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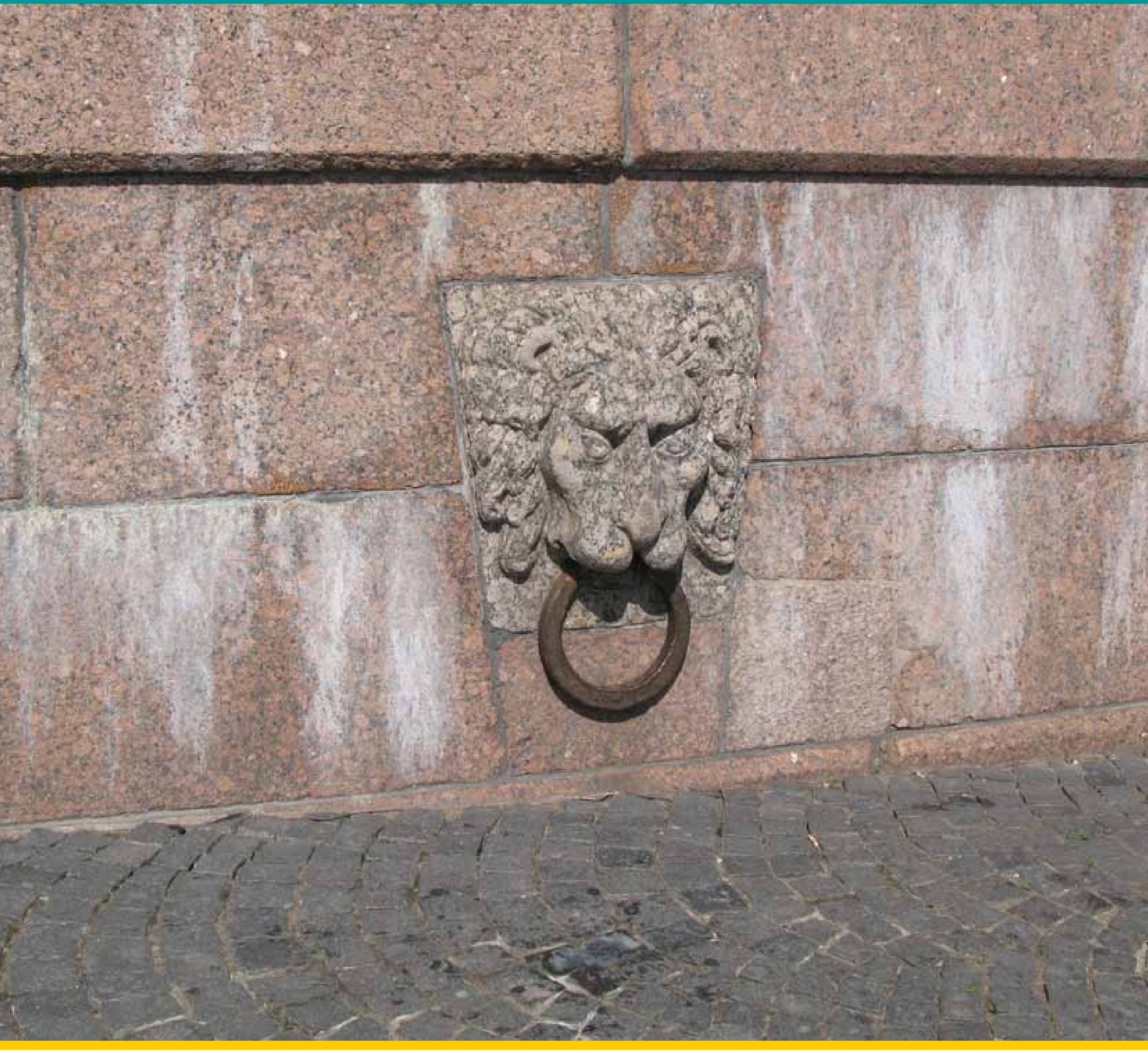

Evaluation of the durability of granite in architectural monuments

South-East Finland - Russia
ENPI CBC 2007 - 2013

Elena Panova, Dmitri Vlasov and Hannu Luodes (eds)

GEOLOGIAN TUTKIMUSKESKUS

Tutkimusraportti 214

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Edited by

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Front cover: Embankment stones of the waterways of St. Petersburg.
Photo: Heikki Pirinen, GTK.

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Evaluation of the durability of granite in architectural monuments was carried out as part of the project "Efficient use of natural stone in the Leningrad region and South-East Finland". The focus of the research was on rapakivi granite, since it is the most common and most widely used local stone material.

The main aim was to examine how the natural stone survives in the city environment on the Baltic Sea coast where the stone is exposed to several annual freezing/thawing cycles, pollution caused by traffic and industry as well as human activities such as reconstruction and maintenance of the infrastructure. The study was concentrated on the various weathering processes and their effect on the durability of rapakivi granite.

As a summary of the results of this study, it can be concluded that the weathering of granite, and rapakivi granite elements in particular, is restricted to few millimetres of the stone surface. The combined effect of physical, chemical and biological weathering causes the mineral structure on the stone surface to disintegrate, which provides conditions for the freezing and thawing of water, crystallization of de-icing salts and settlement of biological growth. The effect of weathering is mostly aesthetic and does not impact on the strength or durability of the elements. Human activities can affect the durability of the stone elements through defects caused in the construction phase, during maintenance or in restoration works. Typical examples include movement of the mounting basement and broken corners or open joints in stone elements.

The project was co-funded by the European Union, the Russian Federation and the Republic of Finland through the South-East Finland - Russia ENPI CBC Programme 2007–2013.

Keywords (GeoRef Thesaurus, AGI): building stone, granites, rapakivi, weathering, urban environment, buildings, Saint Petersburg, Helsinki, Russian Federation, Finland

Elena Panova, Saint Petersburg state university
University Embankment 7/9
St. Petersburg, 199034
Russia

Dmitri Vlasov, Saint Petersburg state university
University Embankment 7/9
St. Petersburg, 199034
Russia

Hannu Luodes, Geological Survey of Finland
P.O. Box 1237
FI-70211 Kuopio
Finland
E-mail: hannu.luodes@gtk.fi

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Graniitin kestävyyttä rakennusmateriaalina tutkittiin hankkeessa "Efficient use of natural stone in the Leningrad region and South-East Finland". Tutkimus keskittyi rapakivigraniittiin, joka on yleisin ja eniten käytetty paikallinen kivimateriaali.

Työn päätarkoituksena oli tutkia, kuinka luonnonkivi kestää kaupunkiympäristössä Itämeren rannikon olosuhteissa, jossa siihen kohdistuu useita vuosittaisia jäätymis-sulamissyklejä, liikenteen ja teollisuuden saasteita sekä myös ihmisen aiheuttamia kunnossapito- ja muutostoimia. Tutkimuksessa keskityttiin monipuolisesti eri rapautumismekanismeihin ja niiden vaikutukseen rapakivigraniittien kestävyyteen.

Yhteenvetona voidaan todeta, että rapautumisen vaikutukset graniitissa ja erityisesti rapakivigraniitissa rajoittuvat kiven pintaosaan, muutaman millimetrin syvyyteen. Fysikaalisen, kemiallisen ja biologisen rapautumisen yhteisvaikutuksesta kiven pinta haurastuu, mikä luo olosuhteet kiven pinnan jäätymiseen ja sulamiseen sekä jäänpoistosuolojen kiteytymiseen ja biologisen kasvuston kiinnittymiseen. Rapautumisefekti on pääasiassa visuaalinen eikä vaikuta kivielementtien kestävyyteen. Ihmisen toiminnan vaikutukset, kuten rakentamisessa, ylläpidossa ja restauroinnissa kivielementtien rikkoutuminen, voi vaikuttaa kiven kestävyyteen. Tyypillisiä esimerkkejä tästä ovat mm. kivien asennuspohjan liikunnat sekä lohjenneet kulmat ja avonaiset raot kivielementeissä.

Hanke kuuluu EU:n Kaakkois-Suomi–Venäjä ENPI CBC 2007–2013 -ohjelmaan, ja sitä ovat tukeneet EU sekä Venäjän ja Suomen valtiot.

Asiasanat (Geosanasto, GTK): rakennuskivet, graniitit, rapakivi, rapautuminen, taajama-alueet, rakennukset, Pietari, Helsinki, Venäjä, Suomi

Elena Panova, Saint Petersburg state university
University Embankment 7/9
St. Petersburg, 199034
Russia

Dmitri Vlasov, Saint Petersburg state university
University Embankment 7/9
St. Petersburg, 199034
Russia

Hannu Luodes, Geologian tutkimuskeskus
PL 1237, 70211 Kuopio
Sähköposti: hannu.luodes@gtk.fi

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PREFACE

Within the framework of the program on Cross-Border Cooperation within the European Neighbourhood and Partnership Instrument (ENPI), geologists from Saint Petersburg and Finland carried out a project entitled "Effective use of natural stone in the Leningrad region and Southeast Finland". The mining companies "Vozrozhdenie" (Russia) as well as Palin Granit and Ylämaan graniitti (Finland) supported the project as associated partners.

The joint project between Russia and Finland was not an accidental idea; it was rather a logical continuation of the historical, geographical and geological conditions of the northwestern part of the East European platform. We have a common history and geology. We see the same rocks in nature, in outcrops, and when we walk about the cities we see the same stone in the architecture. We learn about our history, our roots, in the monumental buildings of our cities. Stone buildings have survived through the centuries, retaining the history.

This is not surprising. If we examine the geological maps of our countries, we see that the old towns were founded in regions rich in building materials such as granite, flag-like limestone, quartzite and marble, which were quarried nearby. For the Leningrad region and southeast Finland, facing stone has recently become the most prospective commercial mineral material.

The most abundant building material in our northern countries is granite, which is still actively quarried in the territory of the Karelia Isthmus and southeast Finland. The extensive use of natural stone in decorating Helsinki and Saint Petersburg has created their magnificent and stately images.

Granite is a strong material, but it is subject to destruction, and it can be fouled by moss and lichen. It is necessary to know how to cure granite from destruction in order to save our cities, our history.

Among the largest industrial megalopolises, Saint Petersburg is a unique architectural monument with a grand historical centre. The high degree of preservation and authenticity of historical areas has formed the basis for including the historical centre of Saint Petersburg with the architectural monuments of its suburbs in the UNESCO List of World Heritage Sites in Europe.

Monuments of cultural heritage realize important social functions in education and culture, the actual formation of patriotic feelings, the moral and aesthetic upbringing of young people. Historical and cultural monuments make up an essential part of the world's cultural heritage, evidence of the great contribution of the peoples of our countries to the development of world civilization. Lately, cultural heritage monuments have become the victims of the "ecological aggression" of modern industrial production, urbanization and other anthropogenic and natural factors. Their state has nowadays become one of the characteristic indicators of ecological conditions. This is why the study of changes in the state of objects of cultural heritage and the influence of destructive factors is necessary not only to save the monuments, but to maintain the control over the environment.

The strategy for the development and improvement of the urban landscape is determined by the formula "preservation through development, development through preservation." This entails interdisciplinary investigations of the processes that destroy historical monuments, as well as the influence of different destructive factors, on the basis of constant monitoring, and the creation based on this knowledge of a system of protective measures.

INTRODUCTION

This book is about stone, which has been quarried and is still quarried on the banks of the Gulf of Finland and Karelia Isthmus. The goal of our investigations by scientists belonging to different branches of science was to study different trends in using natural stone in building and architecture, and to evaluate the characteristics of stone responsible for ensuring the safety of stone constructions, as well as the processes of stone destruction under urban conditions. The aim was to examine how the granite weathers and if the weathering causes problems to durability and usability of the rock. Thus various types of weathering processes, such as physical, chemical and biological weathering, as well as anthropogenic weathering were studied and described.

Granite is truly considered to be one of the symbols of Saint Petersburg, and has been used in construction since the 18th century. The Peter and Paul Fortress and the embankments of the Neva River are faced with rapakivi granite, as well as small bent bridges, and bridges across the Neva and the canals, as well as staircases and ramparts towards the river. The basements of many palaces are faced with rapakivi granite. Enormous granite plates are used as pedestals of monuments; Alexander's column together with the magnificent colonnades of Saint Isaac's and Kazan cathedral adorn the city. Granite was extracted on the islands in the Gulf of Finland and in the quarries near Pyterlahti and Monrepos on the banks of the Gulf.

Later, in Soviet times, the granites from the Karelia Isthmus (the regions of Sortavala, Kuznechnoe and Kamennogorsk) came into use. These granites can be seen along the embankments of the Neva, in modern buildings and in the facing of the metro stations. Nowadays, the pavements of Nevsky prospect and other central streets of Saint Petersburg have been paved with granite.

In the architectural decoration of Finnish cities and towns, granites (rapakivi, granite-gneiss and others) are widely used. The largest fortress in Finland, Suomenlinna, built 250 years ago, is dressed in granite. In Helsinki, many interesting architectural monuments, ensembles and cathedrals are very close in style to the old Petersburg and Vyborg.

Lately, a large amount of cheap stone brought from different countries has appeared, but it is not long-lived under the conditions of our climate zone.

The problem of stone decomposition is of great importance to architects, designers, restorers and stone-mining companies. The most essential are the following problems:

- evaluation of long-term changes in the stone (colour and structural-textural peculiarities);
- influence of the structural-textural peculiarities of the stone on its rate of contamination;
- evaluation of the damage to stone due to temperature fluctuation;
- influence of air quality (mechanical and chemical composition of the air)
- influence of rock porosity on the speed of water absorption and retention of stagnant water;
- the after-effects of contact with the ground;
- long-term service;
- mechanical strength in relation to compression and deformation;
- possibility of using stone for different building purposes;
- dependence of bio-destruction on the type of stone;
- influence of the cement material of joints on the mechanical, chemical and biological destruction of stone;
- prognosis of stone behaviour in relation to climate fluctuation;
- temporal changes in stone behaviour: immediately, gradually and after a long time.

There are more questions than answers. We hope that our investigations into the characteristics of the physical, chemical and biological destruction of granite under urban conditions in Fennoscandia will be employed by different specialists and will help in preserving architectural monuments for further generations.

1 GRANITE IN THE STONE DECORATION OF SAINT PETERSBURG AND HELSINKI

Saint Petersburg is often regarded as a granite city. No wonder that granite is its historical symbol.

Granites from different quarrying places have been used in the buildings of the central part of Saint Petersburg. These include pink granites such as rapakivi, kaarlahtinsky, gangutsky and valaamsky from Antrea and grey granites, namely Serdobol from Antrea and nystadsky from Kavantsaari. All these rocks have their own typical visual features such as colour, granularity and pattern determined by their mineral composition and texture.

Rapakivi granite is the most famous among these rocks. It is used in many architectural ensembles and monuments of Saint Petersburg, which make up its unique image. This granite has a remarkable pattern: large ovoid clusters of K-feldspar with a diameter of 3–5 cm surrounded by a rim of greenish-grey plagioclase are set into a fine-grained matrix of feldspars, quartz and biotite.

Peter I initiated the stone building in Saint Petersburg, while Catherine the Great elevated the image of the city to imperial grandeur. Since 1762, the embankments have been dressed in granite. Facing of the basements of the palaces and houses with rapakivi granite began in the 18th century. The walls of the Peter and Paul Fortress are faced with this granite.

Familiar to many, the monument to Peter I, the "Bronze Horseman", stands upon a great monolith of the rapakivi granite. The embankments of the Moika and Fontanka, Griboedov, Kruykov canals and others are built of rapakivi granite. All the embankments of the pre-revolution period were built from red and greyish-red granites from the Vyborg rapakivi intrusion: vyborgites and pyterlithes, which in practice differ little from each other.

Monolithic columns decorate the church of Archangel Michael inside Saint Michael's (Mikailovsky) (Engineer's) Castle. An inner granite colonnade decorates Kazansky Cathedral (Bulakh 2012). The grand Saint Isaac's Cathedral is adorned with 112 columns of pink rapakivi granite (Bulakh et al. 2010). Granite was quarried on the islands of the Gulf of Finland. The granite blocks for the columns of Saint Isaac's Cathedral and the world's largest granite monolith for the Alexander Column in the Palace square, which is one of the symbols of Saint-Petersburg, were taken from Piterlaks (Pyterlahti) quarry on Hevonniemi cape.

The rapakivi granites used for building in Saint Petersburg were quarried from Vyborg massive, which occupies an area about 1800 km^2. In old times, granite was also quarried near the Finnish town of Hamina (Fredrikshamn). The most famous granite quarries are Pyterlahti and Hämeenkylä. The Pyterlahti stone quarries were situated along the banks of the gulf, and one of them was a small island composed of rapakivi granite. It was the very place from where the stone for the Alexander Column and Saint Isaac's Cathedral were taken.

Rapakivi granite was referred to as Finnish in relation to the occurrences at Vyborg and Pyterlahti. According to the colour and extensive use in building, it was subdivided into pink and red granite. The rock consists of large (up to 5cm) round, ovoid clusters of pink K-feldspar orthoclase surrounded by a white rim of Na-feldspar oligoclase (Simonen 1987). The ovoids are cemented by a medium-grained matrix of pink and white feldspars, grey quartz, mica and hornblende (Rämö & Haapala 2005, Sederholm 1928). The granite was named "Rapakivi" in Finnish, meaning "crumbly stone", due to its rapid weathering (Müller 2007). One can come across boulders of this granite that appear to be a heap of loose balls of ovoids. It is considerably less resistant than fine-grained granite, which undergoes almost no weathering.

After the revolution of 1917 other granites started to be exploited in Saint Petersburg.

Kaarlahti (Kuzhechnoe) granite was quarried in Kuzhechnoe near the town of Priozersk. This granite is pink, porphyry, large-grained and highly decorative, but its pattern is different from rapakivi granite. It is characterized by the presence of large rectangular phenocrysts of microcline in a dark fine-grained matrix.

Gangut granite was used in the construction of St. Petersburg at the end of 19th to the beginning of the 20th century. This granite can be easily processed and polished. It was brought from quarries on a small island near the Hanko (Gangut) peninsular in southwest Finland. This granite has a deep red colour and a weakly banded texture, appearing like gneiss. It is made up of a fine-grained matrix of pink feldspars and grey quartz with thin flakes of biotite. According to Kurhila et al. (2005) the

1830 Ma old Hanko granite is a medium-grained, heterogeneous microcline granite with nebulitic structures.

Valaam granite was named after the quarries on Syuskyuyansaari Island near the northern coast of Ladoga Lake. In old times, these quarries belonged to Valaam Abbey and they were called the Valaam quarries, and the small island was named after St. German. The granite is coloured in different tones of pink up to red and has a migmatitic structure. A similar type of granite was quarried by the Valaam Abbey on St. Sergei Island (Putsaari) near the northwestern coast of Lake Ladoga.

Antrea granite has been used in St. Petersburg since the end of the 19th century. It was quarried near the present town of Kamennogorsk. The colour of this granite is light pink and light grey. It is fine-grained with a regular grain texture, sometimes with phenocrysts of microcline 2–3 mm in size.

Kavantasaari granite (Kavansari) was quarried on the River Vuoksa near Kamennogorsk. It is pink and fine-grained, with phenocrysts of small prisms of pink microcline up to 5 cm in size oriented in parallel, and the fine-grained matrix consists of quartz and dark-coloured minerals.

Serdobol granite was quarried in the neighbourhood of Serdobol (Sortavla) on the coast and islands in the north of Lake Ladoga. Serdobol granite is grey, fine-grained and homogeneous, sometimes having a gneiss-like structure. It consists of quartz, feldspars and biotite. The fine-grained matrix contains small phenocrysts of grey feldspar. There are thin feldspar layers and veins with sulphides.

Nystad granite was quarried near Uusikaupunki (Finland), north of Turku in the Gulf of Bothnia. It is a medium-grained, and in some parts large-grained rock composed of plagioclase, quartz and biotite. Varieties quarried for natural stone contain drop shaped quartz grains and some varieties contain also diopside (Selonen 1998, Suominen et al. 2006).

In modern architecture, natural facing stone occupies an important place as a highly decorative, durable and prestigious material. We can say that the fashion for natural stone has now been revived in St. Petersburg. Granite is widely used in the construction of office and residential buildings, monuments, metro stations and shopping malls. Granites are quarried not far from St. Petersburg, in the Karelian Isthmus, in the Vyborg and Priozersk areas of Leningrad Region. It is difficult to list all monuments and buildings faced with stone from the Karelian Isthmus during the last decade, but granite certainly remains the symbol of our cities.

2 THE REQUIREMENTS OF NATURAL STONE

In the geological understanding, the term “facing stone” means a rock that due to its appearance, mechanical and processing properties can be used for the internal and external decoration of civil, industrial, transport and religious buildings for better aesthetic perception.

The most important characteristics of the rocks suitable as facing or monumental stone are decorativeness, soundness of the deposit and jointing as well as physical-mechanical properties and price (Luodes et al. 2000, Selonen et al. 2000, Härmä 2001, Heldal & Arvanitides 2003, Bradley et al. 2004, Luodes 2008)). Based on Selonen et al. (2000) and Luodes (2008) the quality requirements of natural stone can be divided into the following aspects presented in table 1.

Table 1. Quality requirements of natural stone in Finland

1.	Geological requirements such as colour and appearance, soundness and size of the deposit, mineralogy
2.	Technical requirements such as physical and mechanical properties, production properties
3.	Infrastructure requirements such as environmental conditions, logistical properties, labour force
4.	Commercial requirements such as interesting aesthetical appearance, price and fashion, product range, market situation

According to Russian requirements rocks differ in their decorative properties. Decorativeness is an artistic-aesthetic peculiarity of stone. This term refers to the combination of the external properties of the stone, including its colour and pattern. The colour of the stone is determined by the colour of the minerals that make up the rock, while the pattern is defined by a combination of the texture and structure of the rock. According the decorative properties, there are 4 classes of stone: highly decorative, decorative, poorly decorative and non-decorative.

The blocking of rocks refers to the form of natural blocks, and to the size and output of blocks from the rock mass. It is one of the most important properties for quarrying block stone.

Durability is an important criterion for evaluating stone, and is determined by its durability in buildings. According to the classification of Zalessky and Belikov, who estimated the time taken for rocks to begin degrading, quarzites are rather durable (650 years), while granites, gabbro and diabases are durable (2210–350 years), and marbles, limestones and dolomites are medium durable (75–150 years).

To increase the durability of stone, the stone surface should be cleaned and the texture re-finished every 50–70 years. A polished texture of the surface considerably increases the durability, because pollutants and particles do not remain on such surfaces.

Nowadays the following characteristics are taken into consideration while evaluating deposits of facing stone (Table 2).

Table 2. The main characteristics of facing stone according to the Russian requirements.

1.	Name of deposit
2.	Geographical position (including the presence of railways and motor roads in the vicinity) and size of the deposit
3.	Types of rocks and geological position of the deposit
4.	Mineral composition (rock-forming and accessory minerals)
5.	Decorativeness (colour, texture and structure, types of surface treatment, classification in points)
6.	Jointing and output of blocks (number of joint systems, specific jointing in m/m^2, forecast or actual output of blocks in %)
7.	Radiation safety evaluation (specific effective activity of natural radionuclides in Bq/kg)
8.	Physical-mechanical properties
9.	Roofing rocks (composition and thickness)
10.	Degree of exploration and development
11.	Additional information (group according to the accounting balance of facing stone in the Leningrad region, owner, group according to the complexity of the geological structure, the presence and size of the experimental quarry or volume of industrial production, etc.)

