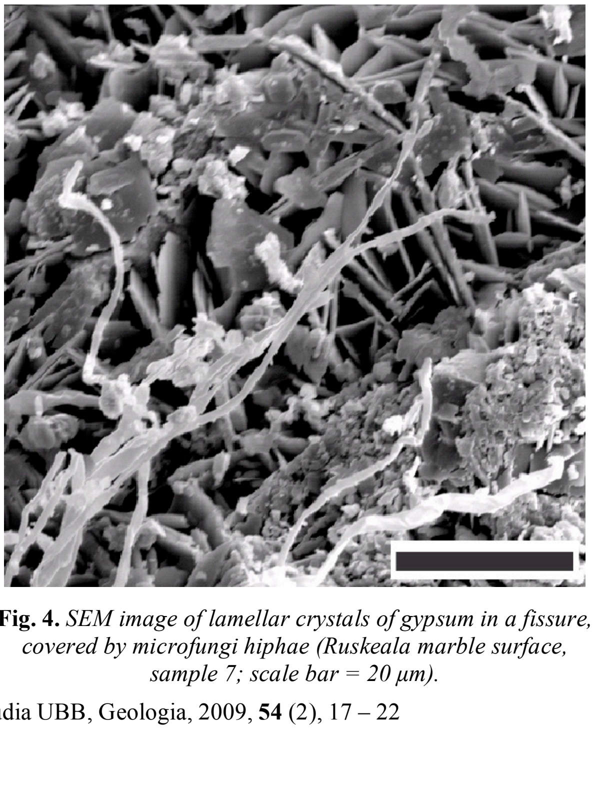


**Fig. 4.** *SEM image of lamellar crystals of gypsum in a fissure, covered by microfungi hiphae (Ruskeala marble surface, sample 7; scale bar = 20 µm).*

On the SEM images of the patina sampled from a vertical surface of the S. I. Lavrov monument pedestal (Putilovskii limestone; samples 9 and 10) randomly distributed fine crystals of gypsum are discernable. The rare gypsum crystals grow locally directly on the rock surface beneath the biofilms (Fig. 5). At other places, the limestone surface is completely covered by a layer of gypsum crystals, among which crystals with rounded forms and average size of 10 µm occur.

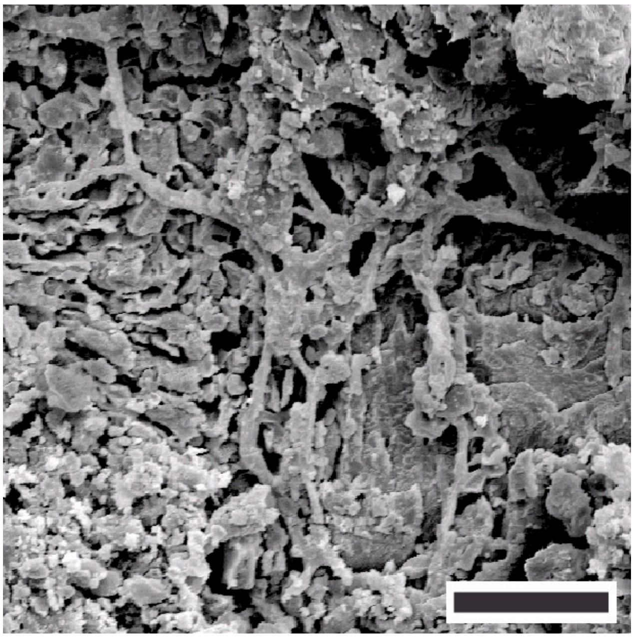


**Fig. 5.** *SEM images of biofilm covering rare and small gypsum crystals (Putilovskii limestone surface, sample 9; scale bar = 25 µm).*

The largest crystals, up to 170 µm in length, were found on the surface of the P.A. Golizina monument made of Pudostkii travertine (sample 11; Fig. 6). Mostly acicular but also large prismatic gypsum crystals are visible. Additionally, more fine laminar gypsum crystals, up to 30 µm in size, occur in hollows. This large variety of forms and sizes of the gypsum crystals is only observed on travertine.

The morphological features of the gypsum crystals developed on the surface of the carbonate rocks in urban environment indicate that the processes of growth and dissolution replace each other, which is typical for metasomatic crystallization. Dissolution, nucleation and growth of crystals take place in the presence of a numerous microorganisms. Three main stages of the gypsum-rich patina formation on the surface of Saint Petersburg carbonate rock monuments were noticed:

- The initial stage, when a thin biofilm is formed on the rock surface. Beneath the biofilm, tiny gypsum crystals occur. This stage is present on the surface of the Carrara marble and Putilovskii limestone (Fig. 5);
- The intermediate stage is characterized by numerous large gypsum crystals. Between them, thin films of microfungi, algae cells and other mico-organisms occur, as could be demonstrated on the Carrara and Ruskeala marbles (Figs. 3b, 4);
- The intensive stage is reached as soon as a layer of gypsum crystals is formed. The micro-organism community develops beneath this gypsum layer, as could be demonstrated on various carbonatic rocks such as the Carrara marble, Putilovskii limestone and Pudostskii travertine (Figs. 3a, 6).

