Chapter

Changes of Granite Rapakivi under the Biofouling Influence

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Abstract

Interdisciplinary study of granite rapakivi biofouling in the natural and anthropogenic environment (St. Petersburg, Vyborg, Southern Finland) was carried out. The biodiversity of microorganisms (cyanobacteria, micromycetes, and organotrophic bacteria) and various types of biofilms are characterized. The influence of external factors on the changes of cyanobacterial biofilms is shown. The features of biofilms localization on the granite surface in an urban environment and in natural outcrops are studied. Differences in the biofilms metabolites composition at the granite quarries and monuments of St. Petersburg are shown. The behavior of chemical elements during the bioweathering of granite is estimated. The role of biofilms in the accumulation of chemical elements on the surface of granite is established. The dynamics of chemical elements leaching from granite may depend on the type of biofilm developing on granite.

Keywords: granite, weathering, biofouling, biogeochemical process, leaching, biodeterioration, microorganisms, environment, model experiments, mobile forms of elements

1. Introduction

Granite is one of the most widespread types of a stone in architecture of northern Russian cities such as Saint Petersburg, Vyborg, Priozersk, Primorsk as well as Finish cities such as Helsinki, Lappeenranta, Kotka, Hamina, Kuopio (Finland). The destruction of granite in the northern cities is a result of interrelated physical, chemical, and biological processes [1]. Biogenic weathering is connected with the impact on the rock surface by microorganisms (bacteria, microfungi, and microalgae) as well as lichens and mosses. They form lithobiotic communities which have a noticeable effect on the state of the stone.

The study of this problem seems to be an interdisciplinary task, the solution of which is possible only on the basis of an integrated scientific approach and the use of modern research methods. Organisms of lithobiotic communities are able to actively influence on the mineral substance chemically and physically. They catalyze the destruction of rocks, contributing to the extraction of minerals from them. Microbial activity in combination with atmospheric pollution is one of the features of urban ecosystems that determine the rate of weathering of granite and other types of stone.

Most microorganisms on stone surface exist in the form of biofilms, which are composed of microbial cells and metabolites. Primary biofilms on granite most often consist of cyanobacteria and green algae. Aerophilic green algae are less resistant to adverse conditions than cyanobacteria and need more moisture. Green biofilm usually can be indicator of increased periodic or constant moisture of a stone [2, 3]. As organic matter accumulates on the surface of the stone, the participation of heterotrophic bacteria and fungi in the microbial community increases [4]. The close cooperation in microbial communities contributes to the successful growth and development of biofilms on stony substrates including granite. Biofilms can penetrate into cracks and pores. As a result, the absorption and retention of water in the rock mass increases, the intensity of diffusion and evaporation of water changes, and the processes of dissolution of the stone take place. The growth of biofilms causes pressure on the structural elements of the rock, acts on individual crystals and grains of stone.

Biochemical activity of microbial communities has a strong influence on mineral substance due to producing chemically active compounds such as polysaccharides, lipopolysaccharides, proteins, glycoproteins, lipids, glycolipids, fatty acids, and enzymes [5, 6]. Biomineral interaction leads to the leaching, formation of secondary minerals, primary soil formation, and thus, prepares the conditions for the further biological colonization of the stone.

The state of the stone surface has a particular importance for the biological colonization. A rough (uneven) surface is colonized much better than a smooth one [7]. Rough surface provides more opportunities for attachment and development of microorganisms (local humidity, microcracking, delay of various contaminants that serve as sources of nutrition for microorganisms, etc.). The biosusceptibility of natural stone may vary depending on the duration and conditions of its exposure in the open air [8].

Thus, natural stone together with biofouling is a peculiar and very complex lithobiotic system, the development of which depends on the properties of the stone, the composition of biological community, and environmental conditions. The aim of our investigation is the analysis of granite biological colonization peculiarities in different environment as well as the estimation of granite changes under the biofouling influence.

2. Materials and methods

2.1 Materials

The objects of research were selected in urban environment as well as in natural outcrops. Peter and Paul Fortress and monuments of the Museum Necropolises were studied in Saint Petersburg. Vyborg castle, fountain, tunnels, and outcrops in the Monrepos park were observed in Vyborg.

Granite outcrops were examined in the natural park Ristijärvi and on the Owl Mountain (Karelia). Also, four old quarries in the south part of Finland were examined: quarry I – (N 60° 34.207′ E 027° 43.835′); quarry II (N 60° 31.855′ E 027° 39.698′); quarry III (N 60° 32.101′ E 027° 39.823′); quarry IV (N 60° 44.413′ E 028° 00.564′). Granite mining at these quarries has long been discontinued. Currently, they undergo a process of natural overgrowth and are ideal model for studying of natural stone biofouling in low anthropogenic influence. More than 500 samples of destroyed rapakivi granite were investigated from 2013 to 2019. Rapakivi granite, as a rule, had its own unique image: large egg-shaped clusters of feldspar with a diameter of 3–6 cm, surrounded by an edge of greenish-gray plagioclase, placed in a fine-grained matrix of feldspars, quartz, and biotite.

2.2 Study of microorganisms

Primary attention was paid to the structure of granite, the presence of cracks, holes, and other surface irregularities, which can serve as a shelter for microorganisms. Traditional cultural methods of mycology and microbiology have been applied for isolation and identification of microorganisms in biofilms on the surface of the granite [9]. Also, metagenomic analysis was used to determine a wide range of microorganisms in biofilms. The work was carried out in the resource center of Saint Petersburg State University "Development of cellular and molecular technologies." Diversity of bacteria in biofilms on granite was carried out on the basis of the 16S rRNA genes analysis. Metagenomic study of fungal diversity in biofilms on granite was carried out with primers for site amplification ITS1-5.8S–ITS2. For the identification of cyanobacteria, direct microscopy of the samples was used. Cumulative cultures were also obtained in distilled water and in the Gromov 6 medium (period cultivation from week to month). Verification of species in accordance with the current nomenclature was carried out using the electronic database AlgaeBase (http://www.algaebase.org/).

2.3 Biochemical analysis

For analysis of small organic molecules in several types of biofilms samples were extracted with 15 mL methanol vigorously mixed and centrifuged (10 min, 400 × g) at room temperature. The supernatant was transferred to a new vial and dryed by a rotary evaporator at 40°C.

The dried extracts were soluble in pyridine (30 μL) and BSTFA (N,O-bis—3-methyl-silyl-3-F-acetamide) (30 μL), incubated at 100°C for 15 minutes. The derivatized samples were analyzed by gas chromatography-mass spectrometry (GC-MS) by Agilent MSD 597, column HP-5MS, 30m × 0.25 mm. Chromatography was carried out with linear temperature programming from 70 to 320° at a speed of 4°C/min. Data were collected using Agilent ChemStation software. Mass spectrometric information was processed and interpreted using AMDIS program (http://www.amdis.net/index.html), standard NIST2005 library, and the library of standard compounds of BIN RAS. Quantitative interpretation of chromatograms was carried out with hydrocarbon using UniChrom program http://www.unichrom.com/unichrome.shtml.