Physical-mechanical properties determine the technology required for mining and processing the stone, and the range and direction of its practical use. It is necessary to take into account the following properties of the rocks: their strength and resistance to freezing and thawing, as well as abrasion, water absorption and radioactivity. Hardness, density, bulk density and porosity are of great importance in the assessment of stone quality.

According to Russian requirements the classification of rocks according to strength requires the definition of 3 groups of facing stones depending on their resistance to compression in dry and water-saturated conditions: strong, medium strength and low strength. For durability, there are 3 categories: very durable (fine-grained massive granites only beginning to degrade after 650 years), durable (syenite, gabbro, coarse-grained granite only beginning to degrade after 220–350 years), and relatively durable, degrading after 25–75 years from the beginning of use.

The above-characterized granites and similar rocks have different strengths (Table 3).

Table 3. Mineral composition (vol. %) and the limit of compressive strength (MPa/cm^3) of different granites (Bulakh, Abakumova 1987)

Granites	Quartz	Microcline (orthoclase)	Plagioclase	Biotite	Horn-blende	Other minerals	Limit of compressive strength
Rapakivi	20–25	20–70	10–15	5–10	10–15	1–2	90–150
Gangut	25–40	12–38	25–50	2–8	–	1–1,6	150–190
Valaam	25–35	24–38	35–47	2–4	–	1–1,5	140–150
Antrea	15–25	18–40	30–40	2–20	0–15	0,5–1	110–200
Kavantasaari	30–35	40–50	10–15	8–10	–	0,7	200–260
Serdobol	10–45	5–50	15–50	2–15	0–2	1–2	200–330
Nystad	30–35	2–7	47–61	7–8	–	0.1–0.3	150–160

As we see, the strongest are Serdobol, Kavantasaari and Gangut granites. Rapakivi granite is the least resistant to crushing and it is the worst at withstanding polishing.

The properties of natural stones for specified uses in construction are controlled with standardised tests (Luodes 2010). In the European level the European Committee for Standardization (CEN) arranges the standardisation work and prepares EN standards for testing methods, products and definitions. According to the EU Construction products regulation 305/2011 (The European parliament and the Council 2011) it is mandatory to use CE marking for quite a number of natural stone products within the region of European Union and European Economic area (EEA). CE marking can be given to a stone product based on tests that have been carried out according to the EN standards. It declares basic properties of the product in a systematic way used in all the Europe.

3 RESEARCH ON GRANITE DESTRUCTION IN THE NATURAL ENVIRONMENT AND THE LABORATORY

As pointed out in the previous chapters, rapakivi granite is subjected to weathering more than the other types of granite. In natural conditions, over a long (geological) time, rapakivi granite disintegrates into ovoids and a fine-grained mass. In general, rapakivi granite is a strong rock and 300 years of experience of its use in architecture has not made it look weathered. However, in comparison with the other types of granite, the weathering processes in this rock are more intensive. Hence, more attention was paid to rapakivi granites while studying the weathering processes. The weathering of rapakivi granite has been studied since the late 19th century by e.g. Sederholm (1892), Eskola (1930), Kejonen (1985) and Härmä & Selonen (2008).

The project area belongs to temperate climate zone with cold humid winters (Peel et al. 2007) representing typical Nordic climate conditions. The minimum winter temperatures can be below -30°C and the maximum summer temperatures can exceed +30°C. Typically due to the influence of the Baltic Sea the winter temperatures are mild. This means that there are several cycles of freezing and thawing during the year. The winters can be snowy requiring maintenance of the streets including ploughing of snow and usage of de-icing substances such as salt for the aid of the pedestrian and car traffic.

As the objects for our study, we chose granites with different structure-texture characteristics and investigated the weathering of the rocks in buildings of different ages, which allowed us to trace the processes of stone destruction during 300 years. In the course of our observations in nature, samples were taken of rapakivi granite in Vyborg (buildings of the 14th century), St. Petersburg (Peter and Paul Fortress, embankments of the historical centre, middle 18th century) and some buildings of the Soviet period. Also, objects for study have included the granite embankments of St. Petersburg, roads, buildings and bridges, among others.

3.1 Methodology of sampling

Stone samples taken in St. Petersburg consisted of chips that had detached from buildings. The surface crust resulting from destructed on the stone samples was sawn away to compare it with the inner unchanged part. Altogether, more than 1000 samples were taken. The sites of sampling were photographed and the types of destruction were determined. In total, more than 2000 photos were taken. In international practice, core drilling is applied to study buildings of different historical periods. The drill core is 2 cm in diameter and 10 cm long. After sampling, the holes are healed (Fig. 1). In all samples, the weathered crust was sawn away from the unchanged granite.

Due to weathering, granite decomposes into separate grains, ultimately transforming into dust, which was also taken as an object of our investigation. In general, the mineral composition of this dust corresponds to that of granite. Moreover, as a result of chemical weathering, clay minerals are formed, which take part in aerosol transport. The dust particles are also a constant factor in the mechanical influence on rocks, causing abrasion of the stone surface.

To study the products of granite weathering, we sampled the dust in the so-called “stone” centre of St. Petersburg, where the buildings are faced with granite, and on the outskirts of the city. The samples of dust were taken in different parts of the city in the autumn of 2012 in dry weather. Weighted samples were collected from asphalt by a small shovel and a brush with a fan-like shape and placed into paper bags.

Investigation of the biological damage to stone should be carried out together with mineralogical and geochemical analysis and sampling to conduct a systematic study of the object. To obtain the most objective picture of the biological destruction of granite in the urban environment, it is necessary to comprehensively consider the conditions of exposure of the object (illumination or shadowing, humidity and temperature conditions, proximity to other objects that are able to influence the properties of the material, place in the cultural landscape and others). Information on the ecological situation within the studied territory and climate conditions in the region could be also vital. Macro- and microclimatic conditions are crucial for the development of bio-fouling, the formation of lithobiontic clusters on the surface of the granite. Their composition and structure can serve as a reflection of environmental conditions that develop in a particular habitat.

The properties and condition of the rock have undoubted importance when selecting objects for observation. This has been shown, for example, in comparative research on bio-fouling of rapakivi granite and granite from Kuznechnoe in St. Petersburg and Vyborg (Panova et al. 2013, Popova et al. 2014). In this case, it is necessary to take into account the history of a particular object. For a monument or building of granite, this may include the year of construction, the year of restoration, and the place of quarrying of the stone used for the building.

Fig. 1a. Core drilling

Fig. 1b. A Sample hole in the basement

Based on the goal to determine the widest range of damage to granite in the urban environment, we have chosen as objects for biological research the granite embankments of the rivers and canals of St. Petersburg, the granite facades of buildings in the historical part of the city and monuments constructed from granite. For comparative purposes, we have examined similar objects in Vyborg, and granite outcrops near the granite quarries on the Karelian Isthmus and in Finland.

The main attention in detecting the damage to granite was focused on changes in the colour and texture of the surface layer of the stone, different forms of fouling and new formations. In describing the nature of the damage, we noted films and stains of various colours, cracks, chips and pits, and evaluated the degree of destruction of the surface layer of the stone. In characterizing the bio-fouling of the granite, we noted the colour of bio-films, their number, thickness, density, connection with certain minerals, cracks or weathered fragments of the stone (selective bio-fouling). We evaluated bio-fouling in relation to the surface relief. At first visually (then in laboratory), we defined the types of bio-film according the dominant species: bio-films dominated by algae, cyanobacteria, phytopathogenic fungi and other organisms. In characterizing the macro-fouling of granite, we recorded the presence of lichens, mosses and seed plants, paying attention to their association with specific components of rocks and structural spaces on the granite. We estimated the total spatial distribution of bio-damage to the object. A compulsory element of the study was a highly detailed description of the visible signs of damage, as well as photography (documentation).

Before sampling, we marked out the sites with visual features of bio-damage and took photos. Samples were taken from the most typical parts of the damaged substrate.

The samples can be divided into 2 groups: samples of collapsing materials and samples taken by non-destructuve methods from the surface of the object under study. In cases where there were significant violations of the integrity of the damaged surface with fragmentation, flaking and shedding of the stone material, the samples were taken into special sterile containers. In addition, scrapings were taken from damaged (colonized) parts of the stone surface in a sterile container or directly onto a nutrient medium in Petri dishes and test tubes. The procedure for sampling stone material for microbiological testing is described in the "Regional temporary construction standards for the protection of building constructions, buildings and structures against aggressive chemical and biological environmental influences", SRF 20-01-2006 (TSN 20-303-2006), approved by the Government of St. Petersburg.

Sampling of the macro-fouling species (lichens, mosses and vascular plants) was carried out according the rules of herbarium collection. Herbarium collections are stored in a herbarium.

Soil samples on the border of the studied objects were taken in order to determine the possible pathways of distribution and accumulation of destructive microorganisms. Samples of primary soil were collected from under the turf moss that had developed on sites of granite destruction. They were used for geochemical studies.

3.2 Analytical methods

3.2.1 Chemical determination

In the course of laboratory analysis of the samples, various modern analytical methods can be applied to studying the mineral and chemical composition of unchanged and weathered rocks. The following research methods were applied in this study:

- sawing off the crust from the fresh part of granite;
- photo-documentation of the prepared samples;
- petrographic study of thin sections;
- scanning electron microscopy and microanalysis;
- confocal microscopy;
- granulometric analysis of the dust;
- X-ray phase analysis;
- infrared spectroscopy;
- determination of C_{org} and S;
- X-ray spectral silicate analysis;
- X-ray spectral analysis;
- ISPMS analysis;
- Hg determination;
- calculation of weathering indices
- statistical analysis of the obtained data.

To study the processes of weathering, we sawed off the crust from the fresh undamaged part of the granite. The crust was generally about 0.5–1.0 cm in thickness.

- *Photo-documentation* of the samples was performed in the laboratory for all taken samples. We took photos of the weathered crust and the sample as a whole. Was also used a high-resolution camera to obtain contrast image details. At the same time, the samples were macroscopically described under a stereomicroscope.
- Petrographic studies and photos of thin sections.
- The main goal of petrographic studies is to investigate the mineral composition of the rock and its micro-texture features.

The studies were carried out with the help of a light microscope with a wide range of magnification from 3^x to 600^x depending on the brand of the microscope. Thin sections of the rocks were used for this investigation. A thin section of rock is a 0.03-mm-thick slice of the rock or mineral that is glued to a glass slide. A standard thin section is 2 × 4 cm in size. Thin sections were made perpendicular to the weathered surface in order to trace changes deep into the granite. The study was conducted in parallel and crossed Nicol prisms (polarisers) that allowed us to identify the minerals using a table of their optical properties. A polarizing microscope has a special device that allows pictures to be taken using polarized light that has passed through the minerals.

To study the fine details of the rock texture and calculate the coefficient of the fractal size, video equipment was used together with software to analyse the video information.

The micro-texture and micro-structure were studied by means of a scanning electron microscope, which is designed to obtain images of the surface of the object with a high (up to 0.25 nm) spatial resolution, as well as information on the composition, structure and other properties of the surface layers. The method is based on the principle of interaction of an electron beam with the object. This method allows the use of a range of magnifications from 10^x to 1 000 000^x, which is hundreds of times higher than the limit of magnification of an optical microscope. The surface is probed by scanning it with a focused beam of electrons. The image is formed using the detection of various signals, including secondary electrons, back-scattered electrons, X-rays and the current through the sample. The main application of scanning electron microscopy is to obtain a visual image of the surface topography (secondary electron image) and of the distribution of chemical elements over the surface (back-scattered electron image, Auger electron and X-ray).

Confocal microscopy is necessary to determine the distribution of organic matter on weathered and fresh granite surfaces. Scanning confocal microscopy means "focal" (in the plane), optically conjugated with the focal plane, where the confocal aperture is placed. This allows recording of the signal from only a thin layer of the sample. Having saved a series of optical slices in the computer memory, it is possible to perform a three-dimensional reconstruction of the object to obtain a three-dimensional image without using time-consuming methods for making and photographing serial thin sections.

The most common application of confocal microscopy due to its high resolution and contrast is the study of the structure and distribution of organic matter. Also, co-localization of two or more organic substances can be studied. This method allows the determination of how organic matter is distributed in granites on the surface and with depth in the sample. The study was performed using a Leica TCS SPE laser confocal microscope.

Granulometric analysis (fraction analysis) is a method to define the concentration of particles with different sizes (fraction size) in loose rocks. Fraction analysis by sieve was used to determine the size of the dust grains. The preparation of samples for the analysis consisted of sifting the sampled dust into fractions through sieves with a mesh size from 0.05 mm to 1 mm and the following weight on a laboratory balance with an accuracy of up to 0.01 g.

X-ray phase analysis is applied to identify of the mineral composition of fine fractions of dust. For this analysis, oriented samples of the clay fraction are placed on a glass plate. The clay fractions were obtained by elutriation in water. The samples were analysed in the range from 3 to 75 degrees on a 2Θ scale in a Rigaku X-ray diffractometer with co-cathode monochromatic radiation, wavelength $X = 1.79021\ A$, voltage $U = 35\ Kv$ and electric current $I = 25\ mA$. The obtained spectra were processed using the software package PDXL-2, and the phases were identified according to the JCPDS card file. To define the characteristics of clay minerals, the oriented samples were saturated with ethylene glycol and again studied on a diffractometer.

Infrared spectroscopy was applied to identify the mineral composition of fine dust fractions. IR spectroscopy determines molecular spectra, and in this spectrum region are the main rotational and vibration molecular spectra. The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. When the frequency of the IR is the same as the vibration frequency of molecules or crystalline lattice, absorption occurs. As a result, the intensity of IR radiation decreases at these frequencies and absorption bands are formed.

Each mineral has its own specific vibration spectrum. The number of absorption bands in the IR spectrum, their position, width and form, together with the value of absorption are determined by the structure and chemical composition of a mineral. This enables information to be obtained on the structure of the substance and qualitative and quantitative analysis of substances and mixtures to be carried out. The mineral composition of the samples under study was defined by comparing the obtained IR spectra with the reference.

IR spectra of aleurite and clay components were analysed in the region from 400 to 4000cm^{-1} on a BRUKER VERTEX 70 instrument with a resolution of 1 cm^{-1}. For analysis, pellets with potassium bromide were used.

Contents of total carbon and total sulphur were determined by means of *infrared spectrometry.* The sample decomposition method is based on the burning of the sample in a resistance furnace in the presence of a catalyst (flux) in an oxygen atmosphere. As the result of burning, all carbon contained in the sample transforms into CO_2 and SO_2. Emitted gases are drawn out by a pump from the oven, drained with anhydrone (magnesium perchlorate) and transferred into a cell, within which their absorption in the infrared region of the spectrum (on the lines corresponding to the energy of the oscillatory motion of the relations of C-O and S-O) is measured. The absorbance value measured in cells is directly proportional to the carbon content and sulphur, respectively. The analysis is performed on an SC-144DR device (LECO Corporation).

Coulometry was applied to determine the carbonate carbon (C_{carb}). The method of automatic titration by the difference in the hydrogen index (pH) was used. The powdered sample (0.01–2 g) is placed in a ceramic vessel, burnt in the tube furnace of the analyser in a gas (argon) current at 1250–1350 **°C. CO_2** gas formed by the burning of the substance is removed by the current into an electrolytic cell and dissolves in the absorbing solution. Acidification of the solution causes changes in the EMF of the electrode system of the analyser. The amount of electricity necessary to neutralize the solution is determined by a scale and the display device in units of element concentration (%). The analysis is carried out on an AN-7529 carbon analyser.

Organic carbon (C_{org}) was determined by the difference between the total carbon content (C_{total}) and carbonate ($C_{carb.}$).

The chemical composition of granite and weathered crust (macro- and micro-element analysis) was performed in analytical laboratory of VSEGEI (St. Petersburg, Russia) and in the laboratories of Labtium Oy at the Geological Survey of Finland.

X-ray spectral silicate analysis was applied to study the macro-composition of granite and weathered crust. Rock-forming elements are determined by the full chemical analysis of the rock, and their concentration is presented as the mass% of oxides. Volatile components are not analysed separately, but in the course of annealing the sample up to 1000 °C, and are marked as “loss at annealing”. Admixture elements are present in the sample in amounts of <0.1%. Their concentrations are calculated in grams per tonne (g/t or ppm).

In the first stages of geochemical investigations to characterize the object as a whole, the samples are analysed by X-ray spectral analysis of 40–50 chemical elements. Furthermore, while solving certain problems, the distribution of groups of elements is examined, such as the group of rare earth elements (REE), which includes La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. Concentrations of elements are determined by ICP MS. The analysis was carried out on an ELAN-6100 DRC device using the software TOTALQUANT.

Analysis of the *mercury content* in the samples was conducted using an RA-915+ mercury analyser and special software. The instrument was calibrated using a set of SDPS-3 with the certified concentration value 300 mg/kg. Each sample was analysed at least twice.

To study samples of granite with signs of *biological damage*, we have applied a complex of analytical methods allowing assessment of the nature of damage to the stone surface, the degree of biological colonization of the rock and the relationship between bio-destructors and the stone. In this case, the methods of mineralogy, petrography, geochemistry, microbiology, mycology, phycology, lichenology and materials science can be used.

In the primary study of the samples of damaged granite, attention was focused on the structure of the granite, micro-cracks, holes and other surface irregularities, which can serve as a shelter for microorganisms and indicate the state of the surface layer of the stone. The magnification of an ordinary binocular loupe allows the determination of the occurrence of biological objects (fungi, algae and lichen) and assessment of the localization of lithobiontic organisms and the degree of disintegration of the surface layer of the stone. The primary observation of damaged granite provides an opportunity to select the most appropriate method for isolating the microorganisms from the analysed sample. For example, when microscopic fungi (micromycetes) are concentrated in the micro-cracks and their isolation from the surface of the stone is difficult, the preliminary activation of micromycetes has been used by placing the sample or its fragment in a moist chamber under sterile conditions for 1 to 2 weeks. After the formation of distinct hyphal structures (the fungus spreads out of micro-cracks on the surface of the rock) they were removed (under a binocular loupe) with a sterile injection needle and transferred to the nutrient medium. In the same way, the selective isolation of microcolonial fungi was carried out, whereby small and compact colonies were transferred whole or in fragments onto the nutrient medium. It is reasonable to select the areas for future investigation by scanning electron microscopy (SEM) during the first visual observations.

3.2.2 Biological determination

Methods of extraction of microorganisms from the samples of damaged granite

Traditional mycological and microbiological methods have been applied for the detection and identification of microorganisms in biofilms on the surface of the granite. In the course of bacteriological studies, the microorganisms were extracted onto an agarosed (solid) nutrient medium: HME-hydrolysed meat enzyme was used to detect a wide range of heterotrophic bacteria and determine the total microbial numbers, as well as the Alexandrov nutrient medium with sand (to extract silicate bacteria), and potato-ammonium agar (for the isolation of actinomycetes). Besides these, it is advisable to use a liquid nutrient medium for the extraction the chemolithotrophic bacteria. The bacteria were quantified using a dilution method (Tepper et al. 2005).

The following nutrient media were used for primary isolation, sustenance in culture and the identification of micromycetes: the classic Chapek-Doks medium and modifications of it (by adjusting the content of glucose and some salts), agarosed oat broth with the addition of glucose, Saburo agar, potato-glucose agar, DRBC medium (King et al. 1979), water agar, 2% Malz-Agar, and wort agar.

The following methods were used for the extraction of fungi into culture from samples of damaged granite:

1. Sowing of crumbs and small fragments of the substrate on the surface of the medium;
2. The method of flushing from the surface of the substrate, with subsequent dissolution of the suspension and sowing on a nutrient medium;
3. The method of selective isolation of fungi from the surface of the substrate on a nutrient medium with an injection needle.

The combination of different methods of isolation of micromycetes and the different nutrient media listed above enables a full and comprehensive analysis of micromycete species diversity on the stone substrate (Vlasov et al. 2001). Species are also detected that differ in growth rate, their relation to the sources of nutrition and development strategy (Fig. 2).

Identification of bio-destructors of granite

Identification of the microorganisms damaging the granite takes place after their extraction into pure culture. The duration of cultivation of various microorganisms prior to their identification varied significantly. It depended on the rate of devel-

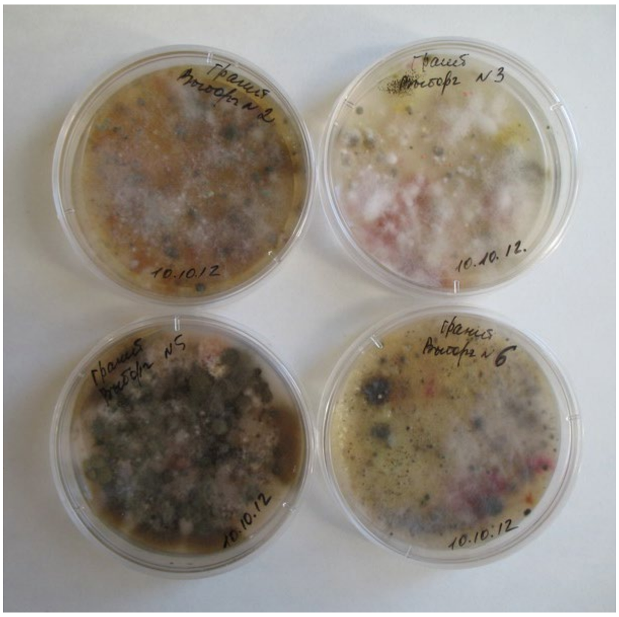


Fig. 2. Extraction of micromycetes from the surface of granite into pure culture.

opment of the microorganisms in culture and time taken for the formation of the taxonomic characteristics used to define the species. For example, in the course of identification of micromycetes, the obtained cultures were incubated in a thermostat for 2–3 weeks at 25 °C until sporulation followed by the study of colonies using light microscopy. The species of most of the obtained isolates were determined in the presence of pronounced sporulation using Russian and foreign identification guides (Guba 1961, Litvinov 1967, Barnett 1967, Barron 1968, Raper et al. 1968, Pidoplichko & Milko 1971, Ellis (1971, 1976), Pidoplichko (1972, 1977, 1978), Boerema & Dorenbosch 1973, Levkina, 1974, von Arx 1974, Bilai 1977, Kirilenko (1977, 1978), Raper & Fennell 1977, de Hoog & Hermanides-Nijhof 1977, Egorova 1986, Smitzkaya et al. 1986, Lugauskas et al. 1987, Bilai & Koval 1988, Bilai & Kurbatskaya 1990, Melnik & Popushnoi 1992, de Hoog & Guarro 1995, de Hoog et al. 2000, Satton et al. 2001).

Mycological and bacteriological analysis of the samples of granite was carried out in the laboratories of St. Petersburg State University. Lichens were identified according to standard techniques at the Department of Botany SPbSU under the leadership of D.E. Gimelbrant, and mosses were identified at the Botanical Institute of the Russian Academy of Science under the leadership of L.E. Kurbatova.

Methods of investigation of lithobiotic systems

To determine the full characteristics of a lithobiontic system it is necessary to use complementary methods to evaluate not only the development of living organisms on granite, but also to determine the changes occurring in the surface layer of the stone.