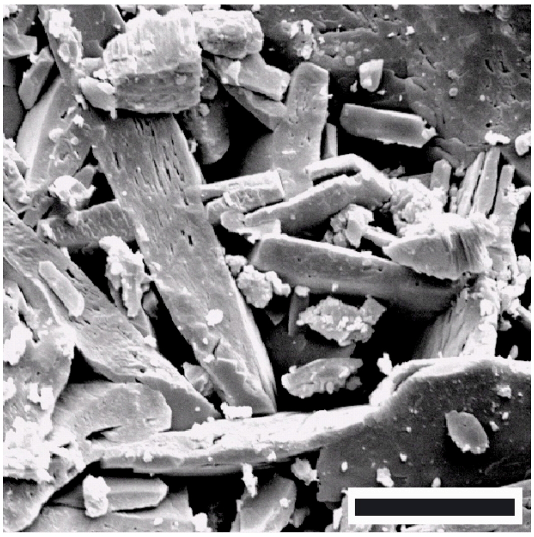
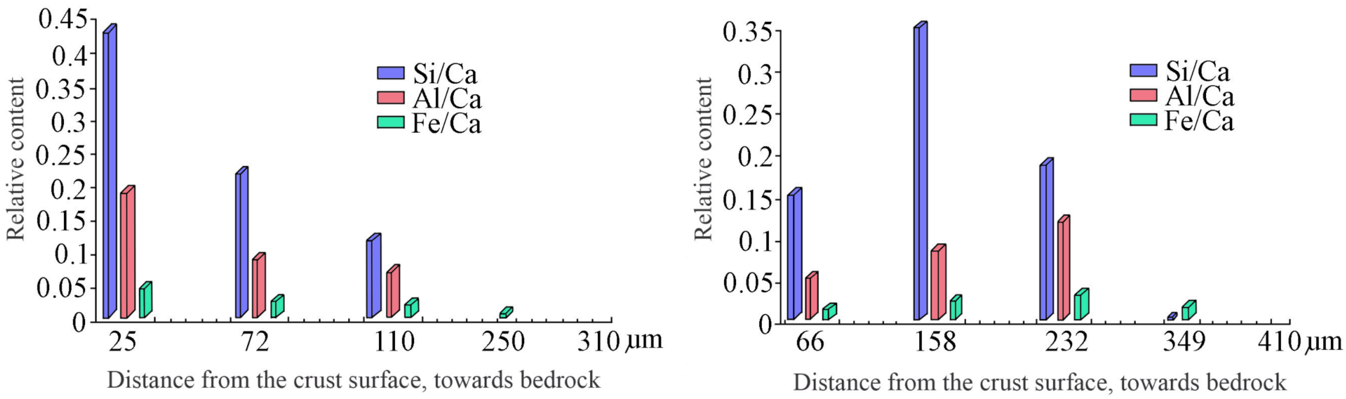


**Fig. 6.** *SEM images of large prismatic gypsum crystals formed on the Pudostskii travertine surface (sample 11). Scale bar = 20 µm.*

The EMP analyses of the gypsum crusts formed on the surface of the A. I. Kosikovskii monument (Table 2) show that the composition of patina is related to both, the environment exemplified by polluted air, acid rain and dust, and the mineral composition of the bedrock. The sulphur content across the thickness of the crust is practically constant and decreases sharply only at the very contact with the bedrock. The content of the main impurity elements essentially varies and can reach the following values: 13 wt.% for $SiO_2$, 5 wt.% for $Al_2O_3$ and 4 wt.% for FeO, respectively. In the thinner crusts (<100-200 µm thickness), the highest silica and aluminum content is found near to the crust surface; it smoothly decreases towards the fresh rock (Fig. 7a). This suggests an origin of these elements from the environment. The content of iron either remains constant, or has the lowest value in the center of crust. In the thicker crusts (200-400 mµ thickness) the highest concentration of silica and aluminum is found in the middle part of the crust, whereas the Fe content remains the same or slightly increases towards the center of a crust (Fig. 7b). The presence of numerous micro-organisms in the gypsum crust supports the hypothesis that the selective diffusion of some chemical elements into the patina crust might be connected with micro-organisms acting as biogenic carriers.




a b

**Fig. 7.** *The variation of relative content of Si, Al, and Fe across the gypsum crust formed on Carrara marble of the A.I. Kosikovskii monument (the Si, A,l and Fe content are normalized to Ca content): a) thin crust, sample 5, profile 1; b) thick crust, sample 2, profile 3; see also Table 2.*

## CONCLUSIONS

Summarizing, it could be shown that a gypsum-rich patina develops on various marble and limestone monuments, in particular on those with complicated forms. The degree of carbonatic rocks sulphation depends on the local conditions, fissuring and porosity of the rock, structure/texture peculiarities and mineral composition of carbonatic bedrock. They are equally important. A complicated relief of the monument promotes the moisture accumulation. For this reason, the high artistic monuments made of homogeneous Carrara marble, with a complex relief, as well as the monuments made of highly porous Pudostskii travertine suffer most from the sulphation.

The metasomatic crystallization of gypsum, occurring on the carbonate rocks surface in the urban environment, is contemporaneous with the activity of many micro-organisms. The mechanism of this bio-mineral interaction is not clear yet and experiments improving its understanding are in progress.

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