2.4 Scanning electron microscopy

Scanning electron microscopy was used in order to study peculiarities of localization of microorganisms in the surface layer of the stone and to characterize the relationship between lithobiotic organisms during colonization of the granite. Samples of the damaged stone (0.5–1.0 cm × 0.5–1.0 cm) were initially examined under binocular loupe. The criterion of selection for SEM analysis was the presence of structures of microorganisms on the stone surface as well as transformation of the granite surface. The material was examined (after fixation) under the scanning electron microscope in the range of magnification from 100× to 10000×. SEM studies were performed on electron microscope ABT-55 (Japan) and TM 3000 (HITACHI, Japan, 2010) with an attachment of an energy-dispersive microanalysis OXFORD in SPbU Resource Center "Microscopy and Microanalysis."

2.5 Geochemical study

The determination of elemental composition in fresh granite and various types of crusts was carried out using inductively coupled plasma (ICP MS, Agilent 7700) in the chemical laboratory of the All-Russian Geological Institute.

For the experiment on the dynamics of granite bioleaching, we took three types of samples from the surface of granite rapakivi from the Monrepos Park (Vyborg): surface layer of granite without biofilms, granite with black (lichens + fungi + cyanobacteria), and with gray (lichens + alga) biofilms. There are no local sources of pollutions in this area. Previously, the samples were powdered. Samples part (2 g) were diluted with 10 mL of bidistilled water each (in a ratio of 1:5) and mounted on a vibration panel for constant mixing of the sample and placed in a thermostat. The experiment lasted about a month. During this period, the temperature in the thermostat was 25^0C at normal pressure. Aliquots of the solution were taken from the upper part of the flasks in the following time intervals: 1, 3, 6 hours from the beginning of the experiment; then after 1, 3, 8, 11, 14, 18, 22, 28, 32 days. The solution was analyzed with the following parameters: pH, particle size (HORIBA LA-950 nano-sizer), and composition of elements (ICP-MS, Agilent 7700).

3. Results and discussion

3.1 Main types of granite biofilms (outward, biodiversity, and metabolism)

There are different types of granite destruction in St. Petersburg, Vyborg, and quarries in Finland: fissuring, granular disintegration, flaking, exfoliation, loss of color, crusts, biofilms of different composition, ovoid weathering, and macro-fouling. Primary biological colonization usually connected with the formation of pigmented biofilms. The color and structure of biofilms usually depends on the dominance of certain groups of microorganisms (cyanobacteria, algae, microscopic fungi, and lichens).

Cyanobacteria typically prevailed in primary biofilms, especially in natural outcrops of granite. They formed the basis of lithobiotic communities in most of the studied habitats. Both mono-species and multi-species communities dominated by cyanobacteria were noted. The dominance of specific species often determined the morphology of the whole biofilm. So, on granite in quarry I, a rich biofilm with a dominance of *Stigonema ocellatum* Thuret ex Bornet & Flahault (Dillw.) was formed in the place of natural water seepage (**Figure 1**). This species forms the interwoven filaments, which are clearly visible in the SEM image. The upper part of the biofilm has a greenish-olive color and is represented by *Stigonema ocellatum*. In the lower part of the biofilm, a change in color to brown-red can be seen due to the change of the dominant species by *Gloeocapsopsis magma* (Brébisson) Komarék et Anagnostidis. Other representatives of cyanobacteria also appear in the lower part of the biofilm: *Lyngbya* sp., *Leptolyngbya foveolarum* (Rabenhorst ex Gomont) Anagnostidis et Komarek, *Synechocystis salina* Wislouch.

Lighting also plays an important role in the formation of biofilms on the granite surface. Thus, it was shown by comparative studies of the species composition of cyanobacteria in the Vyborg granite tunnels (with scarce of light) and open areas of granite near tunnels. Under natural lighting, six species of cyanobacteria were identified (for 1 sample): *Gloeocapsopsis magma*, *Nostoc commune* Vaucher ex Bornet et Flahault f. Commune, *Calothrix parietina* (Nägeli) Thuret ex Bornet et Flahault f. *parietina*, *Scytonema hofmannii* C. Agardh ex Bornet & Flahault, *Aphanocapsa* sp. 1, *Aphanocapsa* cf. *fusco-lutea*. In the same time, no more than three species of

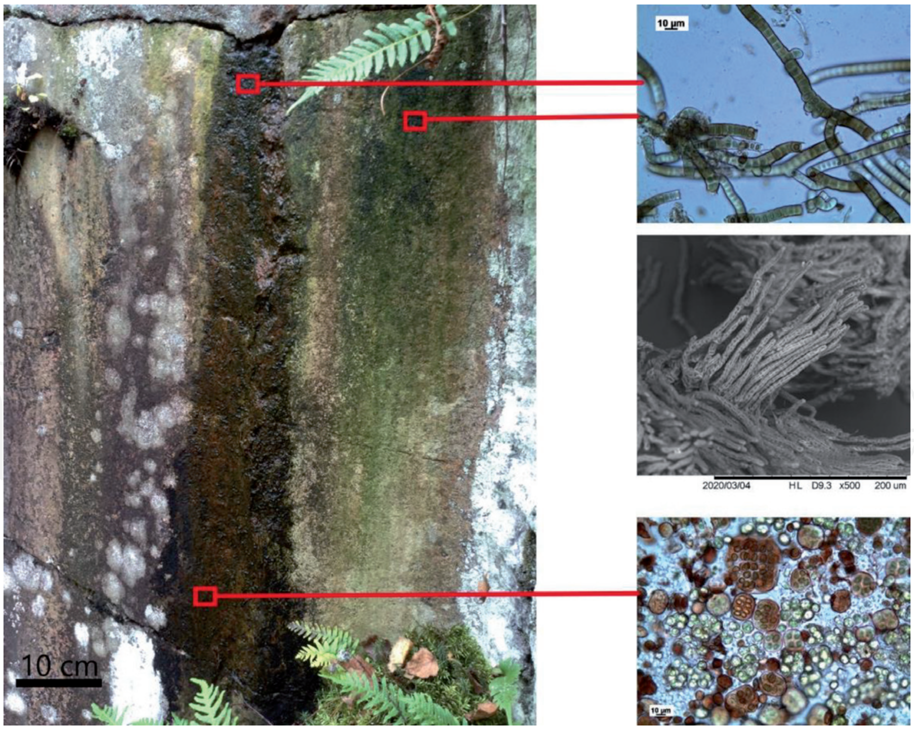

Figure 1.
Stigonema ocellatum *dominated biofilm on the surface of granite rapakivi in the quarry I.*

cyanobacteria were detected in each of the studied samples which were collected inside the tunnels. Moreover, the diversity of biofilms types inside tunnels was much lower than in the open air. In total, only three types of biofilms with the dominance of cyanobacteria were found in the tunnels (**Figure 2**).

a. Dark green to black biofilm is represented by the dominant species *Chroococcus* sp. 1 with the participation of *Aphanocapsa* sp.;

b. Green algae predominate in the green biofilm; cyanobacteria *Chroococcus* sp. 1 and *Aphanocapsa* sp. also found;

c. White deposits represent a mineral layer and contain neither cyanobacteria nor microalgae;

d. Cyanobacteria *Gloeocapsopsis magma* dominates in the reddish-brown biofilm.