Petrographic analysis was applied to describe the microstructure of the rock, the characteristics of the distribution of minerals and the degree of weathering of the rock. Zones with lithobiontic organisms and the sites of their accumulation are often well seen in thin sections. Furthermore, this method allows an evaluation of the penetration depth of destructors into the rock along microcracks and structural spaces in the surface layer of the stone.

Scanning electron microscopy was used in order to study characteristics of the distribution of microorganisms in the surface layer of the stone, and identify the main areas of colony localization and pathways of destructors into the substrate. This method also gives the opportunity to characterize the relationship between lithobiontic organisms during colonization of the granite, to analyze the dynamics of the colonization of stone depending on its properties and external conditions and to determine the ability of microorganisms to cause the destruction of the rock. The high magnification and good resolution achieved using a scanning electron microscope makes possible to study biological objects directly on the surface of crumbling granite. Samples of the damaged stone (0.5–1.0 cm x 0.5–1.0 cm) were initially examined under a binocular loupe. The criterion of selection of samples for SEM analysis was the presence of structures of microorganisms on the surface of the stone, as well as information on the possible localization of micromycetes in microzones (inhomogeneous areas, cracks, cavities) of the rock. In some cases (long-term storage of material), the samples were kept in a humid chamber to enhance the development of micromycetes, after which the material was fixed by the following method:

- Fixation of samples using 4% glutaraldehyde in 0.1m buffer solution for 2 hours;
- Rinsing after fixation in 0.1 m buffer solution for 1.5 hours;
- Drying to the critical point;

- Mounting of samples on tables for examination in the scanning electron microscope using a special glue;
- Coating of the surface of samples with gold.

The material was examined under a scanning electron microscope in the range of magnification from 100x to 10 000x. SEM studies were performed using an ABT-55 electron microscope (Japan).

3.3 Evaluation of the condition of a building by qualimetric method

Evaluation of the state of historical monuments in the course of natural observations was carried out by measuring and evaluating a complex of features. Qualimetry is defined as a scientific approach and art of estimation involving the measurement and rating of the condition of any object that has grades of quality. Qualimetry has been introduced due to the urgent demand for quantitative estimation of the initial quality and present condition of any object, product or artefact (object of art), because only a numerical value can be used in monetary calculations of the economic effectiveness of different activities. The application of certain (standard) ways to calculate this number results in the most objective assessment in comparison with any oral characteristic. It provides the possibility to compare the condition of any objects (e.g. buildings, sculpture, pictures, household utensils, antique arms and jewelry) estimated by different experts at different times under different conditions of expertise.

Within the five-point rating system of estimations, an estimation from 1 to 1.8 points refers to the near collapse or catastrophic state of the object, from 1.8 to 2.8 indicates an unsatisfactory state, from 2.8 to 4.0 a satisfactory state and from 4.0 to 5.0 evidence that repair work or restoration of the object is unnecessary (Expertise 2005). This system allows a comparison of the condition and quality of an object before and after restoration.

The roots and development of qualimetry, its terminology, theory and modern state have recently been discussed in four scientific publications (Qualimetric expertise 2008, Qualimetric monitoring 2010, Marugin 2009, Bulakh & Marugin 2013, Marugin & Azgaldov 2008, Marugin & Azgaldova 2010). There are three main principals in modern qualimetry. The first is that estimation is carried out in steps, the second principal that each part has its own weighted value, and according to the third principal, estimation must be carried out by several independent experts.

The procedure for experts and leaders of the evaluation is more closely presented in the Appendix 1 of this document.

3.4 Experiments of modelling the biological weathering in this study

The problem concerning the forms and alteration of the forms in which the elements occur in the rocks is vital when studying the processes of rock weathering. It is known that many chemical elements are included in minerals as isomorphic inclusions, replacing major anions in the crystal lattice. Some of them are accumulated in gas-liquid inclusions and others are in a colloid-dispersed form in the pore spaces of the rock. Weathering causes the disintegration of rocks, and chemical elements can be leached from the pore space, resulting in the establishment of new physical-chemical conditions favourable for the further destruction of the rock.

Pore solutions from rocks have been the subject of serious investigation in geochemistry. Porous waters differ in their features from other types (of water?) by their higher concentrations of and enrichment in microelements and their lower mineralization (Kruykov 1971, Krainov et al. 2004). P.A. Udodov and colleagues have demonstrated that pore waters contain enormous numbers of microbes, up to 10^8 in 1 ml of solution, and these take an active part in bio-inert interactions (Udododv 1983).

Leaching as a method for the selective extraction of some elements is often applied to study the mobile forms of chemical elements in geochemical and environmental investigations. For instance, leaching with sodium pyrophosphate is used for samples enriched in organic components, hydroxylamine dissolves most manganese and iron oxides, oxalic acid dissolves all of the oxides and partly weak silicates, a mixture of potassium iodide and ascorbic acid dissolves oxides of iron, manganese and aluminium, and extraction with hydrochloric acid is used for acid-soluble components. Water extraction is used to determine water-soluble salts.

The study of *mobile forms of chemical elements* in unaltered granite and the crust by the experimental study of aqueous extracts has been carried out to investigate the chemical destruction of granite.

To study the water-soluble component of the pore solution, a method of extraction and analysis of the nano-fraction of the rock has been developed. The nano-fraction is contained in the porous and inter-grain space of the rock, where chemical elements are in ionic, molecular and colloidal forms (Oleynikova & Panova 2011). The extracted solution is not considered as an aqueous extract that characterizes the "true soluble" forms of elements, but rather as an independent fraction in terms of the weight, particle size (up to 1000 nm) and properties (of the particles it contains?). It has been called the nano-fraction (NF) to distinguish it from other fine fractions according the size of its particles. In colloid chemistry, 1 μm is a conventional boundary of the colloidal state above which (>1 μm) the substance is considered as a separate solid phase (Fridrikhsberg 1984).

Crystalline rocks have small porous spaces, and as a result, a small share of NF. Weathered crust has a more porous texture and the volume of pores can reach 5 vol%.

The NF extraction procedure included crushing and powdering of the rocks to a particle size of <74 μm. The experiment with the rocks requires their preliminary grinding to open the pores and microcracks and ensure the access of the extractant (water) to free and adsorbed salts and colloidal particles. Powdering of the sample is the usual practice while analysing rocks, because it provides the desired homogenization of the sample and the contact between the solid particles with the solvent during the experiment. The increase in the degree of abrasion at <74 μm leads to deterioration of the wettability of powders, which is not favourable for the experiment.

After powdering to <74 microns, the sample was mixed with deionised water and periodically stirred for 5 hours, and then left for a day to stabilize the resulting colloid-saline solution of NF. The solution was drawn into a syringe and passed through a "Sartorius" membrane filter, guaranteeing the selection of particles less than 1 micron in size. Part of the solution was analysed by ICP MS and the other part was placed in a pre-weighed Petri dish for evaporation of the solution to determine the proportion of the nano-fraction in the sample as a whole.

Another part of the sample was analysed by the standard procedure of "full" decomposition using concentrated nitric, hydrofluoric and perchloric acids. Full analysis of the sample and aqueous extract was performed by ICP MS. The solution was analysed using an ELAN-6100 DRC device (Perkin Elmer).

One of the most effective tools for studying *biological processes* on solid natural substrates is their modelling in experimental conditions. In order to create an experimental model of granite destruction by microorganisms, it is necessary to understand well the main stages and factors in the colonization of the rock. We attempted to create a structural model of this process, which would take into account the most significant factors determining the sequential biological colonization of the substrate. Micromycetes were taken as the main test objects. The most important parts of the model are: availability (accumulation) of the inoculum potential, the transfer of propagating structures onto the rocky substrate, the initial stage of colonization of the stone surface (adhesion, germination and others) and, finally, the colonization of the substrate (surface growth, penetration into the material, the structural exploration of space, i.e. microcracks in the surface layer of the stone), which leads to alteration of the substrate properties.

The dynamics of granite exploration were determined by two groups of factors (Fig. 3). On the left side of the main axis are the ecological and physiological features of a settler that ensure its ability to grow on the rock. On the right side from the main axis in the model there is a complex of abiotic factors that play a crucial role at every stage of colonization of the substrate. The scheme, in our opinion, rather fairly reflects the relationships and processes that define the various types of biological colonization of granite in the urban environment. It is based on accumulated data from our studies and the literature. It is unlikely that we would be able to reproduce this model experimentally under laboratory conditions. However, laboratory experiments allow us to analyse the individual components of the model.

For artificial seeding (inoculation) of granite fragments, we used cultures of certain types as

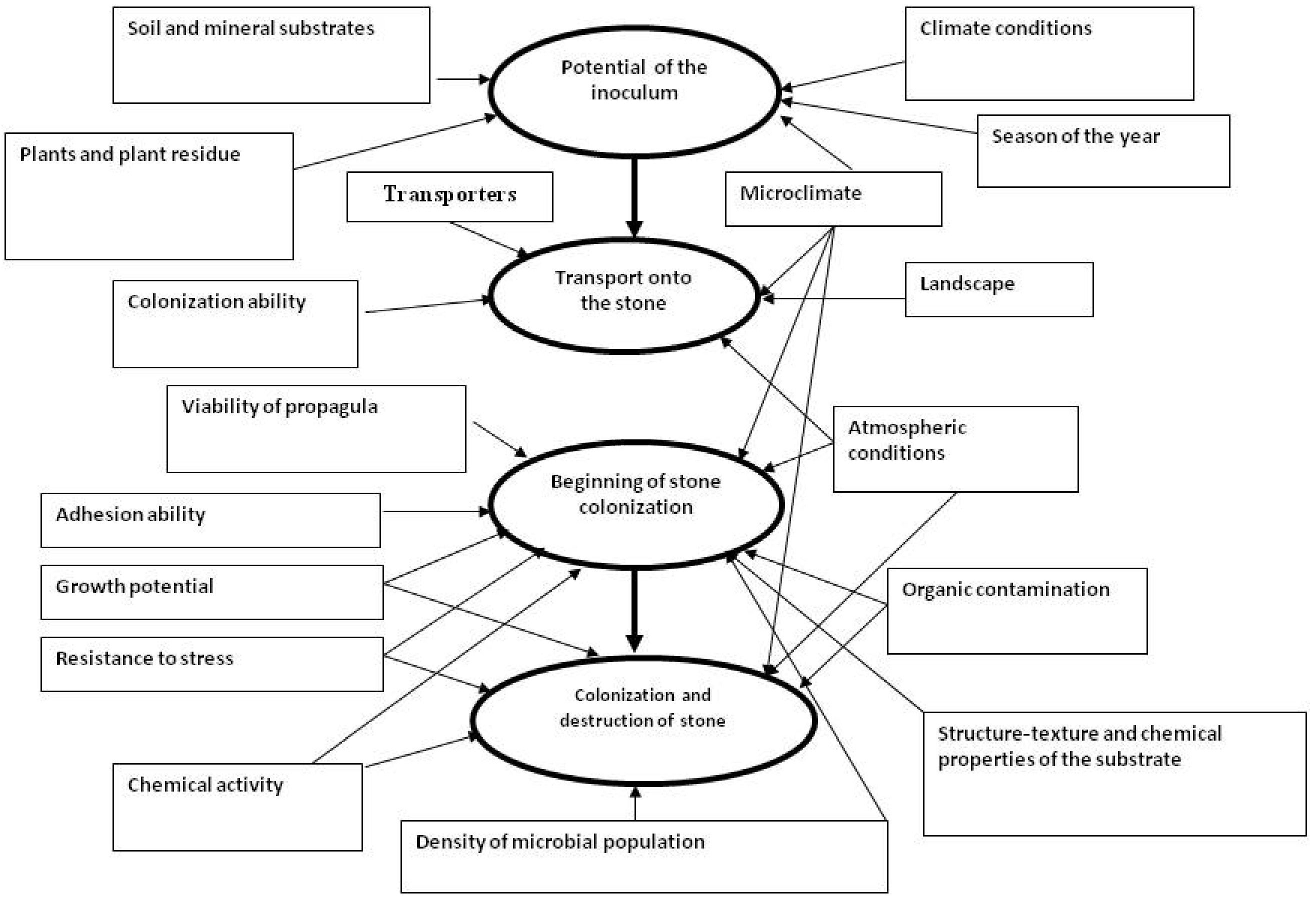


Fig. 3. Scheme of the sequential biological colonization of the substrate by micromycetes.

well as combinations of microorganisms (micromycetes and bacteria) that had previously been observed in the natural environment. The choice of test cultures was based on the available data on the occurrence of microorganisms on the surface of stone undergoing destruction. Sterile granite blocks (1.5–2.0 × 1.5–2.0 cm) were inoculated with a spore suspension, cells or cell clusters. The concentration of the suspension for each species was calculated separately. One drop of suspension (0.02 ml) was applied onto the surface of the sample. The minimum amount of Chapek-Doks liquid medium with 0.5% glucose was placed on the surface of the stone at the time of inoculation. Further nutrient solution was not added, and inoculated samples were humified at an interval of 1–2 weeks. The duration of observation of the growth and development of the microorganisms differed between experiments depending on the speed of colonization of the substrate. For example, the observation period for the colonization of granite by bacteria of the genus *Bacillus* was 45 days (Fig. 4). SEM investigation of the surface of colonized fragments of granite was carried out at the end of the experiments.

On the basis of experience in using a variety of research methods to assess biological damage to granite and taking into account the necessity for a comprehensive approach to the assessment of granite bio-destruction in the urban environment, we have proposed a sequence for analysing the bio-fouling of granite that consists of several stages (Fig. 5). The presented scheme combines methodological approaches with field observations, the sampling of field material, its laboratory analysis, as well as the formulation of the model experiments. Analysis of interrelated biological and physical-chemical processes of granite destruction will allow an objective picture to be obtained of the processes of transformation of this rock under the influence of environmental factors.

a b

Fig. 4. Experiment on the artificial inoculation of granite with bacteria of the genus *Bacillus*: a) experiment in a liquid medium; b) experiment on a solid medium.

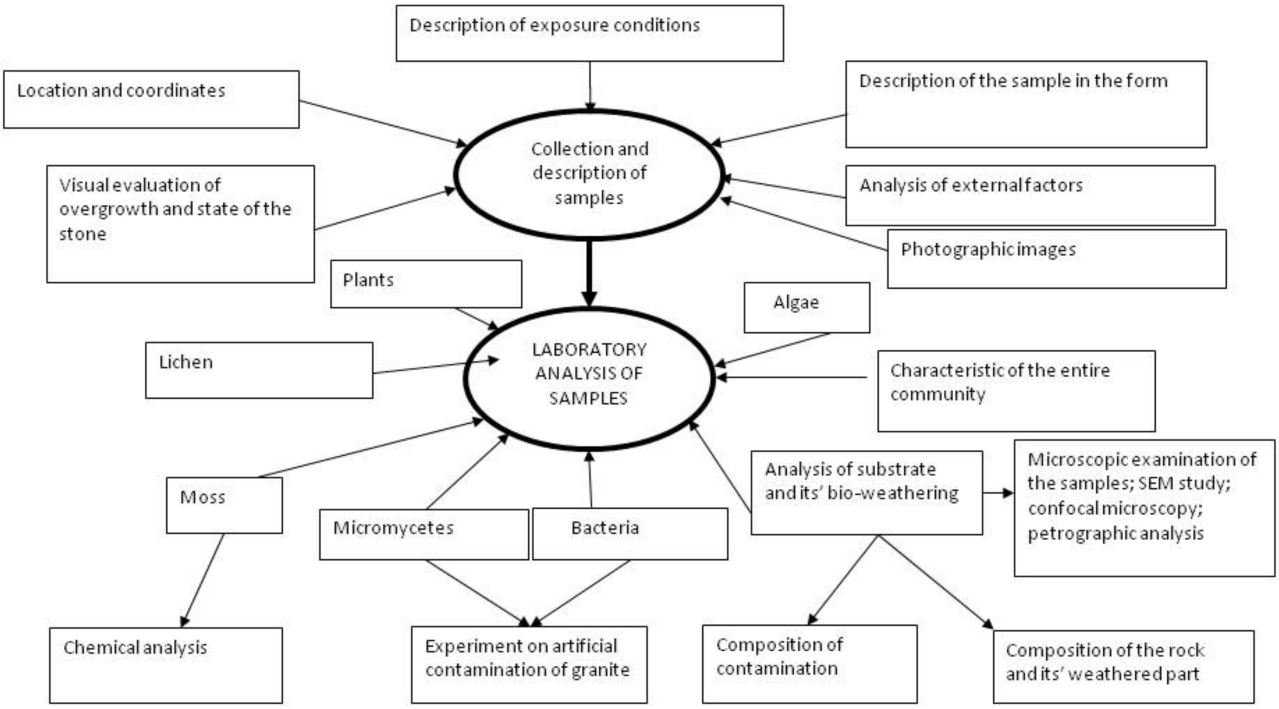


Fig. 5. Main stages of analysis in the bio-fouling of granite.

4 WEATHERING OF GRANITE UNDER URBAN CONDITIONS

Weathering is a process of mineral and rock destruction under the influence of physical, chemical and biotic factors (Panova et al 2014). Weathering is subdivided into physical (or mechanical), chemical and biogenic forms.

Physical weathering is the destruction of rocks without considerable changes in the composition of the fragments. Physical weathering mainly takes place under the influence of temperature fluctuation, the freezing and thawing of water, the crystallization of salts contained in the capillary water, wind, the impact of biotic communities and the root system of plants.

Temperature weathering is the destruction of minerals and rocks due to temperature fluctuation (Fig. 6). On heating and cooling, the volume of solids changes, which is typical for rocks and minerals. As a result of daily and seasonal temperature fluctuations, two types of stress appear in the rock.

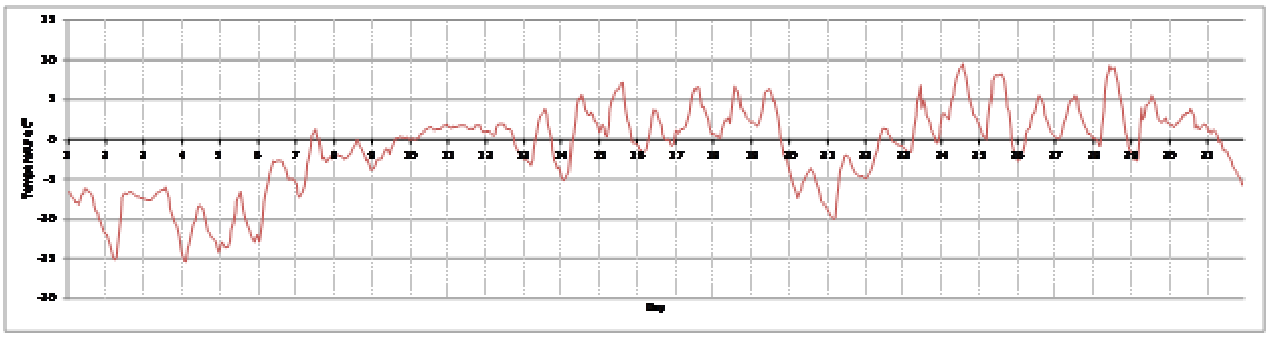


Fig 6. Temperature variation at the Kaisaniemi measuring station in the centre of Helsinki during March 2003. COPYRIGHT: ILMATIETEEN LAITOS. Data © The Finnish Meteorological Institute.

In stress of the first type, a gradient in the volume associates with uneven heating of the surface of the stone and its deeper parts. Cracks directed parallel to the surface appear due to differences in temperature and consequent expansion, resulting in the peeling and exfoliation of rocks, known as desquamation. This phenomenon has historically been used by miners to split large boulders (Heldal & Storemyr 2015). They used to create a fire around the stone, which then started to fall apart in a stratified manner like an onion, with layers parallel to the surface.

The second type of stress within the rock and mineral is connected with differences between minerals in the coefficient of thermal expansion and contraction. When heated by 1 °C, minerals increase in volume and length by different amounts, and these coefficients differ dramatically between different minerals. For example, each quartz grain in granite increases in volume by 15% when the rock is heated to 50 °C. Since the temperature during the day varies, the differences in the coefficients of volumetric and linear expansion lead to the weakening of links between grains. This type stress begins with the splitting of mineral grains, initially along cleavage cracks, leading to the formation of particles with a size up to hundredths of a millimetre. Dark-coloured minerals and rocks are destroyed more quickly, and also coarse polymineral rocks with large differences in coefficients of expansion between the constituent minerals. Daily temperature fluctuations are manifested to a depth of 1 m. The most active temperature weathering occurs on exposed areas of the rocks due to the lack of vegetation and topsoil. Ice pressure leads to expansion cracks and the splitting of rocks into separate fragments.

<u>Frost and salt weathering</u> is the destruction of rocks due to the periodic freezing of water in cracks. On freezing, water turns into ice and increases its volume by 9%. This causes the destruction of the rock along the cracks. The pressure of ice leads to the expansion of the cracks and splitting of the rock into fragments. In coastal areas, salt crystals may also form in the open spaces of the rock surface. Salt can be transported by the wind from the sea as an aerosol, or it can originate from road maintenance in the winter as de-icing salt. Both the freezing and thawing of water and salt crystallization produce more empty spaces and pores on the rock surface, leading to roughness of the surface and providing an opportunity for the biological growth to settle.Salt frost weathering has been studied e.g. in Jerwood et al. (1990) and Goudie (1999).The process has been discussed in detail e.g. by Steiger et al. Chapter 4, Weathering and Deterioration, in Siegesmund and Snethlage (eds) (2014).

The mechanical action of the wind, corrasion, is an important factor in physical weathering. This is especially the case in large metropolitan areas because of the large amounts of dust, which has an abrasive effect on the rock. Contaminated air has one of the most powerful, permanent impacts on stone in the architecture of large cities. The solid particles in air have recently received increased attention in connection with understanding of their significant contribution to the destruction of monuments (Manta et al. 2002, Zereini et al. 2005, Jönsson 2011, Fernandez-Camacho et al. 2012, Bityukova & Kasimov 2012, Soubbotina 2004, Rampazzi et al. 2010, Sverlova 2009).

Dust consists of fine solid particles, which can have both a natural and an anthropogenic origin. The mechanical and chemical properties of dust depend on its composition. The products of weathering of facing stone and buildings and soil are sources of particles of natural origin. Technogenic particles enter the atmosphere as emissions from industry and traffic.

Chemical weathering is a process of chemical alteration of minerals and rocks under the influence of water, oxygen, carbon dioxide, organic acids and biochemical processes. The main general factors affecting the intensity of the chemical weathering are the surface area and particle size, rock type, location, climate and time.

The main agents of chemical weathering are water, carbonic, sulphuric, nitric and organic acids, oxygen, hydrogen sulphide, methane and ammonia, aomng others. There is also a considerable amount of data on heavy metals accumulated in dust (Rampazzi et al. 2010, Sverlova 2009, Anisimova 2008, Ufimtzeva & Terekhova 2005). In air monitoring, the following air pollutants are detected: PM, CO, NO_2, SO_2, HF, Cl_2, HCl, P_2O_5, H_2S, CS_2, aerosols of H_2SO_3, H_2SO_4 and HPO_3, CH_2O, HCN, heavy metals (Fe, Cd, Co, Cb, Mn, Ni, Cr, Zn, Pb, Te, Hg), inorganic compounds of As, nitrogen and aromatic amines (Roshydromet 2013, Winkler 1997).