It is interesting to note that only five taxa were found in Monrepos Park (Vyborg). This is due to the super dominance of certain species of cyanobacteria in biofilms on the surface of granite (**Figure 3–5**).

In total, 78 cyanobacteria taxa belonging to 5 orders, 18 families, and 29 genera were identified in the studied habitats. Quarry IV was the richest in the number of species (**Figure 6**).

The largest number of families (4), genera (8), and species (29) was noted for the order Synechococcales, followed by the order Chroococcales (25 species). The most diverse is the genus *Leptolyngbya* (**Figure 7**). It occurs most often. Cosmopolitan species predominated among the identified cyanobacteria.

The most common in the studied areas are *Calothrix parietina* Thur. ex born. & Flah., *Gloeocapsopsis magma* (Brébisson) Komarék et Anagnostidis, *Leptolyngbya foveolarum* (Rabenhorst ex Gomont) Anagnostidis et Komarek, *Gloeocapsa atrata* Kützing, nom. illeg. (**Figure 8**).

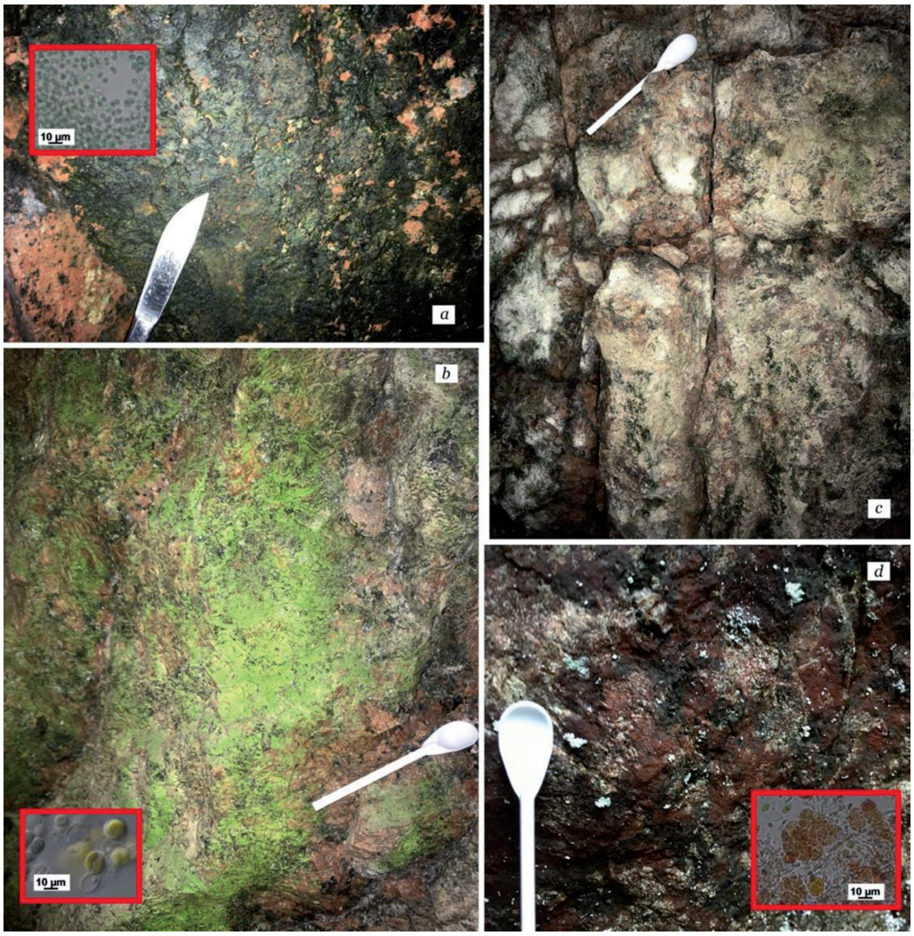

Figure 2.
Different types of biofilms and deposits in the Vyborg tunnels.

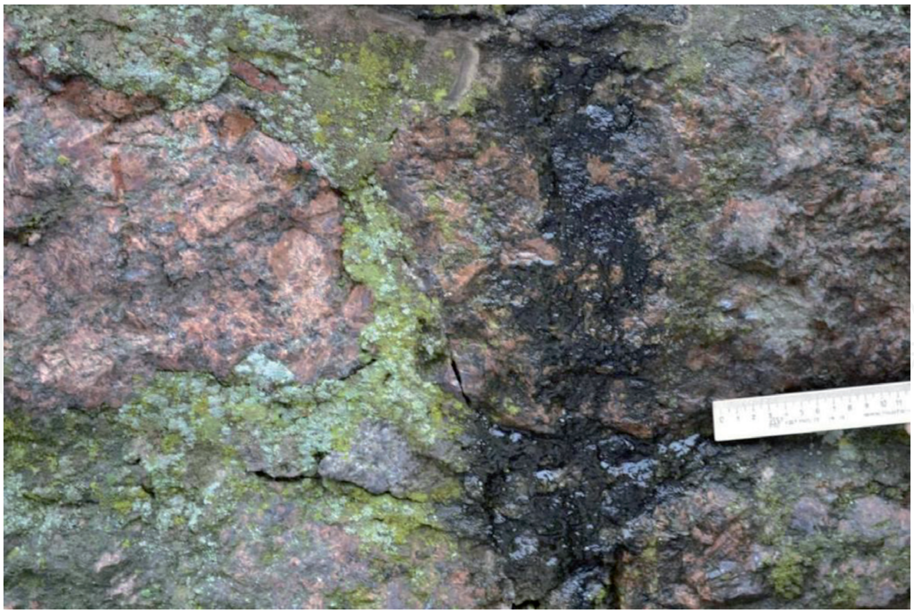

Figure 3.
Biofilm formed by the cyanobacteria Microcoleus vaginatus *Gomont ex Gomont on the granite wall of the Vyborg castle (Vyborg).*

Organotrophic bacteria were also characterized by significant diversity at various granite sites in the city of Vyborg, including Monrepos Park. Their number reached 10^7 cells per 1 gram of material. A similar picture was observed in St. Petersburg (on the granite monuments of Museum Necropolises). The results of

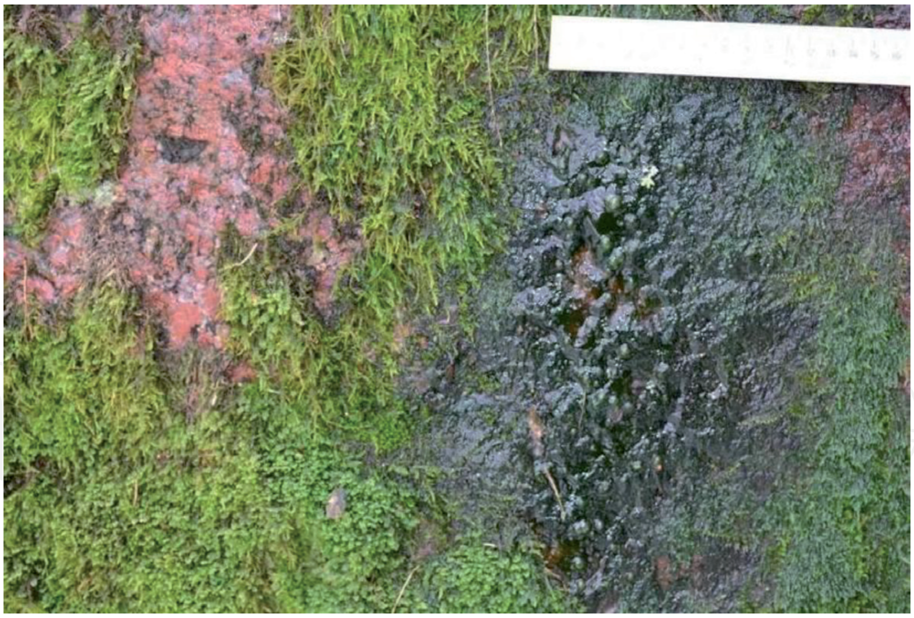

Figure 4.
Biofilm formed by the cyanobacteria Lyngbya martensiana *Meneghini ex Gomont on a granite block in Monrepos Park (Vyborg).*

Figure 5.
Biofilm formed by the cyanobacteria from the genera Lyngbya *and* Synechococcus *on a granite wall in Monrepos Park (Vyborg).*

metagenomic analysis show that two main bacterial phyla dominate in biofilms on the granite rapakivi in city environment: Bacteroidetes and Proteobacteria. The Bacteroidetes phyla were characterized by a large presence in black biofilms. A significant part of the lithobiotic communities in all samples of granite was represented by actinomycetes. Acidobacteria were also isolated in a significant amount from black biofilms (**Table 1**).

In the heterotrophic block of biofilms on the surface of granite, a significant diversity of micromycetes was noted. In total, 64 species of micromycetes were isolated and identified (47 – St. Petersburg, 42 – granite outcrops, and 25 – common species). The domination of dark-colored fungi in biofilms on the granite

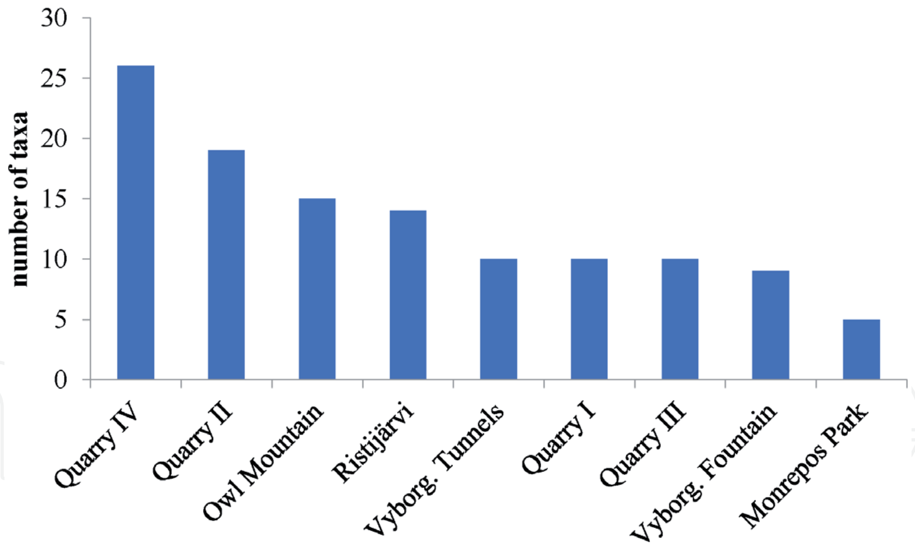

Figure 6.
The number of cyanobacterial taxa revealed on the granite in study areas.

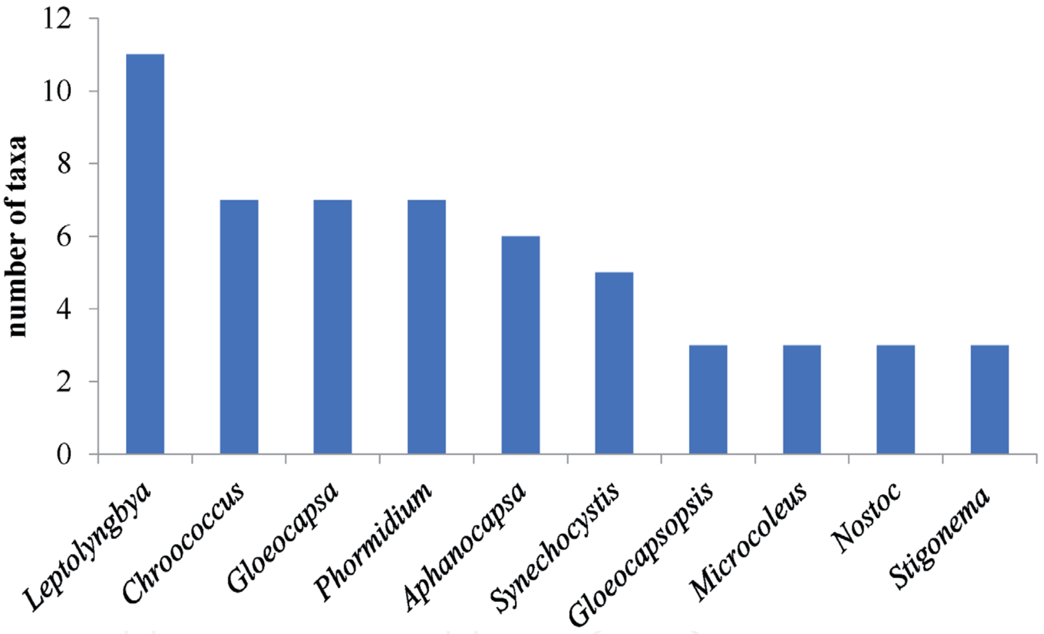

Figure 7.
Number of species in the richest genera.

surface was typical for the urban environment. It is interesting to note that some microfungi were superdominants in biofilms on granite in an urban environment (*Cladosporium*, *Alternaria*, *Aureobasidium*, and also black yeast-like fungi). Species of ascomycetes prevailed in the taxonomic relationship, which was shown using metagenomic analysis. Microcolonies and hyphae of microscopic fungi were typical for damaged granite surface (**Figures 9–11**). According to scanning electron microscopy study (SEM-analysis), microcolonies can be considered as the dominant form of the fungal existence on granite. Small compact clusters and chains of thick-walled cells (short hyphae) were noted in the granite surface in natural outcrops as well as in urban environment. Fungi are able to penetrate through microcracks into the rock substrate while causing weakening of the surface layer of granite. Fungal microcolonies were formed usually on feldspar and mica. Long hyphae were usually connected with the microrelief of K-feldspar. They were more typical for granite rapakivi in Saint Petersburg (**Figure 11**).