Besides the above, the atmosphere contains sulphur, nitrogen and complex organic compounds, which include chlorides, nitrogen, technogenic radionuclides, viruses and germs. Moreover, dioxin one of the most dangerous carcinogens, can be detected in the atmosphere, as well as chemicals such as benzaperen, phenols, formaldehyde and carbon disulphide. Ash and soot contain such toxic elements as lead, tin, chromium, cobalt, nickel, strontium, beryllium, niobium, tungsten, molybdenum, zinc, manganese and copper.

Chemical elements can interact in the air with other pollutants as a result of photochemical processes (Batraki 1998, Fernandez-Camacho et al. 2012, Hinds 1998, Puttonen 2011, Sverlova 2009, Levine & Schwarz 1982).

Under the influence of carbon dioxide and sulphur dioxide on granite and cement, gypsum and calcite crusts discolouring the surface of the stone appear. Historical masterpieces lose their original appearance (Bortz et al. 1993, Nord et al. 1994, Elsen 2004, Bruno 2004, Franzini 2000, Sabioni 2001).

The main chemical processes of weathering include dissolution, leaching, oxidation, hydration, carbonization and hydrolysis. In the course of weathering, the removal of chemical elements, oxides and hydroxides occurs in the form of true and colloidal solutions and of suspensions of clay particles.

Water has the properties of a weak electrolyte dissociating into H^+ and OH^-. The degree of dissociation of water increases with temperature and intensifies the processes of decomposition of rocks. Being a good electrolyte, water may gradually dissolve the minerals.

The value of acidity or alkalinity (pH) plays a significant role in the processes of chemical weathering. The pH indicates the concentration of hydrogen ions and significantly affects the solubility of components such as SiO_2, Al_2O_3, $Fe(OH)_3$, $Al(OH)_3$ and others that are formed, in particular, by chemical weathering. Several factors can lower the pH of rainwater. Among these are human activity, together with natural sources of acidity such as volcanic activity, as well as dust and salts in the atmosphere. Sulphates have the strongest effects of the substances in the atmosphere. The combined effect of sulphates and chlorides in coastal areas is also prominent (salt from the sea leads to hydrochloric acid in rain water).

The redox potential (Eh) is a very important parameter of the physical-chemical conditions of dissolution and migration.

Chemical alterations take place as a result of oxidation and hydration (for example, pyrite alteration: $FeS_2 + mH_2O + nO_2 – FeSO_4 - Fe_2SO_4 – Fe(OH)_3 – Fe_2O_3 \times nH_2O$), as well as dissolution and hydrolysis. Hydrolysis reactions play a special role in ion exchange between solids and water, leading to the destruction of even the very stable structures of silicates, accompanied by their hydration and removal of elements from the lattice.

Another important feature of water, without which the chemical alteration of rock is impossible, is the "delivering" of agents (extraction) of chemical weathering and the removal of reaction products. The transport of substances occurs in the form of true and colloidal solutions.

According to the theory of weathering, the beginning of the process of chemical weathering is accompanied by the extraction of alkali and alkaline earth elements (calcium and sodium) from the crystal structures of silicates. Silicates at this stage undergo hydrolysis, forming clay minerals (hydromica, montmorillonite, beidellite, kaolin and others). The most mobile elements, i.e. chlorine and partly sulphur, can be leached by water. A result of further development of the weathering process is the formation clays rich in aluminium, i.e. kaolinite and halloysite, and iron oxides and hydroxides.

According to the general trend of weathering, there is certain regularity in the mobility of elements that allowed B.B. Polynov to categorise the migration of elements in weathering crusts (Table 4).

Table 4. Categorisation of the migration of chemical elements in the weathering crusts of silicate rocks.

Intensity of migration	Chemical elements
Very strong migration	Cl, S, B, Br, I
Strong migration	Ca, Na, Mg, Sr, Zn, Mo, U, F
Moderate migration	Si, K, Mn, Ba, Ni, Co, Cu
Weak and very weak migration	Al, Fe, Ti, Zr, Y, Nb, Ta, Sn, Pt

Thus, stone in urban environments evidently undergoes considerable chemical influence due to air contamination.

4.1 Biogenic weathering

Biogenic weathering is connected with the influence of flora and fauna on the rock. The biochemical impact on the rock starts with the colonization of the surface of the rock by microorganisms, lichen and mosses. The biochemical component has a strong influence on mineral substances. On the one hand, it produces chemically active compounds (organic acids), while on the other hand, it stimulates the extraction of mineral substance from the minerals and contributes to the destruction of the rock. Bioinert interaction leads to the appearance of primitive soil and thus prepares the conditions for further colonization of the stone by embryophytes (higher plants).

In the course of bio-weathering together with the presence of moisture, chemical elements are absorbed by plants from the destructible rocks in accordance with their biological needs. These elements include P, S, C1, K, Ca, Mg, Na, Sr, B and at a lesser degree Si, Al, Fe and some others.

Carbon dioxide and humic acids, released during the decomposition of organic residues, enter the water, which consequently increases its destructive ability. Vegetation contributes to the accumulation of moisture and organic substances in the soil, thereby increasing the time of exposure to chemical weathering. Bacteria, which are ubiquitous, form substances such as nitric acid, carbon dioxide, ammonia, and others that stimulate the rapid dissolution of minerals in rocks.

Bio-fouling is usually understood as the development (accumulation) of living organisms (microorganisms, plants, fungi, animals) on a solid substrate. Often, this term stands for “biological colonization” (biological colonization). Bio-fouling takes place in both air and water. This process may have a differing duration and be accompanied by the gradual destruction (destruction) of the substrate.

Biodestruction is a special type of destruction of rocks and materials by living organisms or their metabolic products. This is defined by a combination of reactions that modify the properties or destruction of the material, mainly caused by a group of organisms (Р В С Н 20–01–2006, St. Petersburg 2006). A biodestructor is an organism that damages a material or an agent of biodamage. The development of destructive processes may lead to the loss of the essential properties of the material, its consistent and complete destruction. The processes of biodestruction affects almost all known natural and artificial materials.

Different groups of living organisms may cause biodestruction of granite. These destructors include bacteria, microalgae and fungi, mosses, lichen, embryophytes, invertebrates and vertebrates. However, most researchers consider that the main damage to granite buildings is caused by microorganisms, which have very high destructive activity (Berthelin 1983, Warscheid & Braams 2000). The mechanisms of their influence on granite are very diverse, so it is necessary to specify the composition of the microorganisms as well as lichens that can colonize the granite. The characterizations of micro-organisms, lichens as well as mosses and seed plants are presented in the appendixes 2, 3 and 4 respectively.

4.2 Abiogenic weathering

The processes of destruction of natural stone in technogenic ecosystems are accelerated and are caused by the complex impact of closely interrelated physical, chemical and biological factors.

Photographic documentation of granite in the architectural buildings of St. Petersburg allowed us to compile a representative database and classify the damage to granite as follows (Table 14). We defined three groups of destruction, which can be visually determined: abiogenic (physical and chemical), biogenic and anthropogenic.

The classification we developed can be correlated with that published by B. Fitzner (Fitzner B. & Heinrichs K. (2004). Photo atlas of the weathering forms on stone monuments, www. Stone. rwth-aachen.de). However, in the published atlas, very little attention is paid to granites. In our atlas, weathering is considered only for granites in the climate conditions of Saint Petersburg. Moreover, the classification is grounded in the types of weathering and has a genetic approach.

4.2.1 Physical weathering

Observations carried out in natural environment have allowed the following types of physical weathering to be defined (in parentheses, type of weathering classified by Fitzner): IA coarsening of the surface (Rr); IB caverns and deepings (R); IC exfoliation (S); ID cracks (L); and IE splitting and loss of fragments (O) (Fig. 20).

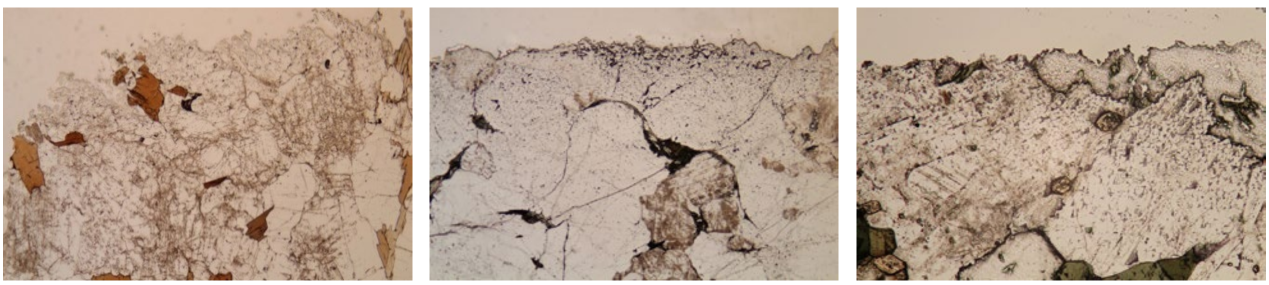
As presented in *IA Coarsening of the surface (Rr)*. Coarsening of the surface is the most widely represented type of mechanical destruction, which is typical for open surfaces of granite, but develops with different intensity depending on the position of the surface relative to the direction of the wind rose, and the vertical or horizontal position. Coarsening of the surface is the process of grains loss, and it is stimulated by the participation of mineral particles in the air that are formed during the destruction of granite and cause the abrasion.

Table 5. Resistance of minerals to weathering

Very stable	Stable	Instable	Very instable
Quartz (zircon, rutile, corundum, anatase)	K-feldspar Plagioclase (albite) Muscovite (monazite, xenotime, cassiterite, fluorite, magnetite, ilmenite)	Plagioclase (andesine) Pyroxene Amphibole (apatite, hematite, garnet)	Plagioclase (anorthite) Biotite Chlorite (pyrite, pyrrhotite)

As presented in Table 5, quartz, potassium feldspar and albite are the minerals that are most resistant to weathering.

Coarsening of the surface can be well observed under a microscope. The study of petrographic thin sections prepared in parallel to the weathered surface allows the character of surface alterations to be clarified (Fig.7). The surface of granite is uneven with cracks, which gradually leads to the loss of grains.



A B C

Fig. 7. Weathered surface of granite (the upper part of the photos). Nicols parallel, magnification 90X.

IB Caverns and deepings (R). Caverns and deepings appear on the surface of rock due to deep weathering and the loss of numerous mineral grains. Typical rounded deepings in the rock are explained by the loss of large ovoids.

IC Exfoliation (S). Exfoliation leads to the appearance of thin plates on rock surface, which consist of granite and are the products of its destruction. As mentioned in section 3.1, exfoliation occurs as a result of the heating of the stone surface to a certain depth, the differences in coefficients of expansion of the minerals and the formation of weathered crust (plate) that is in parallel to the surface of the bedrock.

ID Cracks (L). Three types of cracks can occur: micro-cracks, micro-cracks of weathered crust and inner cracks caused by the textural and mineral heterogeneity of granite.

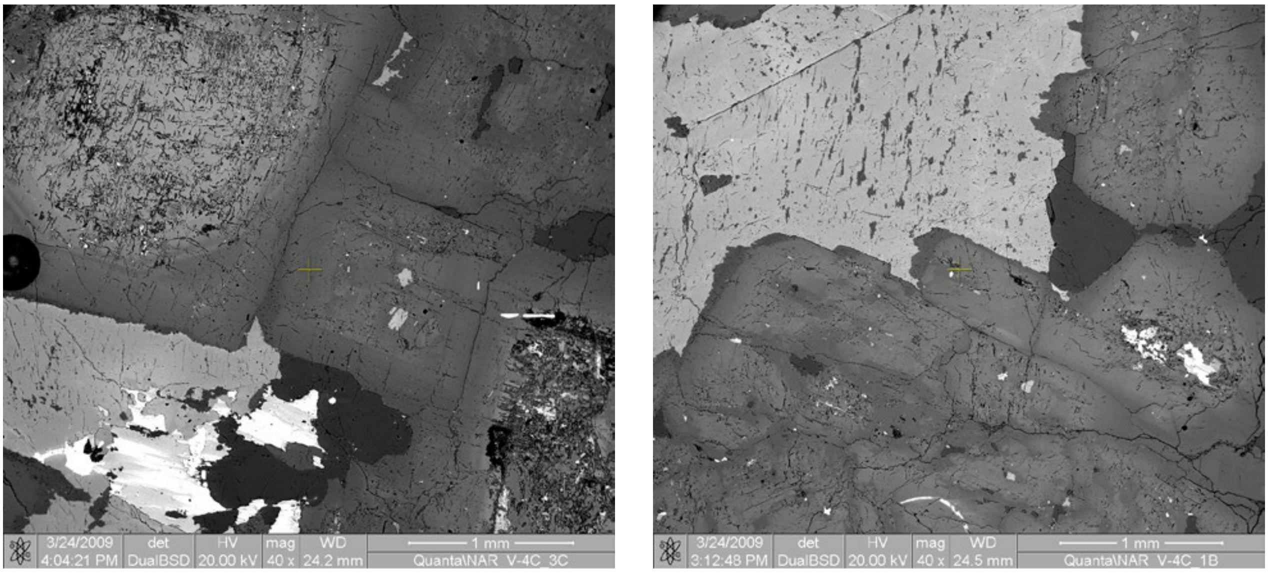
Cracks of jointing are well seen in quarries. During quarrying, about 80% of rocks can be discarded and form waste or secondary material deposition due to fracturing of the rock. Cracks can appear over time in the produced blocks. These are well seen on the paving slabs laid in the 18th century and in modern masonry.

Micro-cracks in the weathered crust appear during the course of weathering. They can be seen in thin sections made perpendicular to the weathered surface of granite. The crust of granite is split by the smallest cracks, the number of which decreases inwards from the surface (Fig. 8)

Fig. 8. Cracks in the weathered surface of granite (upper part of the photo). Nicols crossed, magnification 90x.

It is necessary to note the peculiarities in the destruction of certain minerals. Fracturing firstly affects feldspars and amphiboles due to their cleavage. The quantity of quartz crystals, which are less susceptible to mechanical destruction, thus increases in the crust.

The microheterogeneity of the rock and ultramicrostructure of minerals may be observed by means of scanning electron microscopy. The inner structure is defined by the presence of perthites (regular intergrowths of potassium feldspar with plagioclase) and micro-inclusions. Such a microstructure creates the conditions for increased



A B

Fig. 9. Electron-microscopic images illustrating the microheterogeneity of granite.

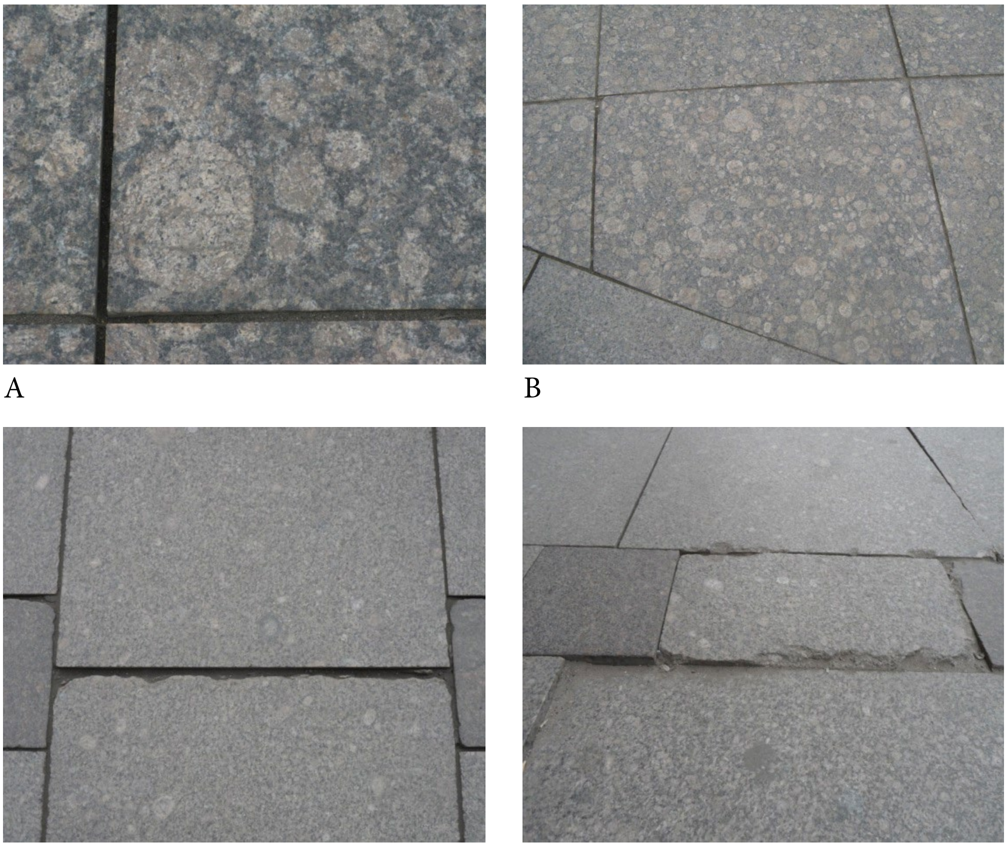
A B

Fig. 10. Insertions of granite without matching the colour (left) and using the same stone (right).

moisture between the crystals, makes their drying difficult and, consequently, as a result of freezing, expansion of the cracks and the appearance of internal stresses, creates the conditions for the accelerated destruction of the stone, especially when there are sharp annual and daily fluctuations temperature, and hence freezing and defrosting (Fig. 9).

IE Splitting and loss of fragments (O). At the site of cracks, chips are often formed, resulting in the loss of fragments. This causes aesthetic damage to architectural buildings, which is amplified by careless restoration (Fig. 10).

The process of physical destruction may be traced by comparing recently laid slabs with the state of the stone used for paving sidewalks in the 18th century (Figs 11 & 12).



A B C D

Fig.11. Modern paving with slabs, laid in 2013 (upper photos) and 2009 (lower photos).

A

B

Fig. 12. Granite paving stones laid in the 1760s and gaps between them (right)

In modern masonry, stone edges are cut and fitted to each other. Under mechanical impact on the slabs of the pavement, the splitting of crystals first takes place, which contributes to the further destruction of the rock. This process usually begins with feldspars, which have cleavage and split along it. Intensive splitting is especially characteristic of large phenocrysts, the loss of which significantly disrupts the integrity of the stone (Fig. 13).

The splitting of crystals takes place along the edges, and this process gradually widens the gaps between the plates. On the embankments of Saint Petersburg, paved in the 1760s, these gaps are on average 1–3 cm in width (up to 8 cm). Upon weathering of the granite, the grains of quartz and feldspar, with lesser amounts of micas and amphiboles, accumulate in the gaps, from where they are dispersed by the wind, turning into urban dust. Organic soil particles also accumulate in the gaps. These particles are clearly visible between the plates in the bright sun. In the space between plates, mechanical differentiation of grains takes place, with mica accumulating at the top and quickly being carried away by the wind. Quartz, feldspar and clay minerals remain in the gaps. Moisture is retained for longer in the gaps than on a flat surface of stone, which contributes to the weathering of the stone.

Dust produced in physical weathering

Granulometric analysis has demonstrated that in general, the dust of St. Petersburg contains particles of various sizes, but the predominant particles are 0.1–0.25 mm in diameter (Fig. 14). However, in the city centre, the predominant fraction has a particle size of 0.25–0.5 mm, and on the outskirts of the city, a fine particle fraction occurs (0.05–0.1 mm).

Large particles are to a greater extent responsible for impact and abrasion, while particles of a small size can accumulate in the surface defects.

The colour of dust particles is very variable, including white, black, red, pink, yellow, blue and green, as well as colourless particles. However, dark coloured particles predominate (35 vol.%),

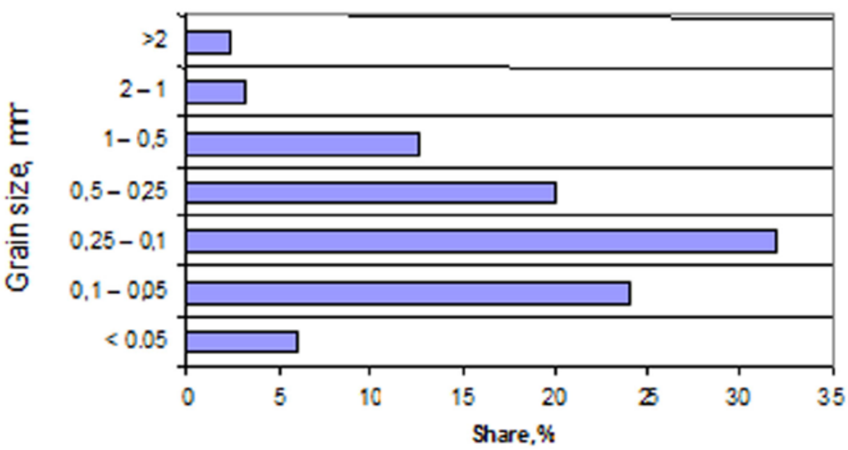


Fig. 13. Average size of dust particles in Saint Petersburg.

while colourless particles make up 27 vol.%, white 17 vol.%, red 10 vol.%, blue, green and pink 5 vol.% each, and yellow 1 vol.%.

The shape of particles is as diverse as their colour range. We have observed rounded and acute-angled particles of different shapes. In general, the predominance of acute-angled grains over rounded particles should be noted, indicating a significant contribution of local sources of dust in comparison with the aerosol transfer from afar. Acute-angled particles make up 70 rel.% and rounded particles 30 rel.% (Table 6).

Particles of technogenic origin are found in the dust. They have a different morphology and shape and are represented by metal particles, spherules and ash. The particles can be clearly identified by scanning electron microscopy and microprobe analysis (Figs 14 & 15).

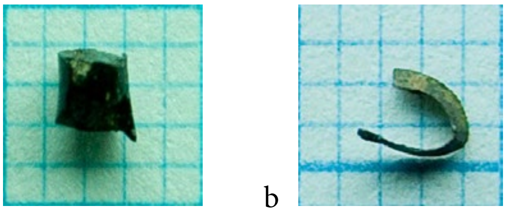
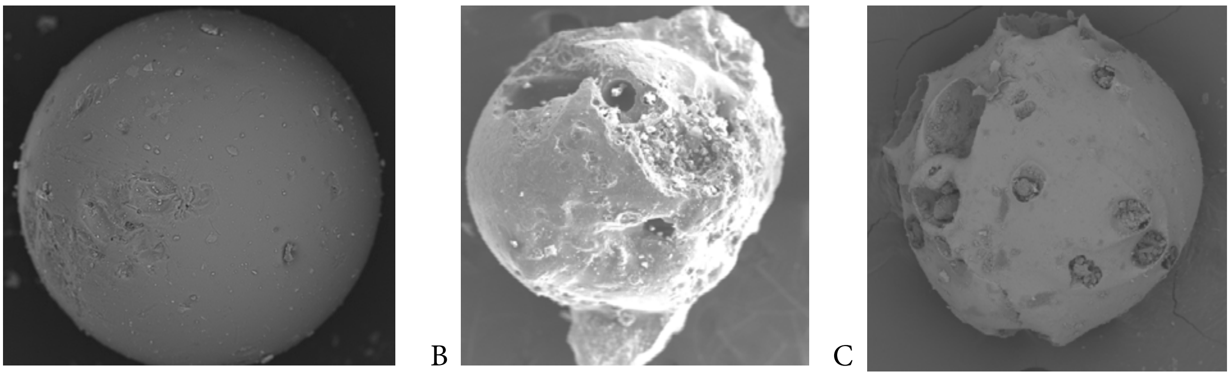


Fig. 14. Technogenic particles of dust. Grid squares 1 × 1 mm.