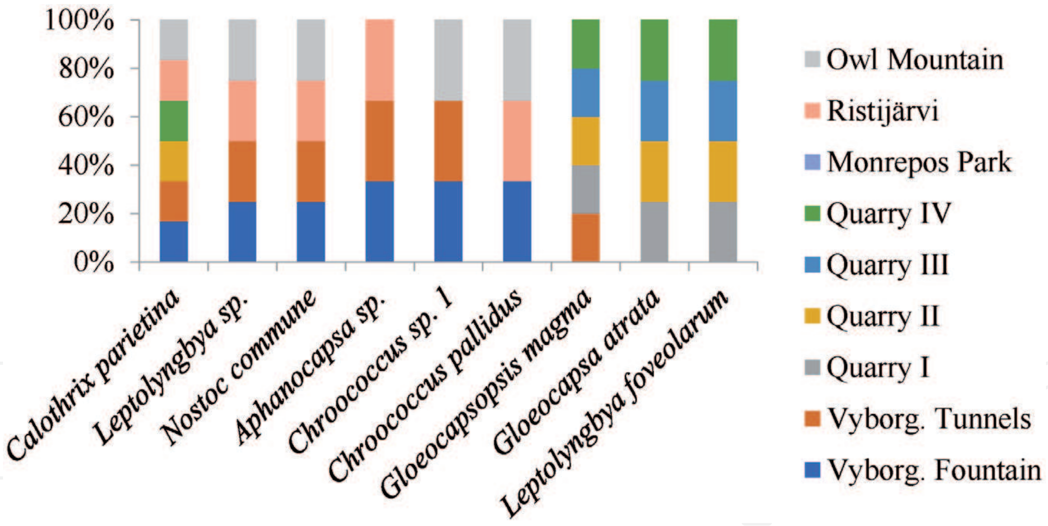

Figure 8.
The presence of common taxa of cyanobacteria in biofilms on granites in the studied places.

Bacteria phyla	Green biofilm	Black biofilm
Acidobacteria	0.2	6.6
Actinobacteria	15.2	7.5
Bacteroidetes	13.3	40.5
Firmicutes	2.7	0.0
Proteobacteria	48.7	33.4

Table 1.
The dominant groups of organotrophic bacteria in biofilms on granite at the monuments of the Museum Necropolises in St. Petersburg (share according to the results of metagenomic analysis).

As a result of biochemical studies, more than 200 different compounds were found in biofilms samples from granite quarries. Among them were identified: mono, di, and trisaccharides, aliphatic carboxylic acids, amino acids, sugar alcohols, phenolic compounds, diterpenes, sterols, ethanolamine, phosphate, glycerol-3-P, and urea. In samples of biofilms taken in an urban environment only about 100 different low molecular weight organic compounds were identified. In general, the biofilm samples from granite in urban environment had a significantly lower molecular diversity of metabolites than the samples taken in the quarries in Finland. At the same time, the quantitative content of some compounds, primarily sugar alcohols, was significantly higher in biofilms in the urban environment. Most likely, the revealed differences are associated with the species composition of microorganisms in biofilms.

The general patterns of the distribution of small organic molecules depending on the type of biofilms were similar for samples taken in the quarries and in Museum Necropolises (Saint Petersburg). In biofilms with a predominance of algae and cyanobacteria, the amount of mono- and disaccharides, amino acids and organic acids in free form was significantly higher in comparison with other types of biofilms. In samples dominated by fungi, the amount of free-form organic acids was lower and concentration of polyols was higher compared to algae.

Sugar alcohols and phenolic compounds predominated in the fouling formed by lichens. In samples of primary soil with a moss cover, the greatest variety of low molecular weight metabolites was observed; however, their quantitative content was lower than in other samples. The data obtained show the possibility

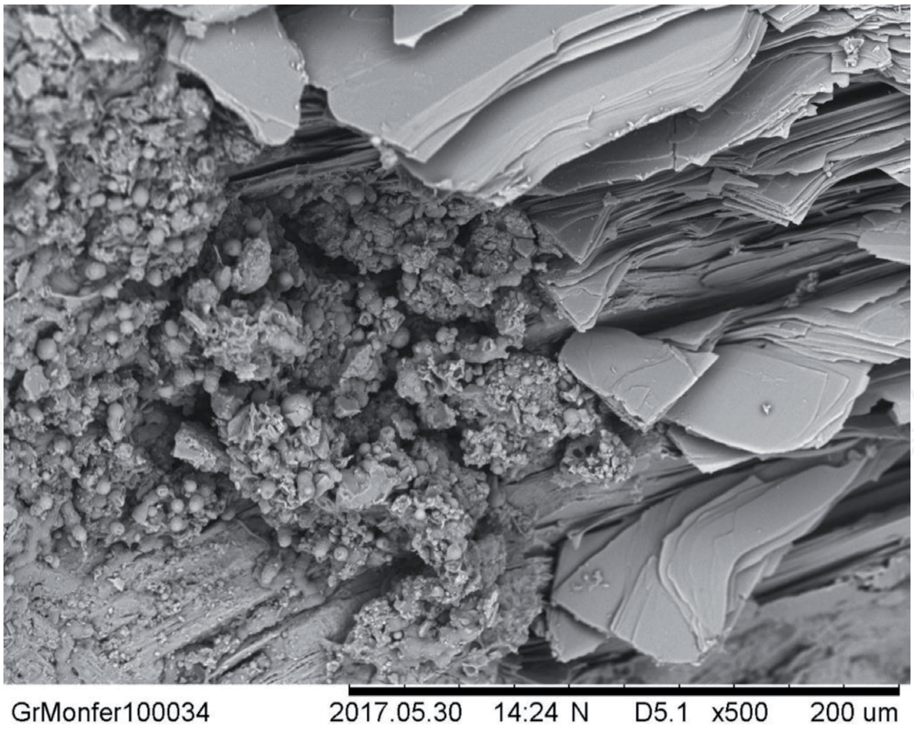

Figure 9.
Fungal microcolonies on the border of mica (Quarry I).