Table. 6. Shape of dust grains in Saint Petersburg.

Shape of the particle	**Sketch**
Rounded	
	
	
Acute-angled	
	
	
	
	



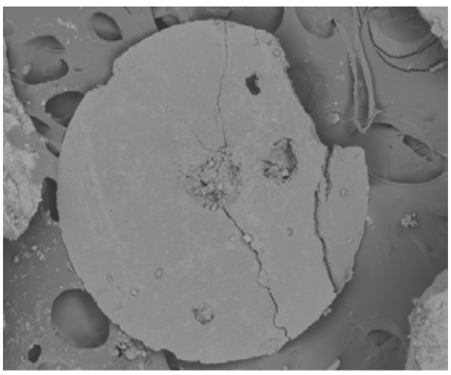


Fig. 15. Morphology of technogenic particles of dust (SEM-images). Magnification 200ˣ.

Analysis of heavy concentrates was performed for the grain-size fractions >1 mm, 0.5–1 mm and 0.25–0.5 mm. The results demonstrated a dominance of quartz in the fraction 0.25–0.5 mm in all analysed samples (up to 60 rel.%), while feldspars comprised about 35 rel.% and technogenic particles about 25 rel.%. Biotite and muscovite each made up 5 rel.%, while amphibole, pyroxene, calcite, dolomite, magnesite, corundum, rutile, hematite, cinnabar, apatite, fluorite, talc, chlorite, alunite, kaolinite, hydromica, montmorillonite and fragments of rock made up less than 5 rel.% of the particles. Technogenic particles clearly dominated in the large grain-size fraction (up to 60 rel.%).

Dust in the centre of the city is enriched in quartz, feldspars, fragments with a quartz-feldspar composition and technogenic particles. The defined distribution of minerals is determined by the use of granites in the facing of buildings in the historical centre, which enrich the dust with unrounded particles of quartz, feldspars and rock fragments as a result of destruction. The dust of the outskirts of the city is characterized by the accumulation of a wide variety of minerals, and at a certain site by the predominance of clay particles, which is determined by soil erosion.

Defining mechanical resistance of the granite by fractal analysis

In general, the mechanical resistance of granite can be estimated by calculating the coefficient of fractal dimension of the grains.

Features of the spatial distribution of individual members of the rock provide important information about the patterns of structural regularities of crystalline rocks. These features can be described using the theory of fractals. A fractal is infinitely self-similar geometrical figure, each fragment of which is repeated on scaling down. The problem concerning the analysis of granitoids was studied in detail by Vistelius (1987). The studies have shown that sufficiently long linear sequences of quartz and feldspar grains have the properties of Markov chains, the order which was subjected to statistical evaluation that suggested the presence of spatial correlations between individual members.

According the features of various granites, there are two main types of granite textures: porphyry and equigranular. The most important among them are: (A) inequigranular, porphyritic granites of the standard type with large crystals of feldspars and a random arrangement of different-sized quartz grains of irregular shape; and (B) equigranular granites with isometric feldspar grains and a chain-aggregative location of quartz grains (Fig. 16).

To establish quantitative criteria for dividing granite rocks and their destruction, research was carried out on the textural patterns which repeat the regularities of the spatial structure observed in these clusters of grains. The morphometry of quartz aggregates is based on fractal statistics of $M(R)\mu R^D$, taking into account the exponent dependence of the square of cross-section units *M* from their linear size *R*. Samples for the study were selected so that there were no signs of tectonic influence on the rock.

In morphometric analysis, digitized colour images of flat sections of granites (20 x 20 cm or 10 x 10 cm in size) were converted to a black and white (bitmap) format. To calculate the fractal dimension, *M* and *R* parameters of numerous quartz aggregates were measured, and the D value was estimated as the slope coefficient of the linear regression of variables by the method of least squares. According the features of various granites, there are two main types of granite textures: porphyry and equigranular. The most important among them are: (A) inequigranular, porphyritic granites of the standard type with large crystals of feldspars and a random arrangement of different-sized quartz grains of irregular shape; and (B) equigranular granites with isometric feldspar grains and a chain-aggregative location of quartz grains (Fig. 17).

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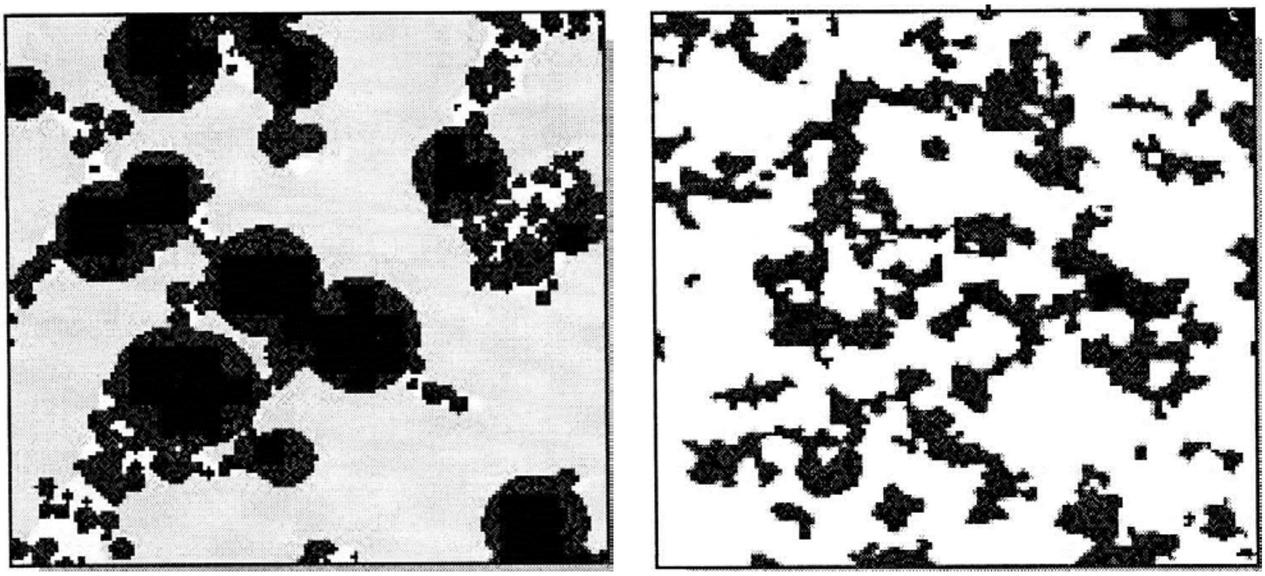


A B

Fig. 16. Textural patterns of rapakivi granite (left) and Kuznechnoe granite (right).

Table 7. Results of analysis of the texture of granite.

Sample	Type of granite	Mode of quartz, Q	Fractal dimension, R
	Rapakivi	0,32	1,75±0,05
		0,37	1,81±0,08
		0,30	1,77±0,06
		0,33	1,79±0,09
		0,31	1,78±0,10

sion of variables by the method of least squares.

The obtained D values vary within the range of 1.46 to 1.89 and may be divided into two practically non-intersecting groups according the types of granites. With a reliability of 95%, the granites of A type have persistently high (1.75–1.81), and granites of type B lower (1.63–1.70) fractal dimension values (Table 7).

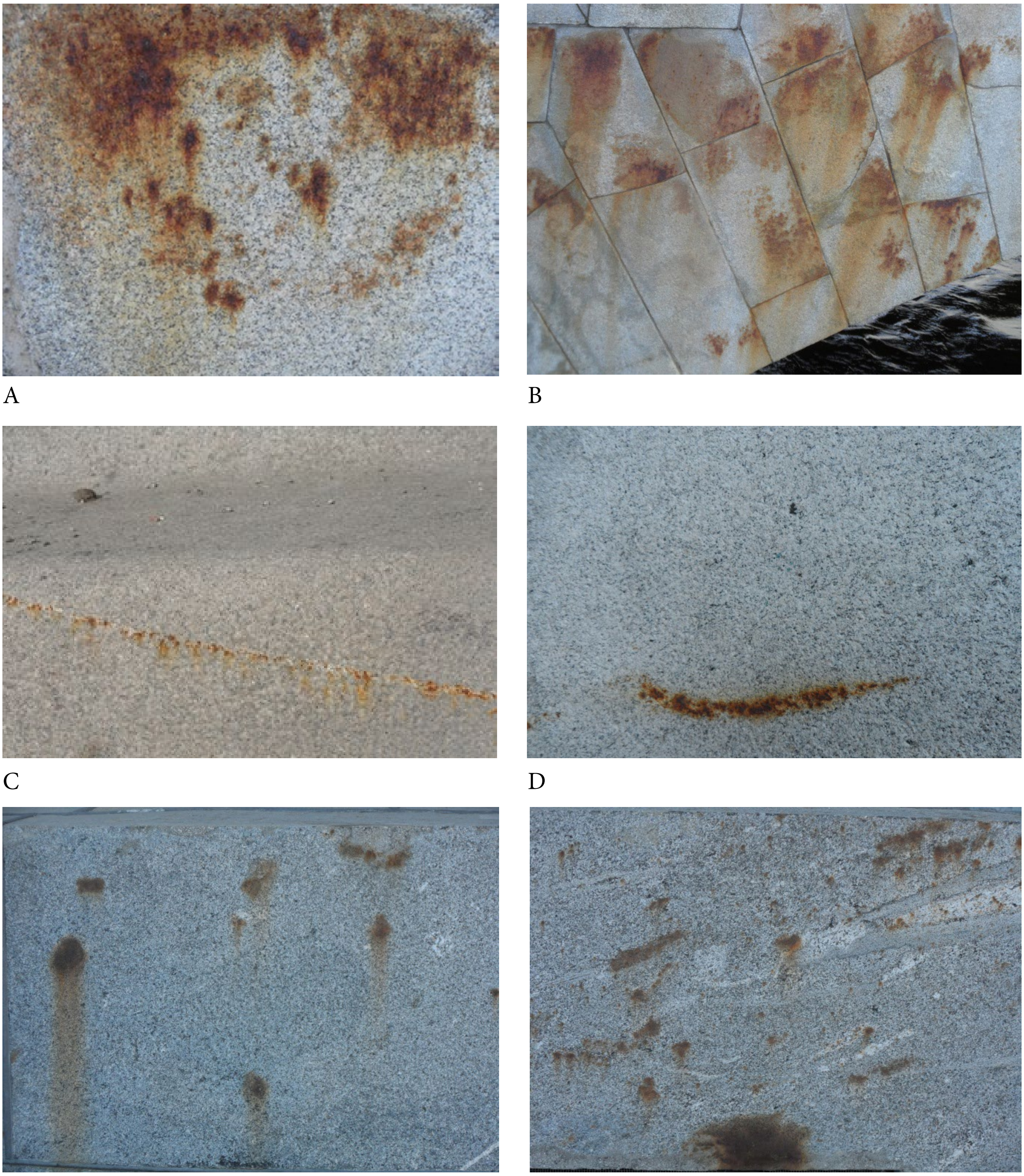
Thus, granites with higher fractal dimension values are more susceptible to physical weathering.

4.2.2 Chemical weathering

Chemical weathering belongs to the abiogenic type of weathering and in our classification has the index IF. In the classification by B. Fitzner, such weathering was not defined.

Chemical weathering can be observed as a change of colour caused, first of all, by the decomposition of sulphides with the formation of iron hydroxides (Fig. 17). The presence of sulphides in granite leads to their oxidation in urban conditions and the appearance of brown spots on the surface of the stone. If sulphides develop along cracks in the rock, brown stripes are then formed. On vertical walls, the brown colour flows downwards from sulphide accumulations, forming vertical stripes. This effect can be avoided by the appropriate choice of stone for building, i.e. without sulphides.

Mechanical links between the parts of stone are the first to be destroyed under the influence of water, wind and temperature fluctuations. Water penetrates the cracks and micro-cracks in the rock, creating a favourable environment for chemical reactions. Gases and substances from the air and water have harmful chemical impacts. When dissolved, they form carbonic acid, resulting from the dissolution of carbon dioxide in the air and rain water, which begins the acid leaching of rocks.



A B C D E F

Fig. 17. Chemical weathering of granite shown as formation of iron hydroxides.

Due to oxygen in the air, oxidation and the transformation of chemical elements into protoxides take place.

In thin section, it is clearly evident that at the transition from unaltered to weathered rock, the grains of rock-forming minerals (K-feldspar, plagioclase and quartz) become more cracked and the cracks become filled with brown iron hydroxides (Fig. 18 a, b). A mixture of clay minerals develops along the cracks in K-feldspar and its crystals gradually grow turbid (Fig. 32 c). Alteration of plagioclase starts with development of iron hydroxides in the mixture with clay minerals in the form of irregular spots oriented in the direction of cleavage (Fig. 18 d).

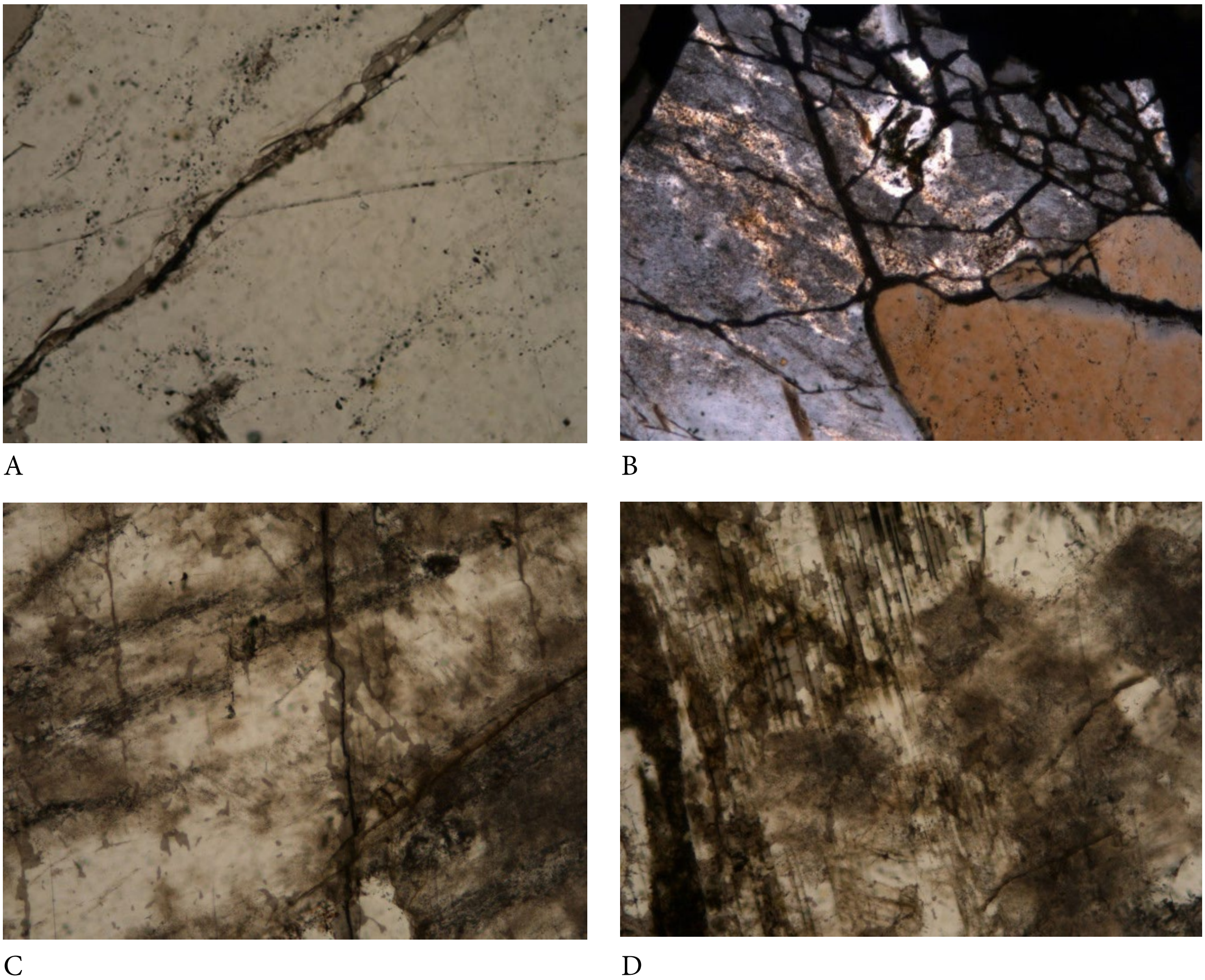


Fig. 18. Alteration of rock-forming minerals in granite.

A, b – quartz, c – K-feldspar, d – plagioclase
a, c, d – Nicols parallel, d – Nicols crossed.

Dark-coloured minerals are replaced by an aggregate of chlorite and iron hydroxides on the edges of biotite grains and along the cleavage in amphibole (Fig. 19).

Porphyry and equigranular granites are characterized, in general, by a small amount of biotite and its weak chloritisation. The latter causes a decrease in the density and, consequently, an increase in the total moisture capacity of the rock. Gradually, the rock-forming minerals such as micas, pyroxenes, amphiboles and feldspars are transformed into clay minerals and leached from the rock. The processes of oxidation and substitution of minerals leads to more micro-cavities and micro-cracks and, as a result, to an increase in mechanical destruction.*IF* Chemical weathering

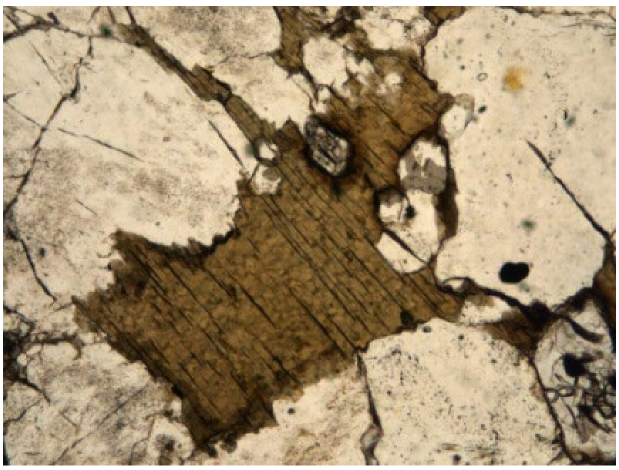


Fig. 19. Development of iron hydroxides (brown) around biotite and zircon grains.

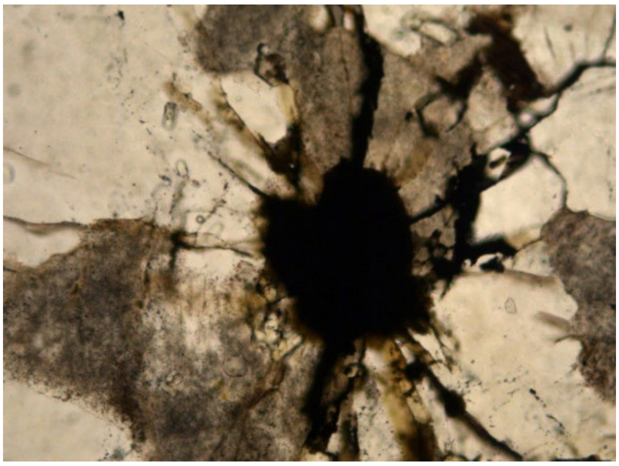


Fig. 20. Pleochroic halo around a grain of thorite.

The presence in the granites of radioactive minerals causes radioactive decay and the appearance of radial cracks around them (pleochroic halo), which accelerates mechanical destruction (Fig.20)

Radioactivity

Radioactivity of rocks is an important property, which is normalized and determines their value and possibility for use as inner or outer facing. To study the natural radioactivity of rocks, we carried out measurements in the environment by means of a radiometer, which was used for a survey of the city on foot. Our measurements demonstrated that rapakivi granite stands out among other types of granite due to its high background radiation, with values for pink rapakivi granite, porphyry granite of 45–53 μr/h and grey rapakivi granite, porphyry granite of 43–47 μr/h. Granites from the other massifs have lower values (pink granite and porphyry granites from Priozersk, 29–31; grey fine-grained granites from Sortavala, 16–19), and the values for the background radioactivity of facing stone are 15–23 μr/h. In General, the level of radioactivity of granites is not dangerous when it is used for facing the buildings, but its application in the internal poorly ventilated indoor spaces may cause accumulation of radon (European Commission 1999).

Higher values of background radioactivity depend on the presence of radioactive minerals in the rock. Average uranium concentrations in different types of ovoid granites are 4.3–10.5 g/t, and those of thorium 14.0–49.0 g/t. To identify accessory mineralization, we have studied samples of granites by scanning electron microscopy and microprobe analysis. The following accessory minerals have been identified: thorite, zircon, bastnäsite, allanite and brannerite. These contain thorium and uranium and contribute to the destruction of granite due to the radioactive decay of these elements.

Aerosols

As noted in section 3.1, the aerosol transport of particles and chemical elements leads to increased chemical destruction of granite in the urban environment.

Special attention is paid to mercury as the most characteristic element of aerosol transport in technogenic conditions and belonging to the first toxicity class. Its wide application in industry and the geochemical peculiarity of its behaviour (volatility) have resulted in the intense anthropogenic dispersal of this element.

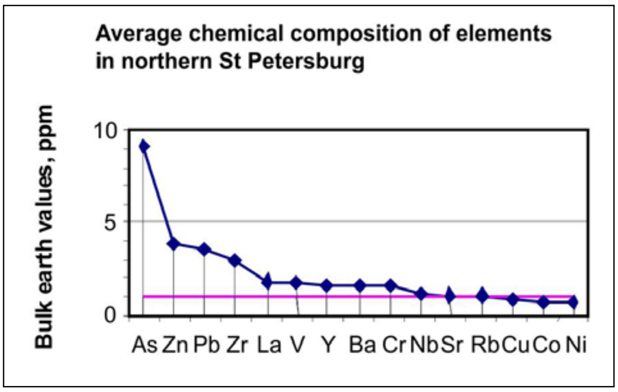
According to measurements carried out higher mercury concentrations are mainly localized in the historical centre of the city, where there are historic buildings with domes that have been gilded with an amalgam of gold and mercury. In the 20th and early 21st centuries, various industrial wastes, industrial drains, solid waste landfill, and landfill of gas-mercury lamps, among others, have become the sources of mercury in the environment that have caused mercury pollution in large cities. Thus, the intensity of mercury accumulation in the weathered crust compared to the unaltered granite shows its anthropogenic accumulation (Table 8.)

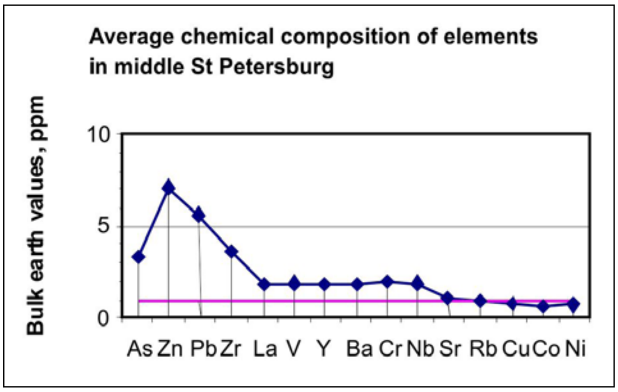
The dust of aerosols may take part in the chemical destruction of granite by accumulating in the irregularities of the surface and reacting with moisture.

Dust particles settling on the weathered surface of stone can change its chemical composition. In the dust of Petersburg, the following chemical elements have been determined (average, g/t): Zr (515), Zn (458), Sr (388), V (172), Cr (151), Rb (135), La (82), Pb (65), Ni (45), Cu (42) and As (13). Concentrations of some elements in the dust are in 2 to 13 times higher than in the lithosphere. The geochemical range of the clarkes of concentration of chemical elements in the dust in general for St. Petersburg is the following: As – Zn – Pb – Zr – V – Cr – La. The distribution of chemical elements is not identical in all parts of the city. The dust in central parts is characterized by the presence of Zn, Pb and Zr, and that in the southern parts by As (Fig. 21).

Table 8. Mercury concentration in rapakivi granite (mg/kg).

Rock	Vyborg	Saint Petersburg
Fresh rapakivi	0,07	0,08
Rapakivi, crust without biological impact	0,09	0, 13
Rapakivi, crust with biological material	0,10	0, 19





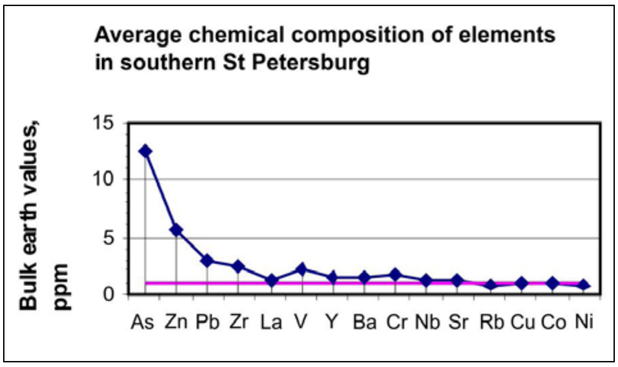
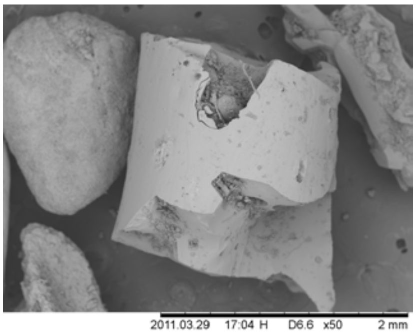


Fig. 21. Average concentrations (ppm) of chemical elements in dust from the northern, central and southern parts of Saint Petersburg.

Micro X-ray spectral analysis of particles of anthropogenic origin revealed the predominance of C, O and Si (Fig. 22). The carbon content in the particles is on average 71.2% t, in some cases reaching 100%. Locally, the following average values (%) have been detected: 14% Fe, 10% Al; 6.2% Ca, 4.9% K, 3.5% Ti, 3.2% S, and 2.5% Mg.

The content of petrogenic oxides and the trace element composition were determined in the crust and relatively unaltered granite to evaluate the degree of chemical weathering of granite in the city. For the reference sample in the centre of St. Petersburg, pairs of samples (granite crust) were taken that displayed the most visible changes in the surface (Fig. 23).



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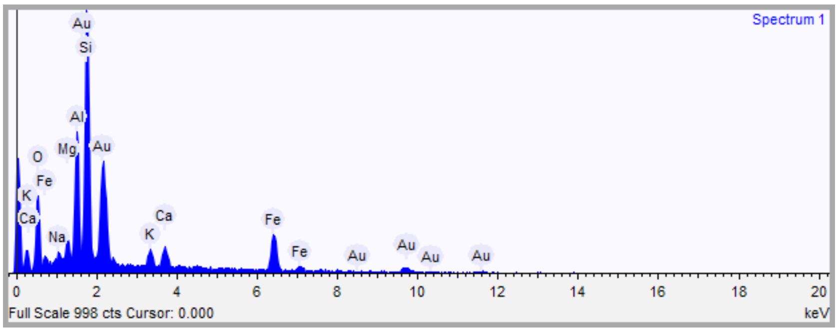

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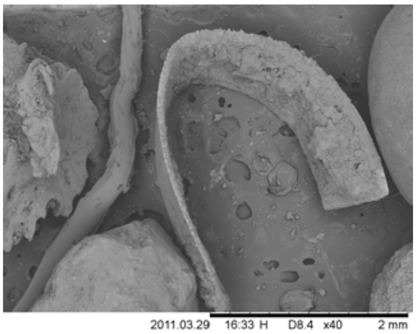

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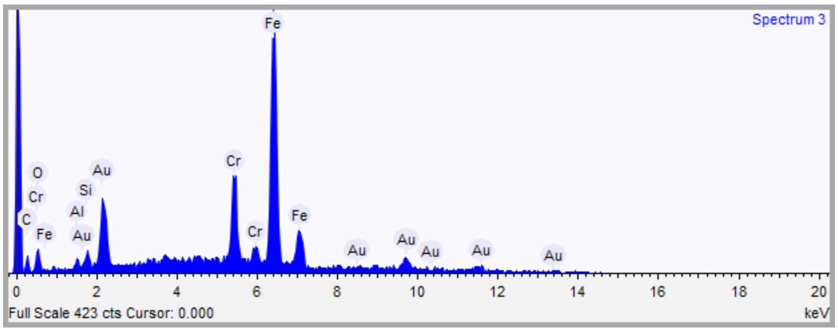

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Fig. 22. Results of micro X-ray spectral analysis of technogenic particles in the dust of Saint Petersburg.

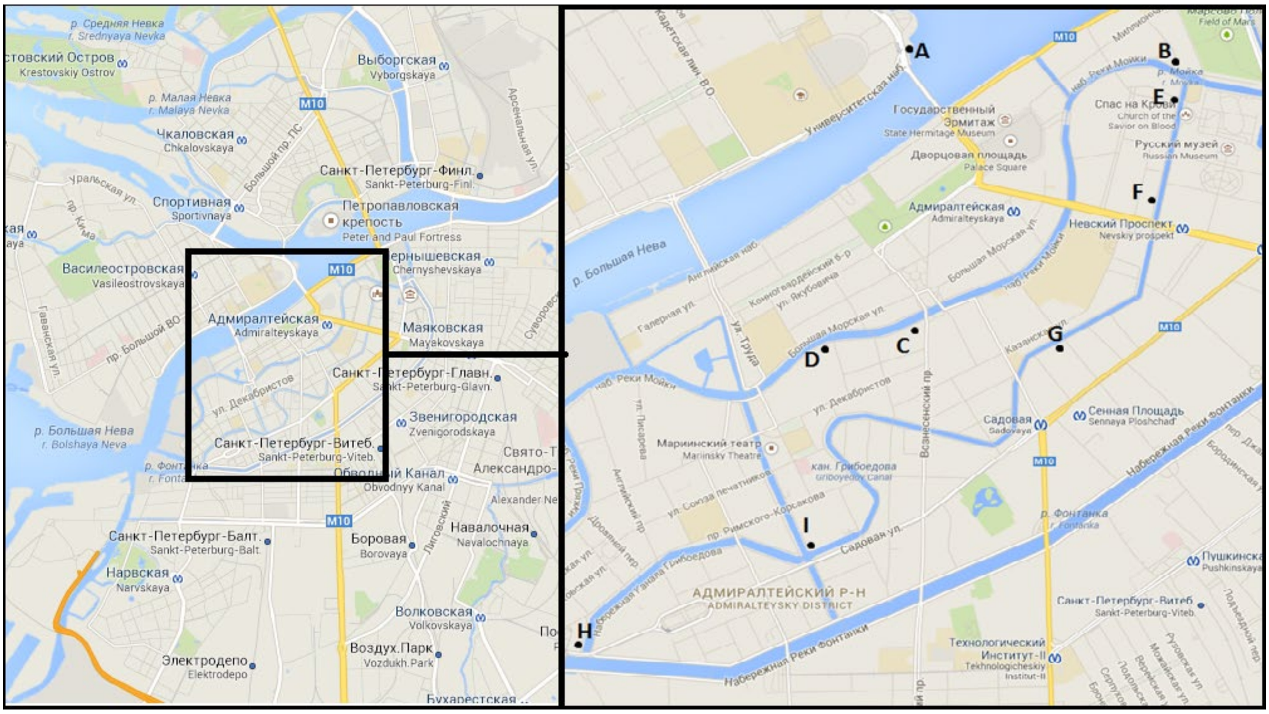


Fig. 23. Location of reference sampling of granite in the centre of Saint Petersburg.

All samples consisted of rapakivi granite from buildings constructed at the end of the 18th to the beginning of the 19th century. The crust had obvious traces of weathering that corresponded to alteration reactions, first of all being composed of dark-coloured minerals. Potassium is leached from biotite ($K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$) and muscovite ($KAl_2(AlSi_3O_{10})(F,OH)_2$), while K, Na and Ca are leached from feldspars ($KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$). The result of the reactions is the formation of kaolin ($Al_2Si_2O_5(OH)_4$), which is noticeable due to its white powdery appearance (Hawkes & Webb 1962). The results of macro-element composition analysis are presented in Table 9.

Table 9. Content of petrogenic oxides in granite and its weathered crust, mass.%.

Location		SiO_2	Al_2O_3	K_2O	Na_2O	CaO	Fe_2O_3	MgO	TiO_2	P_2O_5	MnO	Total
A	Granite	69.10	12.40	5.23	2.44	1.92	7.06	0.39	0.760	0.162	0.075	99.54
	Crust	70.20	14.50	5.31	3.21	2.06	3.54	0.20	0.356	0.106	0.034	99.52
B	Granite	69.30	14.70	5.60	3.18	1.87	4.11	0.25	0.454	0.104	0.043	99.61
	Crust	73.10	12.30	4.80	2.64	1.55	4.38	0.24	0.470	0.104	0.042	99.63
C	Granite	71.30	13.80	5.98	2.71	1.42	3.64	0.20	0.359	0.065	0.032	99.50
	Crust	71.00	14.10	5.88	2.86	1.21	3.93	0.19	0.378	0.072	0.034	99.66
D	Granite	71.50	13.70	5.29	3.03	1.79	3.49	0.17	0.344	0.058	0.032	99.41
	Crust	71.20	13.90	5.48	3.06	1.44	3.83	0.18	0.380	0.063	0.033	99.57
E	Granite	67.90	13.50	5.11	2.93	2.35	6.39	0.41	0.720	0.193	0.066	99.57
	Crust	69.00	15.60	5.49	3.60	1.98	3.39	0.21	0.342	0.092	0.032	99.73
F	Granite	73.70	12.90	6.07	2.65	0.95	2.76	0.13	0.249	0.037	0.021	99.46
	Crust	71.60	14.00	6.76	2.93	0.82	2.84	0.14	0.220	0.038	0.021	99.37
G	Granite	75.50	12.40	5.36	2.72	0.80	2.41	0.14	0.211	0.027	0.020	99.58
	Crust	71.30	14.60	4.78	3.62	1.95	2.82	0.18	0.240	0.041	0.022	99.55
H	Granite	74.70	12.30	5.58	2.49	1.03	2.97	0.13	0.295	0.042	0.026	99.57
	Crust	73.80	12.70	5.61	2.62	1.47	2.89	0.13	0.252	0.121	0.023	99.61
I	Granite	69.90	13.50	5.23	3.02	1.99	4.99	0.28	0.540	0.134	0.056	99.64
	Crust	70.90	13.40	5.12	3.00	1.93	4.44	0.24	0.451	0.152	0.049	99.68
Average for Vyborg massif		72.55	13.05	5.53	2.88	1.43	3.39	0.21	0.33	0.07	0.04	99.48

The data indicate that the crust of the altered granite is enriched in silica, aluminium oxide and sodium and is poor in potassium and calcium compared to the unaltered granite. This is explained by the higher proportion of clay minerals in altered granite, its disintegration into minerals and the removal of clay particles by the wind.

Weathering indices

The intensity of chemical weathering may be evaluated by the calculation of several indices of weathering. These indices are based on the condition that during chemical weathering, the contents of a number of the main oxides, such as Al_2O_3, Fe_2O_3 and TiO_2, remain the same because they are resistant to leaching, while the others, incuding Si_2O, Na_2O, K_2O and MgO, are gradually washed out (Price & Velbel 2002). Most indices are based on data on the composition of petrogenic oxides.

Among the common indexes is the *chemical index of alteration* (CIA) (Law et al. 1991, Price & Velbel 2002, Bahlburg & Dobrzinski 2009). This index is based on the idea that chemical weathering of feldspar as a result of hydrolysis leads to changes in the main cations. It is calculated by formula (1) and for granite rocks it usually varies within the range of 50–55, while for kaolinite it is

100. The results of the calculations are presented in Table 10.

$$CIA = \frac{Al2O3}{Al2O3 + Na2O + K2O + CaO} * 100 \quad (1)$$

The data in the table demonstrate that the samples of crust have a higher CIA than unaltered granite.

The *chemical index of weathering* (CIW) is similar to the CIA and is calculated by formula (2). The value of the index usually varies within the range of 76–59 (Harnois 1988).

$$CIW = \frac{Al2O3}{Al2O3 + CaO + Na2O} * 100 \quad (2)$$

$$WPI = \frac{(CaO + Na2O + MgO + K2O) * 100}{SiO2 + Al2O3 + Fe2O3 + TiO2 + CaO + MgO + Na2O + K2O} \quad (3)$$

The average value of CIW was determined to be 74.97 for granite crust and 75.33 for unaltered granite (Table 20).

The *weathering potential index* (WPI) is calculated according the formula (3) and represents the ratio of the most mobile and immobile components of granite (Price & Velbel 2002). Its value was found to differ by 0.6 units when comparing the crust and unaltered granite samples (Table10).

The *index of composition variability* (ICV) proposed by Cox et al. (1995) may be calculated by formula (4):

$$ICV = \frac{CaO + K2O + Na2O + Fe2O3 + MgO + MnO + TiO2}{Al2O3} \quad (4)$$

As can be seen in Table 20, the ICV for the crust was higher than for the unaltered granite.

The *product index* (PI) is based on the supposition that the proportion of quartz is elevated in weathered crust (Price & Velbel 2002). It may be calculated by formula (5):

$$PI = \frac{SiO2 * 100}{SiO2 + TiO2 + Fe2O3 + FeO + Al2O3} \quad (5)$$

On average, the value of PI was higher for the weathered granite in comparison to the unaltered granite (Table 20).

Data on the micro-element composition were obtained by ICP MS and are presented in Tables 11 and 12.

Table 10. Indices of chemical weathering of rapakivi granite and the weathered cruSaint

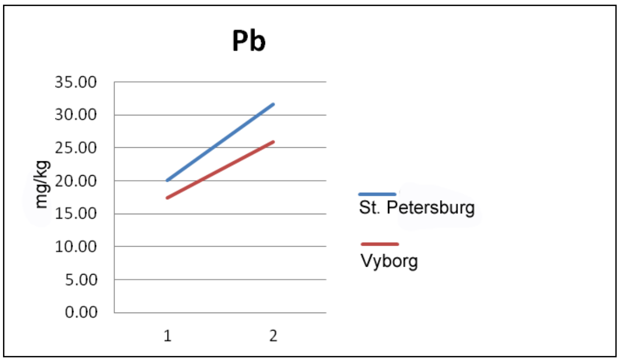
Location		CIA	CIW	WPI	ICV	PI
A	granite	56.39	73.99	10.05	1.44	77.36
	crust	57.81	73.34	10.85	1.01	79.24
B	granite	57.99	74.43	10.96	1.05	78.25
	crust	57.77	74.59	9.28	1.15	81.00
C	granite	57.72	76.97	10.37	1.04	80.02
	crust	58.63	77.60	10.19	1.03	79.41
D	granite	57.54	73.97	10.35	1.03	80.31
	crust	58.21	75.54	10.22	1.04	79.72
E	granite	56.51	71.88	10.87	1.33	76.71
	crust	58.49	73.65	11.32	0.96	78.11
F	granite	57.16	78.18	9.85	0.99	82.25
	crust	57.12	78.87	10.73	0.98	80.76
G	granite	58.27	77.89	9.06	0.94	83.41
	crust	58.52	72.38	10.58	0.93	80.15
H	granite	57.48	77.75	9.28	1.02	82.76
	crust	56.70	75.64	9.88	1.02	82.33
I	granite	56.87	72.93	10.58	1.19	78.60
	crust	57.14	73.10	10.34	1.14	79.49
Average, granite		57.32	75.33	10.15	1.12	79.96
Average, crust		57.82	74.97	10.38	1.03	80.02
σ granite		0.64	2.38	0.66	0.17	2.43
σ crust		0.70	2.17	0.59	0.07	1.22

Table 11. Average concentrations (ppm) of chemical elements in different types of unaltered granites in Saint Petersburg.

element	**granite** Rapakivi (n=13)	Kuznechnoe (n=4)	**Average for SPb** Rapakivi (n=10)	**Average for Vyborg** Rapakivi (n=3)	**Clarke of concentration by A.P. Vinogradov**
Ag	0.13	0.06	0.15	0.11	0.10
Be	0.99	0.20	1.14	1.09	3.91
Bi	0.29	0.05	0.36	0.20	0.01
Cd	0.24	0.11	0.26	0.26	0.1
Ce	181.30	102.90	198.33	183.05	100
Mo	1.66	0.22	1.83	2.33	1
Sb	0.09	0.05	0.09	0.11	0.26
Se	3.19	1.89	3.45	3.29	0.05
Te	0.03	0.01	0.04	0.02	0.001
Th	47.09	25.57	52.70	43.34	18
U	7.37	2.37	8.48	7.37	3.5
W	1.79	0.22	2.26	1.27	1.5
As	11.72	10.32	12.00	11.90	1.5
Ba	119.52	126.05	121.20	105.40	830
Co	3.30	3.89	3.29	2.73	5
Cr	2.92	8.15	2.08	1.43	25
Cu	6.28	7.10	5.98	6.79	20
La	100.33	54.45	110.76	99.30	60
Li	38.28	34.00	40.23	33.80	40
Mn	283.31	153.50	313.33	278.00	600
P	385.80	462.00	376.82	350.00	700
Pb	17.66	7.03	20.07	17.45	20
S	102.01	32.00	111.63	128.70	400
Sc	4.88	4.36	5.10	4.44	3
Sr	12.82	8.10	13.81	13.10	300
Y	54.52	21.65	59.92	63.05	34
Zn	95.35	72.20	100.30	96.25	60

Table 12. Average concentrations of chemical elements in the crust of different types of granite in Saint Petersburg, ppm.

Element	**granite**		**Average for SPb**	**Average for Vyborg**	**Clarke of concentration by A.P. Vinogradov**
	Rapakivi (n=13)	Kuznechnoe (n=4)	Rapakivi (n=10)	Rapakivi (n=3)	
Ag	0.15	0.07	0.15	0.17	0.10
Be	1.25	0.24	1.16	1.65	3.91
Bi	0.34	0.04	0.36	0.29	0.01
Cd	0.32	0.14	0.28	0.48	0.1
Ce	230.06	86.40	207.30	332.50	100
Mo	2.30	0.28	2.07	3.36	1
Sb	0.14	0.08	0.13	0.19	0.26
Se	3.88	1.59	3.54	5.41	0.05
Te	0.03	0.01	0.03	0.03	0.001
Th	42.77	19.92	36.53	70.82	18
U	6.49	2.28	5.84	9.42	3.5
W	2.06	0.28	1.95	2.55	1.5
As	14.83	11.83	13.08	22.70	1.5
Ba	149.00	124.50	145.22	166.00	830
Co	2.99	3.20	2.84	3.66	5
Cr	2.94	8.06	2.91	3.07	25
Cu	7.31	8.42	6.81	9.56	20
La	130.58	46.10	116.49	194.00	60
Li	38.64	28.20	38.07	41.20	40
Mn	304.82	209.50	287.22	384.00	600
P	363.18	397.50	355.67	397.00	700
Pb	30.65	8.03	31.70	25.95	20
S	126.35	38.80	118.32	162.50	400
Sc	4.96	4.58	4.61	6.52	3
Sr	19.16	10.48	18.09	24.00	300
Y	57.90	25.15	52.14	83.80	34
Zn	144.57	74.35	108.48	307.00	60



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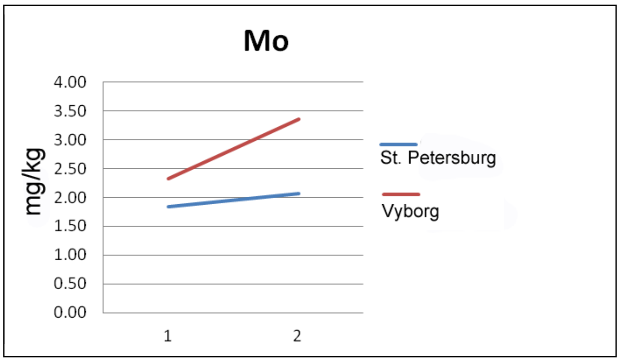

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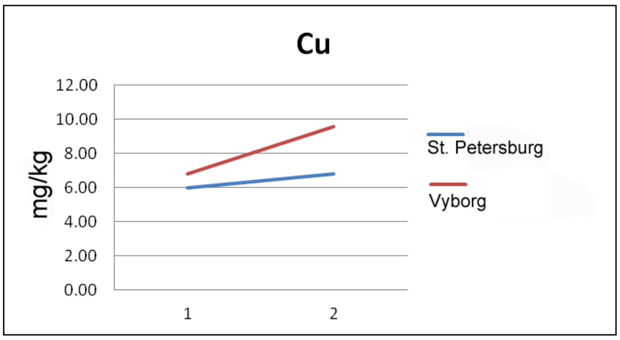

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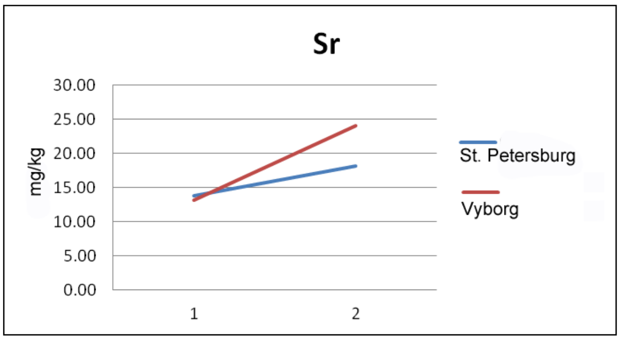

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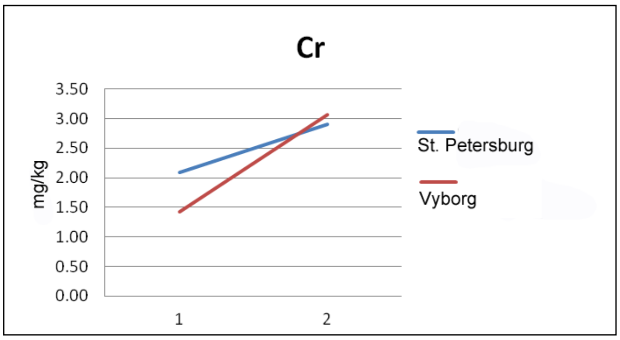

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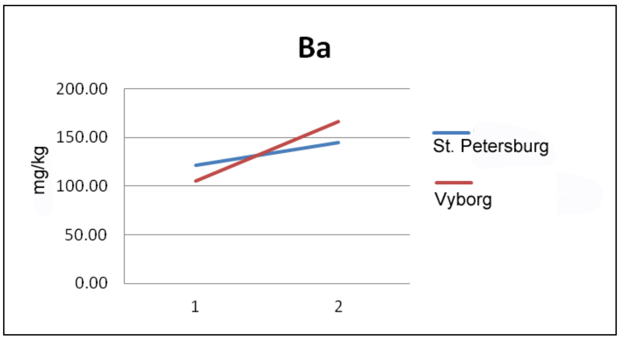

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Fig.24. Changes in the concentrations of chemical elements in unaltered granite (1) and the crust (2). St. Petersburg (blue), Vyborg (red).