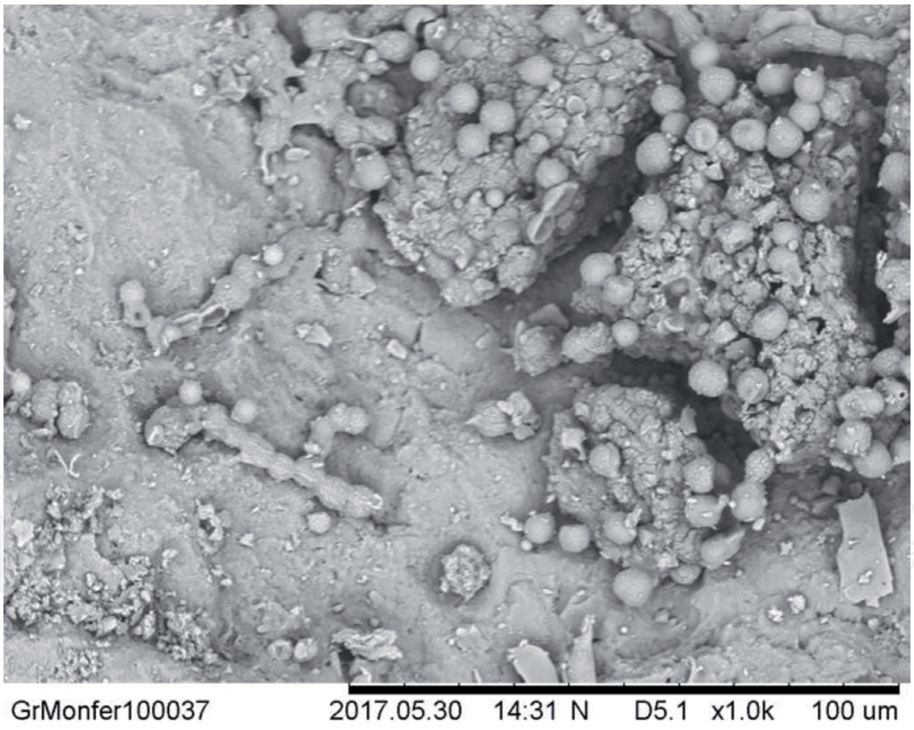

Figure 10.
Fungal microcolonies and short hyphae located on the K-feldspar (Quarry I).

of applying the metabolomic approach to the study of lithobiotic communities in different environment.

3.2 Geochemical peculiarities of granite bioweathering

To assess the effect of biofouling on the behavior of chemical elements during granite weathering, samples of granite rapakivi were taken in natural outcrops

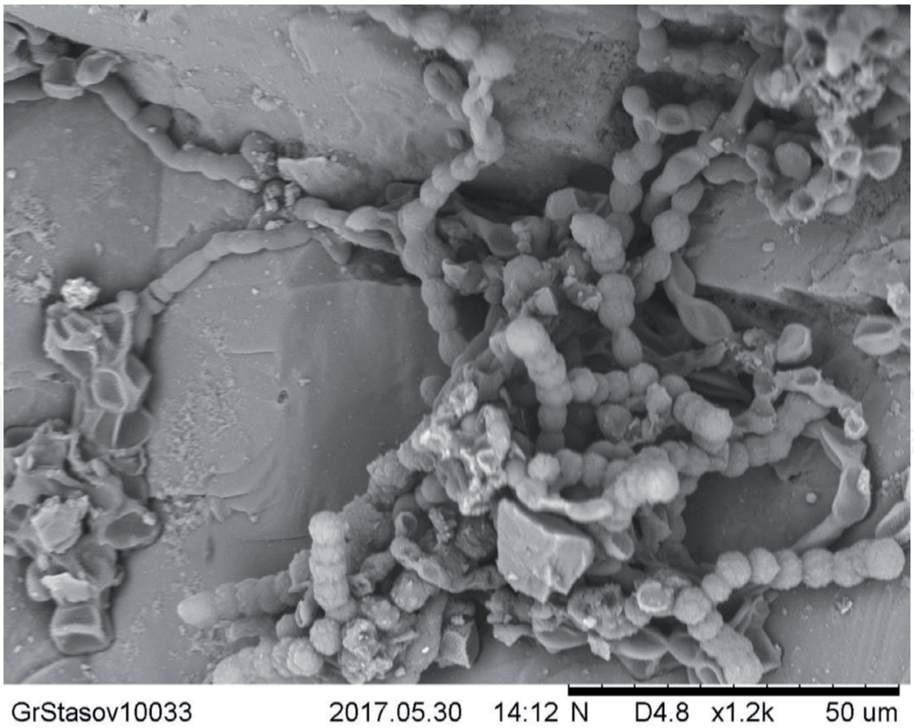

Figure 11.
Fungal hyphae in the granite surface of Stasov monument (Museum Necropolis of Saint Petersburg).

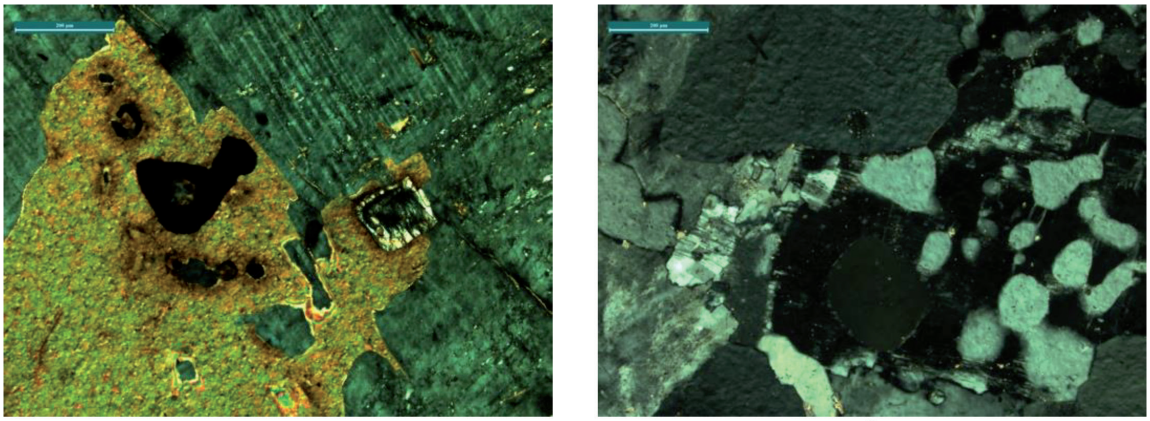
a
b

Figure 12.
Thin skin of rapakivi granite: (a) plagioclase, microcline and biotite with pyrite and zircon; (b) quartz, plagioclase and microcline. XPL (a), PPL (b).