The distribution of some chemical elements in the samples of granite and crust is illustrated in (Fig.24).

Based on the micro- and macro-element composition of the samples, we can conclude that the crust is depleted by a factor of 1.5–3 fold for most of chemical elements in comparison with the unaltered granite. The accumulation of Sb, As, Pb, Cu, S is typical for the crust, which can be explained by the influence of the urban environment.

The geochemical data were analysed by principal components factor analysis. The following factors were defined:

Be 0.7 Bi 0.7 Y 0.68 W 0.60 Mo 0.55 Pb 0.54 Sr 0.53 Ca 0.49
F1(49) ---
Cr 0.88 V 0.86 Mg 0.79 Al 0.71 Co 0.46 K 0.39

Fe 0.88 Co 0.87 P 0.85 Mn 0.80 S 0.76 Sc 0.76 Ti 0.75 Cu 0.67 Ca 0.66 Ba 0.46 U 0.44
F2 (24) ---
Ce 0.20

Th 0.87 La 0.78 Ce 0.77 Se 0.76 As 0.73 Li 0.68 U 0.64 Y 0.48 K 0.44
F3 (13) ---
P 0.24 V 0.21

F4 (10) = Na 0.81 Ba 0.78 Sr 0.74 Zn 0.55 Pb 0.52 Al 0.51 Cu 0.49 As 0.45 S 0.43

Factor 2 represents the type of granite and in Fig. 25 there are two fields of granites: rapakivi and Kuznechnoe. Factor 4 shows the difference in composition of the granite and crust (Fig. 26).

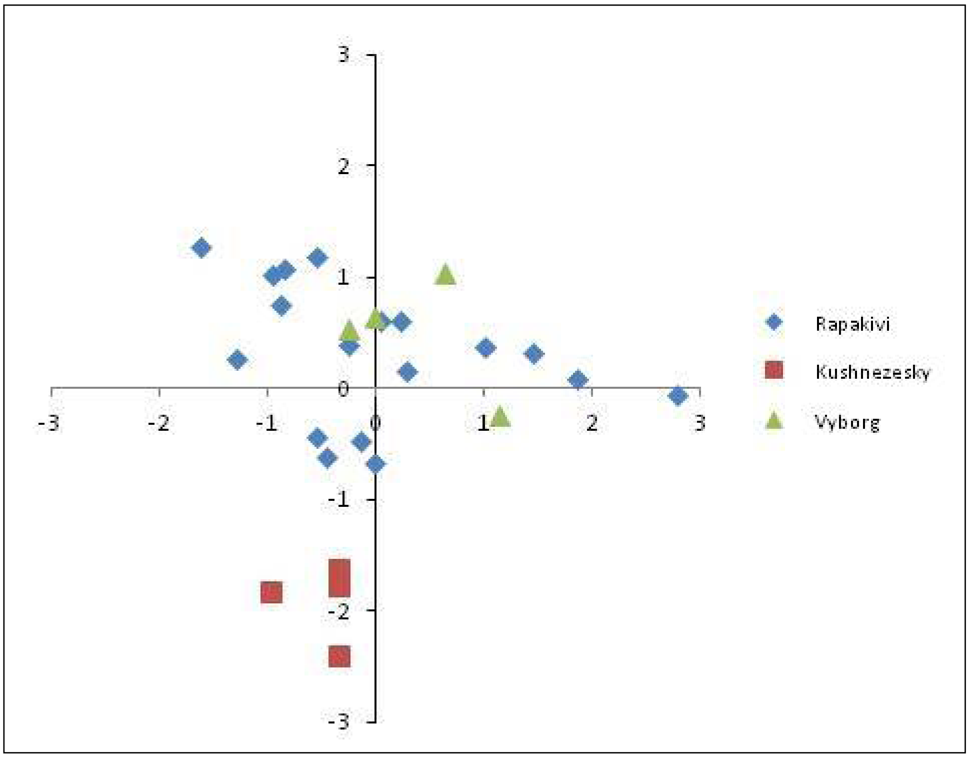


Fig. 25. Diagram of the values for the chemical composition factors of unaltered and altered rapakivi and Kuznechnoe granites (F_I – axis x, F_{II} – axis y).

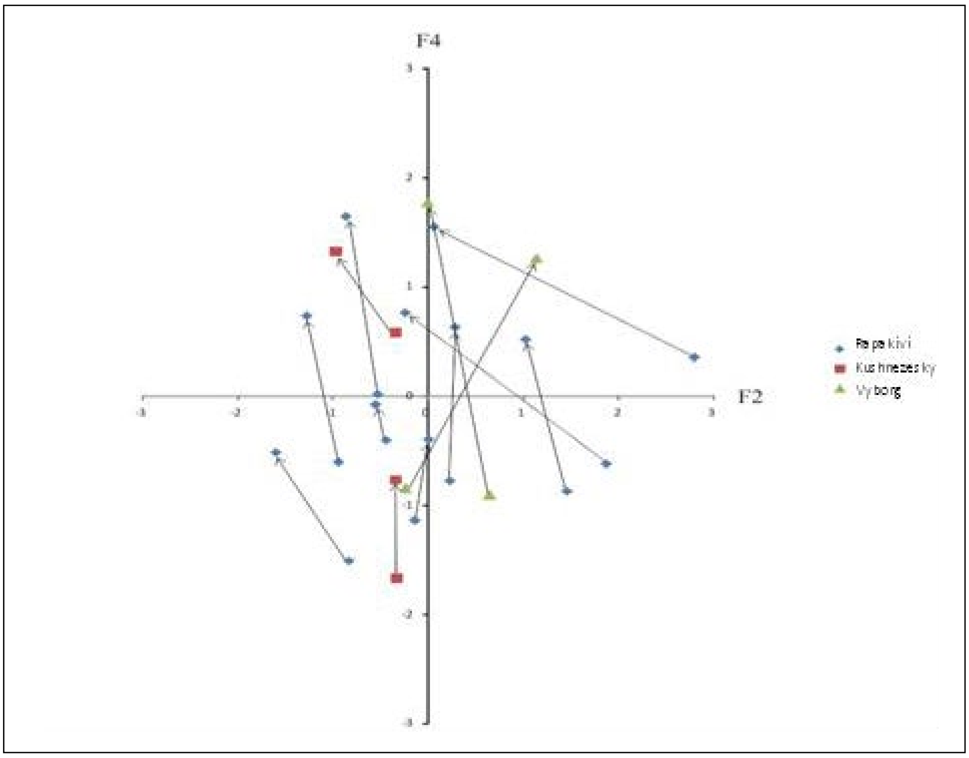


Fig. 26. Diagram of the values for the chemical composition factors of unaltered and altered granites. Arrows are directed from the unaltered granite towards the altered granite.

Thus, as a result of chemical weathering, irreversible changes in the chemical composition of granite take place. During weathering, the crust becomes enriched in elements such as Si, Na, Ca, Sb, As, Pb, Cu and S, which is connected to the removal of clay particles by the wind and the influence of the urban environment. The indices of chemical weathering can provide a measure of the degree of granite destruction.

Experiments on modelling of chemical weathering.

To test the possibility that chemical elements from granite can be leached by water, we performed some experiments that yielded very interesting results.

The method of nano-fractions (NF) separation was applied for extraction of porous water (Oleinikova & Panova 2011). Because crystalline rocks have small pore spaces, their proportion in NF is significantly lower. According to common knowledge, the porosity of the rock reflects the volume of pores, cavities and cracks formed during syn- and epigenesis. Pores are divided according to size into supercapillaries (>1 mm), capillaries (is 0.0002–1 mm) and subcapillaries (less than 0.0002 mm). The porosity of metamorphic and metasomatic rocks ranges from 10 to 25, and rarely to 35 vol.%, while it is 0.1–5 vol.% in intrusive rocks of acid composition, and 0.1–1 vol.% for rocks of basic composition (Kazitzin & Rudnik 1978).

Experiments carried out on extraction of the nano-fraction from the granite and the crust have revealed that for the granite its amount is 0.05 wt.% and for the crust 0.1 wt.% Whole analysis of nano-fractions for rock-forming elements and microelements has demonstrated that the rock-forming components make up 99 wt.% and trace elements about 1 wt.%. Samples of granite, crust and their NF were analysed for 40 elements. Of most interest were the chemical elements, the content of which in the solution of NP was higher than in granite and crust. The accumulation coefficient (K) was calculated as the ratio of the element concentration in NF to the content in the whole rock sample. Table 23 presents the elements that accumulate in the nano-fraction. The highest values of this coefficient, 1.5–10, were determined for Mo, Sr, Zn, Sc, Sb, Ba, Au, Ni, As, Li, U, W, Ag, Cd, Se and Pt. The value of the accumulation coefficient, which reflects the enrichment of the NF by chemical elements, depends on the type of rock and its metasomatic alteration. Such elements as Y, REE, Zr, Nb, Cs, Hf, Ta, Pb and Bi are not typical for the

NF: they are identified in whole rock analysis, and the value of coefficient K is less than 1.

To demonstrate the presence of high concentrations of chemical elements in NF solution, the solutions were evaporated at room temperature and further investigated by electron microprobe analysis.

Deposition from colloidal solutions is a common and widespread method of producing nanoparticles. The method is based on the interruption of the chemical reaction between the components of the solution, leading to the formation of insoluble compounds, at a certain time. The dispersed system is then transferred from a liquid colloidal state to a dispersed solid state. Crystallization of colloids may begin due to the change in reaction conditions. During evaporation of the colloidal salt solution, a gradual increase in the concentration of elements takes place, resulting in the decomposition of the colloidal system: the adhesion of particles into aggregates and micro-conglomerates, the crystallization of chemical compounds, and the formation and growth of fractal structures.

It should be mentioned that on removing water from a nano-fraction solution, crystalline phases are formed reflecting the NF composition, but the forms of elements in the latter differ from those in the pore and grain space of rocks. This is why it should be referred to as the secondary nanofraction (SNF).

Analysis of petrogenic oxides in the SNF of crystalline rocks was performed by X-ray microanalysis at certain points, and if the size of the phases was less than the size of the probe, for an area of 2.5 × 2.5 mm. The results of the analysis are presented in Table 24. The data obtained indicate wide diversity in sample composition. In some cases, from the results of chemical analysis it is possible to determine anhydrite, sulphur, calcium and silicate phases.

Trace elements in SNF from crystalline rocks were determined from an area of 50 × 50 μm by laser ablation followed by ICP-MS (Table 25). The experiment was controlled by analysis of the aluminium foil used as the substrate. Table 25 presents results for those chemical elements that were not detected in the aluminium substrate. The analysis revealed a high degree of heterogeneity in the distribution of trace elements over the area of the samples and also differences between samples.

Thus, experiments on the extraction and analysis of aqueous extracts from the samples of granite have demonstrated that under the influence of water, the leaching of a wide range of chemical elements of granite takes place, contributing to its chemical disintegration.

Table 13. Concentrations of chemical elements (ppm) in unaltered granite (Granite), crust (Crust) and nano-fractions (NF).

Oxides	**Granite**	**$NF_{granite}$**	**Crust**	**NF_{crust}**
SiO_2	71.30	10.64	71.0	44.51
TiO_2	0.36	0.01	0.38	0.64
Al_2O_3	13.80	24.24	14.10	17.39
Fe_2O_3	3.64	1.09	3.93	9.33
MnO	0.03	0.11	0.03	0.31
MgO	0.20	0.90	0.19	3.39
CaO	1.42	23.44	1.21	7.99
K_2O	5.98	3.66	5.88	5.58
Na_2O	2.71	2.25	2.86	1.39
P_2O_5	0.065	0.39	0.072	0.44
LOS	0.45		1.05	

Table 14. Concentrations of chemical elements in the unaltered granite (Granite), crust (Crust) and nano-fractions (NF), ppm.

Element	Granite	$NF_{granite}$	Crust	NF_{crust}
Ag	0.13	0.53	0.15	0.66
Cd	0.24	1.2	0.32	1.4
Mo	1.66	29	2.30	4.1
Sb	0.09	1.3	0.14	1.5
Se	3.19	12.5	3.88	18.4
U	7.37	39	6.49	30
W	1.79	4.1	2.06	10
As	11.72	75	14.83	71
Ba	119.52	1125	149.00	1507
Li	38.28	115	38.64	99
Sc	4.88	87	4.96	110
Sr	12.82	79	19.16	112
Zn	95.35	277	144.57	335

4.3 Classification of destruction in this study

The destruction caused by different mechanisms was classified according to Fitzner et al. (1995) and is presented in the following figure.

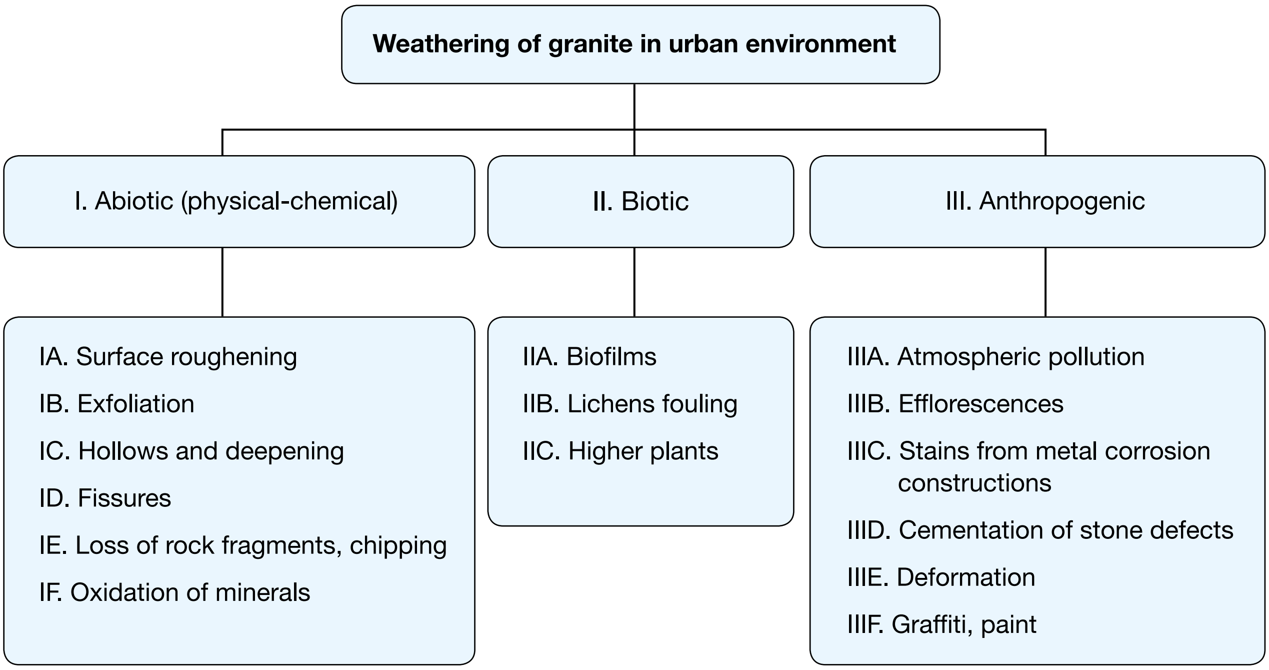


Fig. 27. Classification of destruction according to Fitzner et al. (1995).

The theory of abiotic physical and chemical weathering causing physical and chemical destruction is discussed in sections 3.2.1 and 3.2.2.

4.3.1 Physical and chemical destruction

IA. Surface roughening

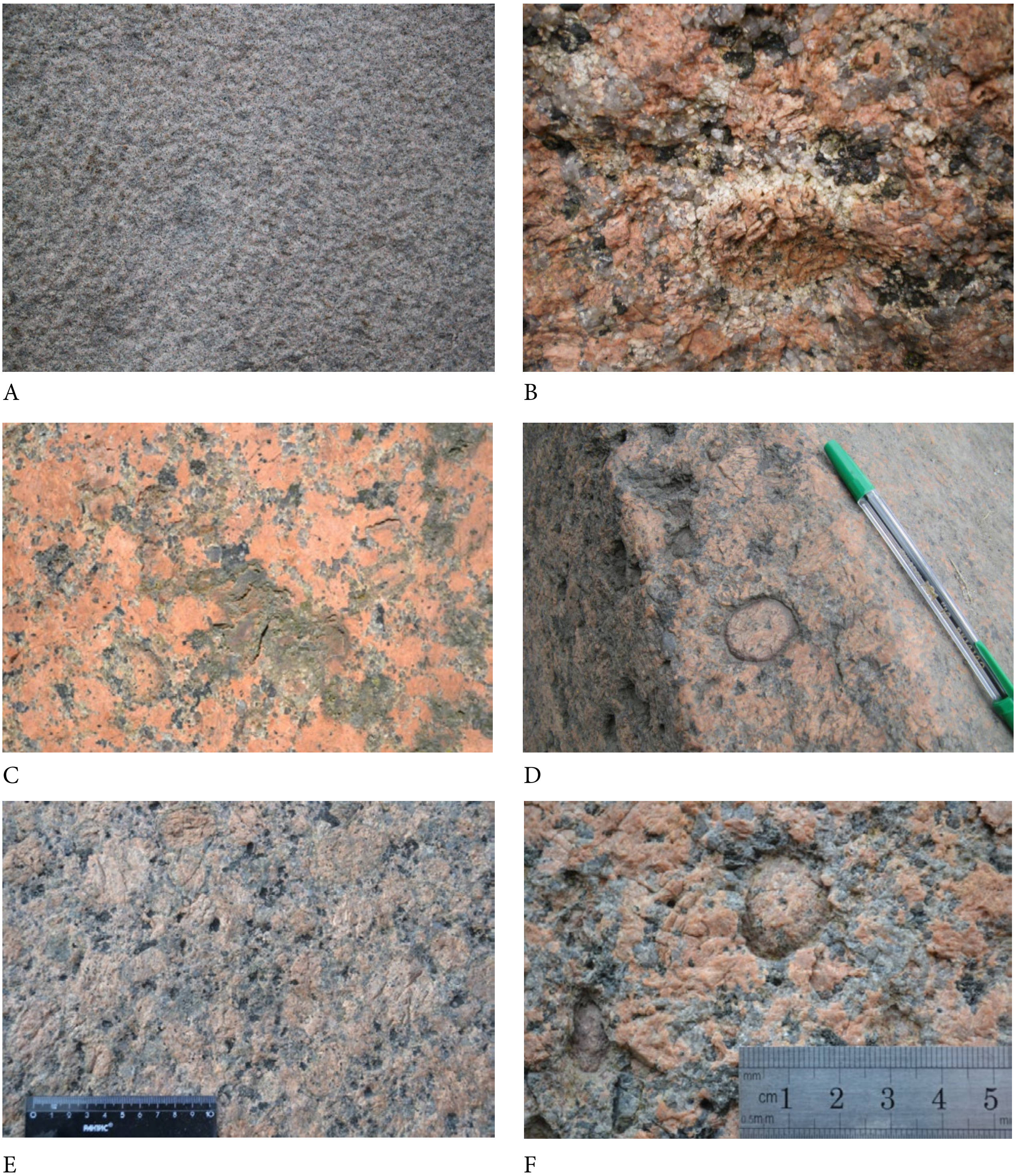


Fig. 28. Examples of surface roughening.

IB. Exfoliation

A

B

C

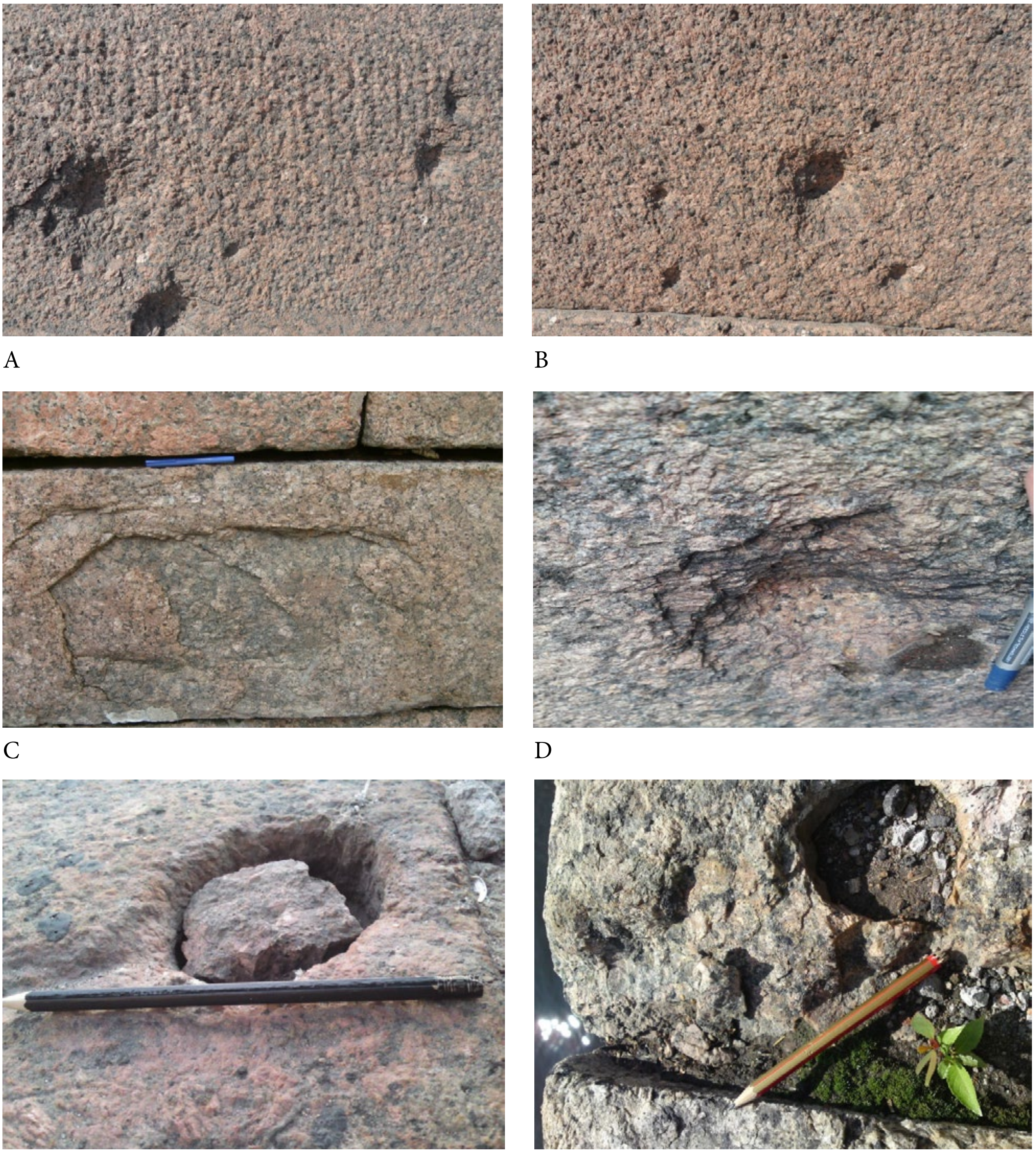
D

E

F

Fig. 29. Examples of exfoliation

IC. Hollows and deepening



A B C D E F

Fig. 30. Examples of hollows and deepenings

ID. Fissures


A


B


C


D


E


F

Fig. 31. Examples of fissures in natural stones

IE. Loss of rock fragments, chipping


A


B


C


D


E


F

Fig. 32. Examples of loss of rock fragments, chipping

IF. Oxidation of minerals

a. Oxidation of sulphide minerals

b. Oxidation of sulphide minerals in a feldspar vein

c. Oxidation of sulphide minerals in a fracture

d. Oxidation of soapstone

Fig. 33. Examples of the oxidation of minerals

4.3.2 Biotic destruction

Biogenic weathering is one of the permanent factors in granite destruction (Table 14). In comparison with the classification by Fitzner, biofilms and lichen fouling have been considered separately and in greater detail.