(granite wall) in Monrepos Park (Vyborg neighborhood) where the influence of the urban environment on natural ecosystem is insignificant. This type of granite is commonly called Wiborgite. Wiborgite is a porphyritic, coarse-grained granite with a typical rapakivi texture composed of round 1–3 cm potassium feldspar ovoids with a plagioclase mantle. The color of this rock can be brown, brownish red, red or green. The essential minerals are potassium feldspar, quartz, plagioclase, biotite, and hornblende (**Figure 12a** and **b**, **Table 2**).

Three types of samples were taken for comparative study: fresh granite, crust without biofilm (3 mm) and crust with biofilm (3 mm). The results of the analysis are presented in **Tables 3** and **4**.

It is shown that the content of almost all petrogenic oxides (except SiO_2), decreases in the crust without a biofilm (**Table 3**). This fact can be explained by the destruction of the granite structure and leaching of the most mobile chemical elements and particles of minerals under the influence of rain and wind. The crust is

Mineral	**Mass %**	**Mineral**	**Mass %**	**Mineral**	**Mass %**
Quartz	24–42%	Muscovite	0–0.1%	Ilmenite	0–0.5%
K-feldspar	28–42%	Allanite	0–0.2%	Rutile	0–0.1%
Albite	7–13.7%	Tourmaline	0–0.2%	Apatite	0–0.3%
Andesine	3–27%	Zircon	0.1–0.2%	Pyrite	0.0
Amphibole	0.2–11%	Kaolinite	0–0.1%	Calcite	0.0
Chlorite	0.0–0.2%	Thorite	0-0.1%	Bastnasite	0–0.9%
Biotite	2.9–7.5%	Magnetite	0–0.1%	Fluorite	0.2–1.9%

Table 2.
Mineral composition of rapakivi granite (Wiborgite).

Samples	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**K_2O**	**Na_2O**	**CaO**	**MgO**	**TiO_2**	**P_2O_5**	**MnO**	**LOI**
Granite (n = 7)	70.78	13.51	3.38	5.57	3.39	2.32	0.22	0.33	0.07	0.04	0.38
Granite crust (n = 7)	72.19	13.05	3.19	5.29	3.11	2.06	0.20	0.34	0.08	0.04	0.46
Granite crust with biofilm (n = 7)	69.51	14.50	3.54	5.41	3.34	2.29	0.23	0.36	0.06	0.03	0.76

Table 3.
Content of pertogenic oxides in fresh granite and two types of crust (mass%).

Elements	**Granite (n = 7)**	**Crust (n = 7)**	**Crust with biofilm (n = 7)**	**CC_1 = crust / granite**	**CC_2 = crust with biofilm/granite**
Ba	119	126	121	1.06	1.02
Sr	12.8	8.1	15.8	0.63	1.18
Li	38.3	34	40.2	0.89	1.05
Sc	4.88	4.36	5.1	0.89	1.05
U	7.37	2.37	12.4	0.32	1.68
Se	3.19	1.89	6.45	0.59	2.02
Mo	1.66	0.22	2.83	0.13	1.70
Cd	0.24	0.11	0.25	0.46	1.08
Sb	0.09	0.05	0.09	0.56	1.00
Ni	12.6	14.6	15.5	1.16	1.23
Co	3.3	3.09	3.79	0.94	1.15
Cu	6.28	6.1	7.98	0.97	1.27
Zn	65.3	72.2	79.1	1.11	1.21
As	11.7	10.3	11.1	0.88	0.95

Table 4.
Content of trace elements in fresh granite and two types of crust (ppm) and coefficient concentration (CC).

relatively enriched with the most stable mineral quartz. The organic matter content LOI (loss on ignition) increases slightly in comparison with fresh granite. In the crust with biofilm the situation is different. Particles of weathered granite can be accumulated in a biofilm. This probably explains the fact that the content of almost all basic elements in the crust with biofilm is close to the composition of unaltered granite. The organic matter content in the crust with biofilm is naturally the highest in comparison with other variants.

A similar situation is observed in the behavior of trace elements. It is shown using the concentration coefficient (CC) calculated as the ratio of the content of the element in the crust to its content in not weathered granite. In the weathered crust, in comparison with fresh granite, the removal of most chemical elements is observed (**Table 4**). The concentration coefficient in this case is less than 1. At the same time, trace elements (Se, Mo, U, Cu, Ni, Zn, and Sr) are accumulated in the crust with the biofilm (concentration coefficient is more than 1).

It is well known that the main environment of migration of chemical elements in the nature is water. Migration of elements in the liquid phase occurs in the form of ions, molecules, and colloidal particles. The chemical composition of water in the hypergenesis zone is formed primarily due to the dissolution of solid phases interacting with water. Granite biofouling may affect this process. For the experiment on the dynamics of granite bioleaching, we took three types of samples from the surface of granite rapakivi from the Monrepos Park (Vyborg): surface layer of granite without biofilms, with black (lichens + fungi + cyanobacteria), and with gray (lichens + alga) biofilms.

As a result, it was shown that the particle size changes over time that reflects the periods of their dissolution and coagulation. On the first day no changes are observed. Further until the 22nd day changes in particles size are observed and then alignment occurs (about 380 nm in size). The curves for the studied variants differ markedly. Largest particle size during the experiment is observed for granite with black biofilm a compared to granite with gray biofilm (**Figure 13**).

A comparison of the graphs of pH changes (**Figure 14**) shows that at the beginning of the experiment, the pH of solutions for the granite without biofilms and granite with biofilms is different. Amplitude of the pH values changes varies from 6.3 to 7.6 and does not connect with the changes in particles size. Correlation analysis confirmed the absence of any linear dependence of the change in the size of nanoparticle in solution on the pH of the solutions.

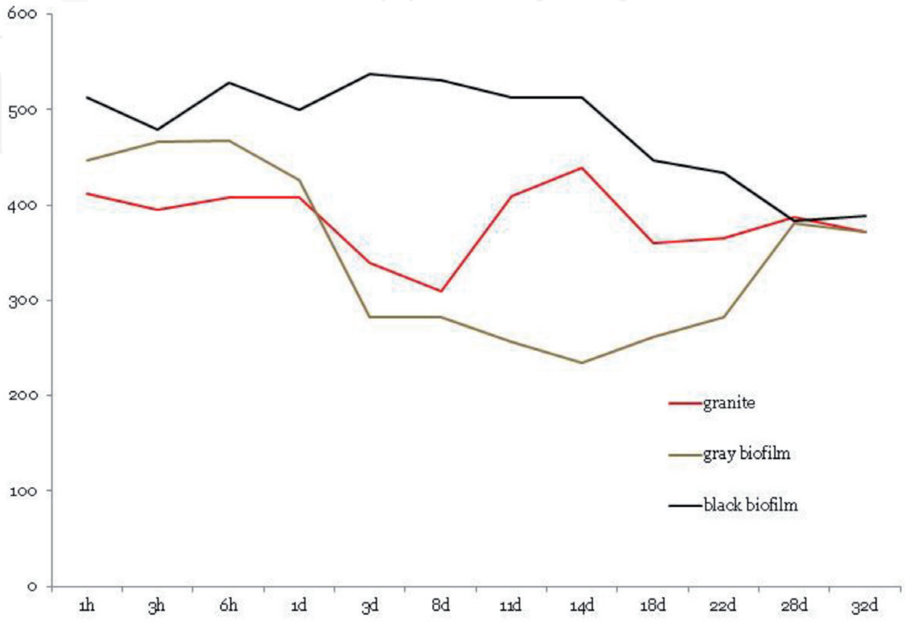

Figure 13.
Particles size changes in time for granite, granite with black, and gray biofilms (nm). h – hours; d – days.

The results show the periodic variation of the acid-alkaline properties of the solutions. As a whole, the variant with the black biofilm are characterized by a more alkaline medium; the variant with gray biofilm has a relatively more acidic medium.

In selected aliquots of solutions, the content of chemical elements was determined by the ICP MS method. The highest concentrations of elements in the solutions were observed for K, Na, Mg, and Ca (an example for calcium is shown in **Figure 15**). This indicates a fairly rapid leaching of these elements from the minerals of the rock, where they are in water-soluble form. Lower contents are typical for a group of elements: Al, Fe, Ba, and Li. Hundreds of mg per liter were found for: Mn, Rb, Sr, and Cs. Thousands of mg were found for the following elements: Sc, V, Ni, Pb, Cu, Zn, Mo, U, Th, Y, La, and Ce. An increased concentration of various groups of elements is observed on the 8th day (K, Na, Ni, As, Cd, and Mo) that can be associated with an increase in the pH of the solution.

The experimental results demonstrate the different behavior of chemical elements in the absence and presence of biofilms on granite. There is also a different

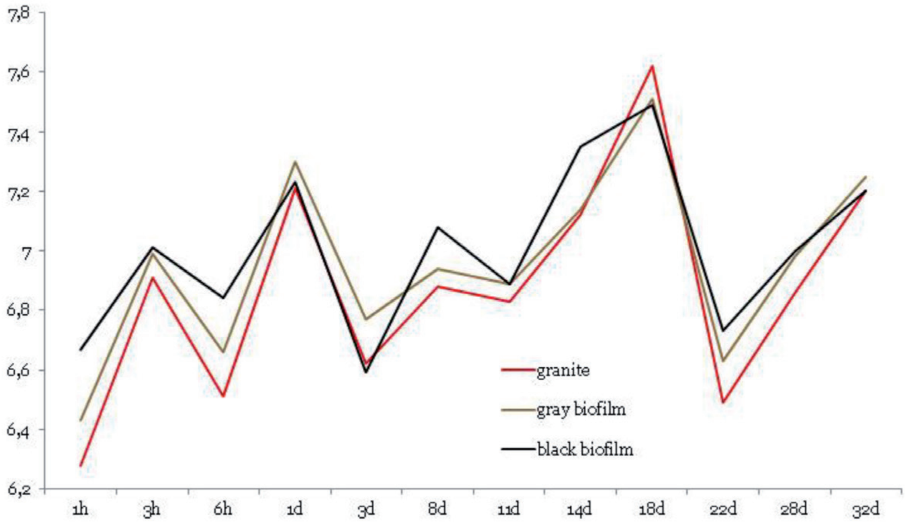

Figure 14.
pH values changes of solutions (granite, granite with black, and gray biofilms). h – hours; d – days.

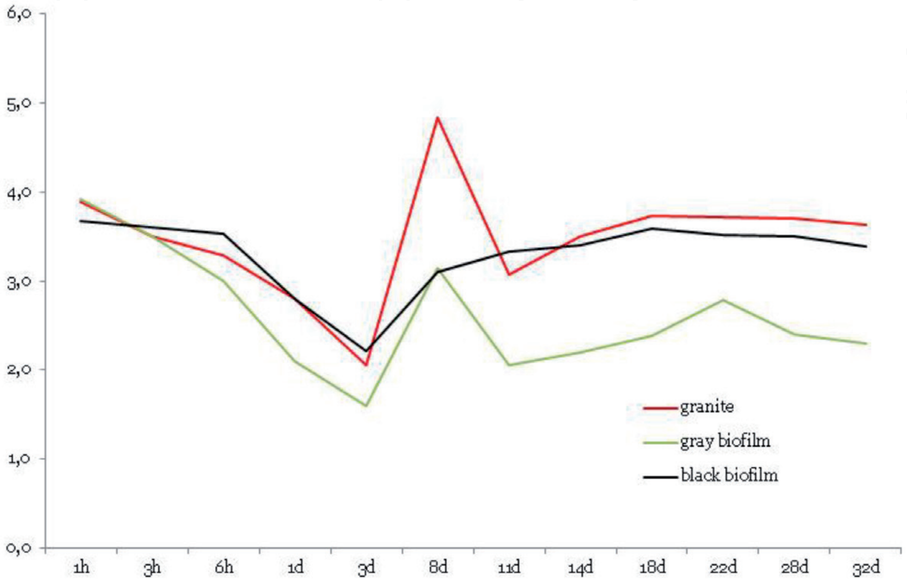

Figure 15.
Dynamics of the calcium content changes in solutions (mg/L) during the dissolution of granite, granite with gray and black biofilms. h – hours; d – days.

behavior of chemical elements in variants with different types of biofilms. The dissolution of granite with a black biofilm is the least intense, which is especially noticeable on the example of Na, Ca, and Mo. The content of these elements in granite with black biofilm practically does not change in solutions over time. Since fungi dominate in the black biofilm, it can be assumed that the migration of elements into the solution may be limited due to the immobilization of elements by fungal biomass. Due to metabolic processes (the release of organic acids and the binding of metals by specific proteins) as well as the physicochemical properties of the cell wall, fungi can efficiently bind metals and significantly reduce their mobility in solution [6].

4. Conclusion

Biogenic weathering of granite is connected with the impact on the rock surface by microorganisms of lithobiotic communities (bacteria, microfungi, microalgae, lichens, and mosses). The biological colonization of granite is a multifactorial process. It depends on the composition of the microbiota, the state of the stone, as well as external conditions. The ecological aspect of the problem is determined by the difference between granite biofouling in the anthropogenic (urban) and natural environment. The biofilms on granite are characterized by a wide diversity of cyanobacteria, micromycetes, and organotrophic bacteria. The species composition often determines the features of the appearance of a biofilm, the features of its development on granite, as well as the biochemical composition and degree of impact on granite. Behavior of chemical elements during the bioweathering of granite depends on the type of biofilm in which some elements can be accumulated. This problem seems as an interdisciplinary task and requires the collaboration of biologists and geologists.

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Conflict of interest

The authors declare no conflict of interest.

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