The classification of bio-fouling is presented in Fig. 34. Aerophilic algae dominate in green biofilms. These films cover the granite basements of buildings, embankments and historical monuments. The surfaces of the monuments at Necropolis are usually covered by green biofilms with a predominance of algae belonging to the phylum Chlorophyta (Figs 35–40). On the monuments, the algae develop in the Indentations on the surface (e.g., inscriptions). High humidity and dim lighting create optimal conditions for the colonization of the granite surface by microscopic aerophilic algae. Green biofilms that cover most of the monuments in cemeteries are irregularly distributed over the granites. The maximum concentration of algae (the most dense green surface patina) is recorded in areas of high humidity (streaks of rain water). Solid green biofilms are often formed in such places (Figs 35–36). Algae can show selectivity with respect to the minerals composition of the granite. Hence, there is a tendency for algal distribution over the inclusions of biotite and around feldspar ovoids (Fig. 38). This is particularly evident on the relatively clean surface of the stone. If there is significant contamination of the granite surface, a continuous biofilm may be formed. The most homogeneous biofilms with algal predominance are characteristic of grey Serdobol granite. Graffiti contributes to the development of green biofilms (Fig. 39). Algae hold moisture, which accelerates the destruction of granite. In addition, their development contributes to the accumulation of organic matter on the surface of granite, which is used by more aggressive destructors, for example, by micromycetes.

SEM studies indicate that unicellular and multicellular (filamentous) forms of algae develop on the granite (Figs 41–46), and the cells of diatoms (Figs 43–46) can be often found.

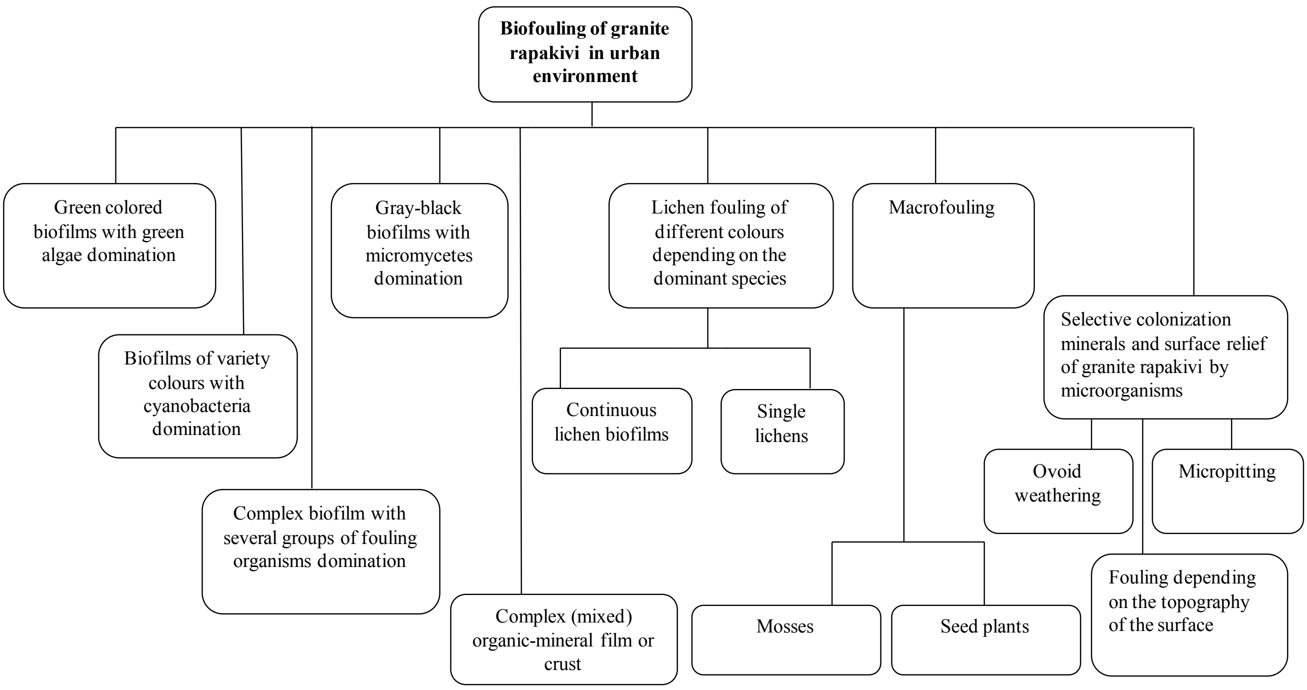


Fig. 34. Classification of bio-fouling of granite in urban conditions.

Fig. 35.A local biofilm dominated by algae on a granite column.

Fig. 36. Extensive biofilm dominated by algae on granite blocks

Fig. 37. Selective colonization of the relief (letters) on rapakivi granite.

Fig. 38. Biofilm dominated by algae on weathered granite.

Fig. 39. Biofilm dominated by algae on the sites of graffiti drawings.

Fig. 40. Biofilm of algae on the relief surface of granite.

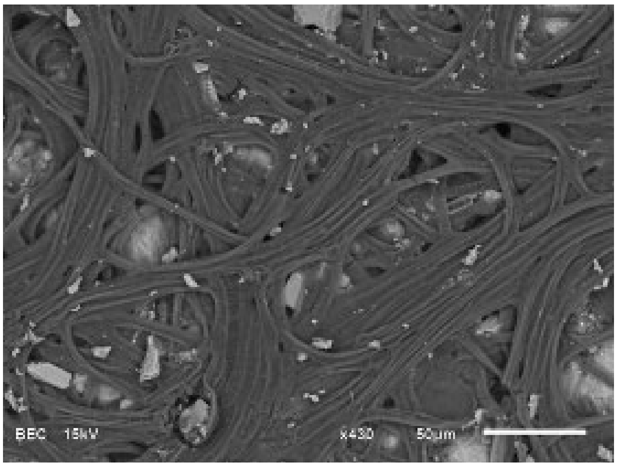


Fig. 41. Threads of algae on the surface of granite (SEM-image).

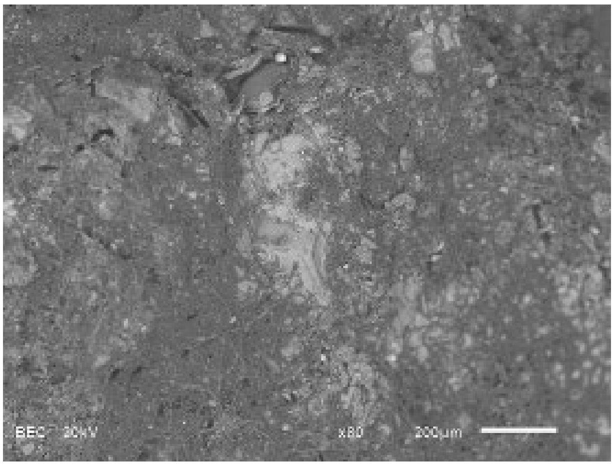


Fig. 42. The surface of granite coated with algae.

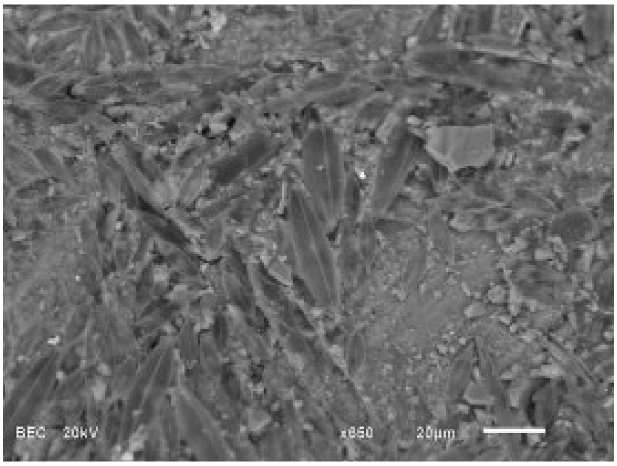


Fig. 43. Cells of diatoms on the surface of granite.

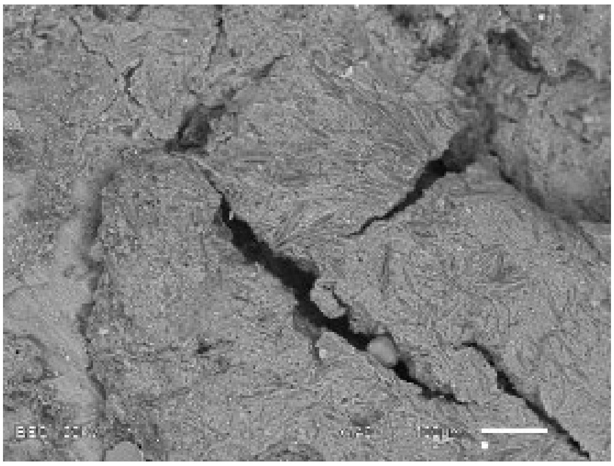


Fig. 44. Cells of diatoms on the surface of the crust covering granite.

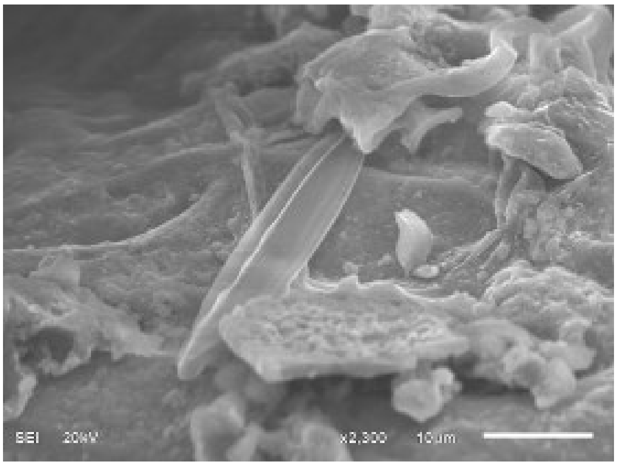


Fig. 45. A diatom cell on granite.

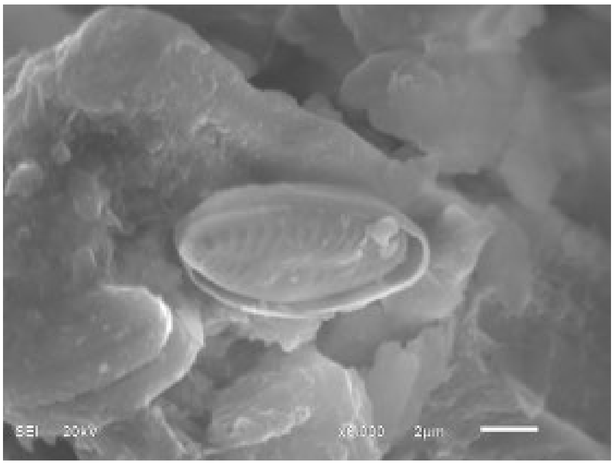


Fig. 46. Cells of diatoms on damaged granite.

Microscopic fungi and bacteria, as a rule, are found in biofilms that have a grey-black colour. Grey-black biofilms are often formed in the direction of moisturisation, often covering large areas of granite in places having a high humidity (Figs 47–52). In many cases, they are dominated by dark-coloured filamentous fungi, as well as microcolonial yeast-like fungi with a black colour (Figs 47–48). In St. Petersburg, they develop on embankments, the basements of historical buildings and the surface of monuments. Atmospheric pollution contributes to the development of dark-coloured fungi. The number of micromycetes in such biofilms can reach 10,000 colony-forming units per gram of sample.

Often, dark films associate with the development of cyanobacteria. Such films can be observed in places with a constant high humidity. They were found on many buildings in Vyborg and the Peter and Paul fortress in St. Petersburg. Their colour varies from dark green to almost black (Figs 49–52). Cyanobacteria secrete mucus, which protects them from drying out. In areas with an intensive development of cyanobacteria, they create the conditions for the development and accumulation of saprophytic bacteria. In our study, their

Fig. 47. Black crust, formed a biofilm (dominated by fungi) and atmospheric pollution.

Fig. 48. Black biofilms dominated by fungi on the surface of granite.

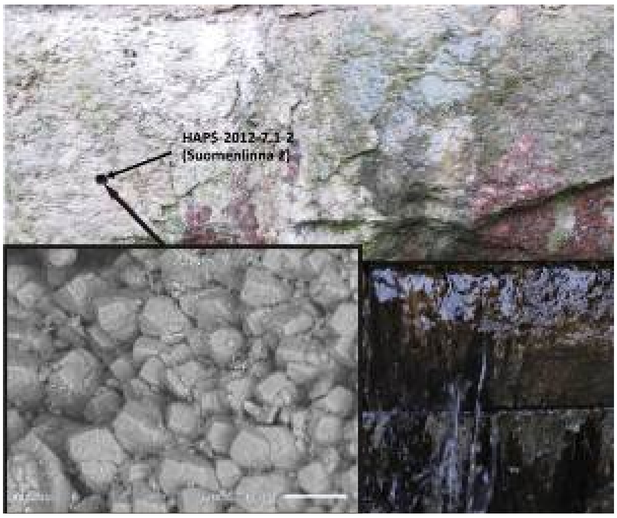


Fig. 49. Dark mucous biofilms on granite (with a dominance of cyanobacteria).

Fig. 50. Biofilm with a dominance of cyanobacteria in a zone of high humidity.

number in mucosal biofilms reached 10^7 per gram of substrate. The composition of the microbial community was dominated by spore-forming bacteria of the genus *Bacillus*. It is known that bacteria of this genus are involved in the weathering of granite (Štyriaková et al. 2012).

An SEM study of granite covered with dark biofilms demonstrated that black microcolonial yeast-like fungi occupy "microzones" in the cracks and caverns of the rock surface (Figs 53–58). They are able to penetrate under the loose flakes of stone. Dark-coloured fungi settle in the space around the crystals of the rock, as well as in the cracks and caverns.

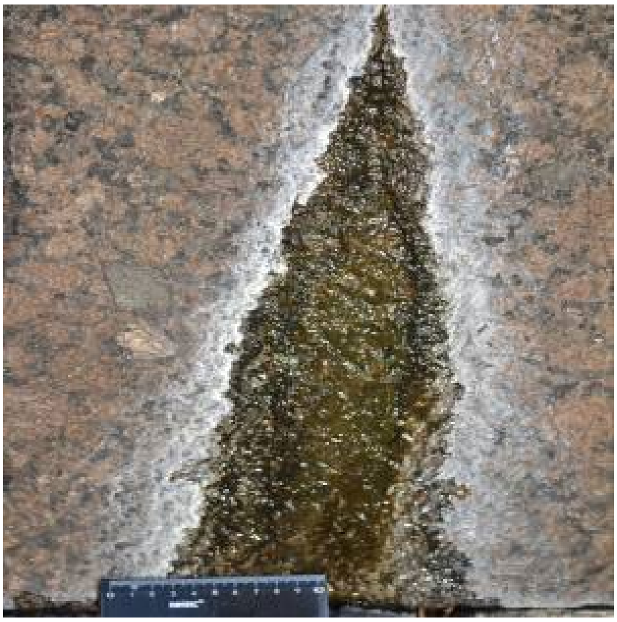


Fig. 51. Biofilm with a predominance of cyanobacteria at the site of infiltration of moisture from a crack.

Fig. 52. Black biofilm dominated by cyanobacteria.

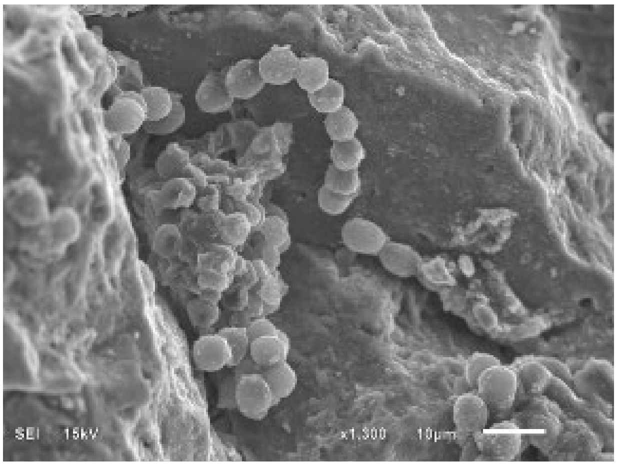


Fig. 53. Short chains of fungal cells (short hyphae) and a microcolony on the surface of granite (Peter and Paul Fortress, rapakivi granite).

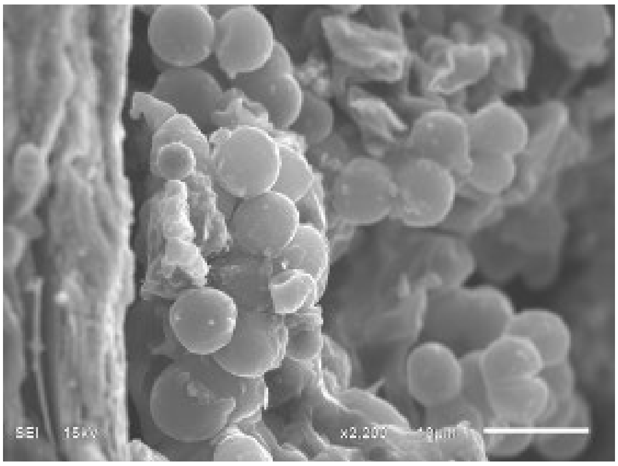


Fig. 54. Fungal microcolony on the surface of granite (Lieutenant Schmidt embankment, rapakivi granite).

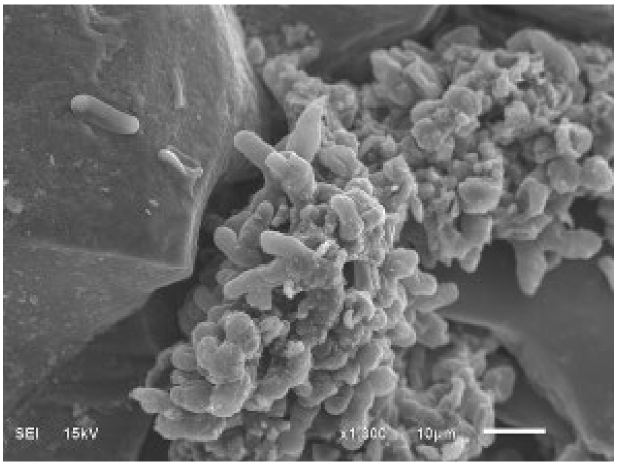


Fig. 55. Fungal microcolony on the surface of granite (in the caverns and cracks) (Kryukov canal).

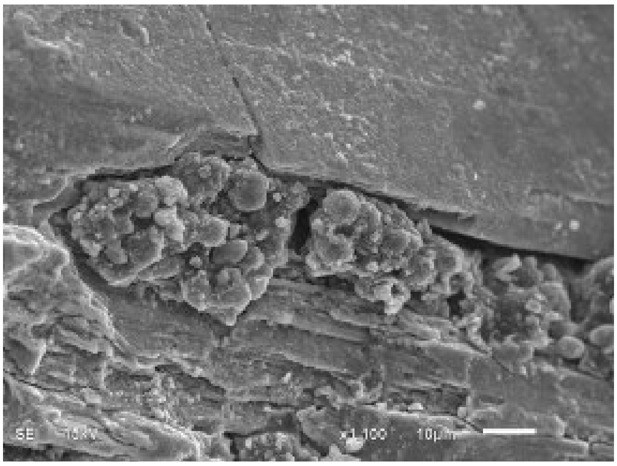


Fig. 56. Fungal microcolony on the surface of granite (Peter and Paul fortress, rapakivi granite).

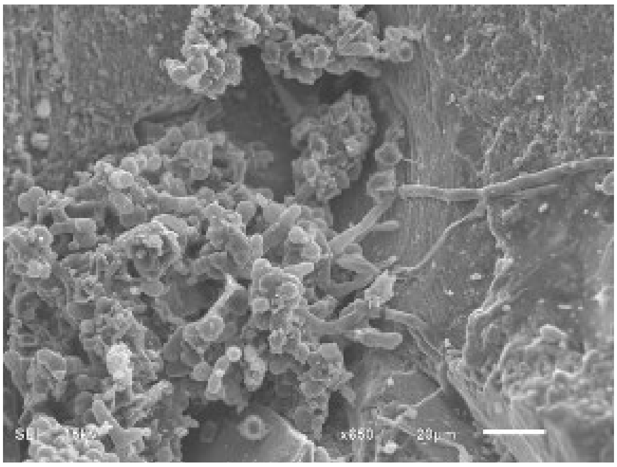


Fig. 57. Fungal microcolony and fungal hyphae in a cavern on the surface of granite (Lieutenant Schmidt embankment, rapakivi granite).

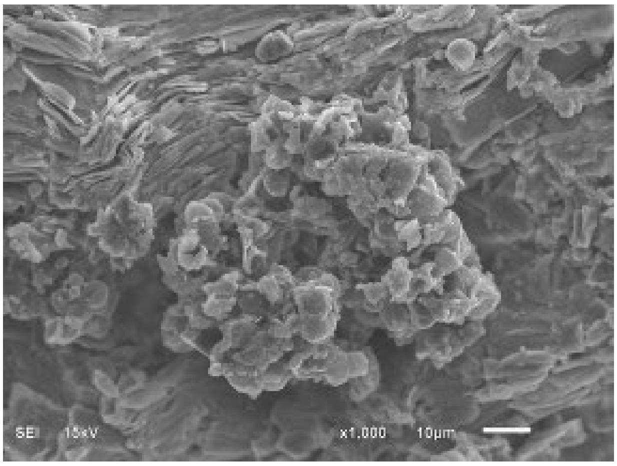


Fig. 58. Fungal microcolony in a cavern on the surface of granite. The fungal microcolony is growing on biotite (Karpovka River embankment, rapakivi granite).

The mycological study identified 29 species of microscopic fungi (Table 12) and sterile light- and dark-coloured mycelia. Dark-coloured anamorphic fungi of the species *Alternaria alternata* and *Cladosporium cladosporioides* clearly dominated on the granite embankments. They are ubiquitous in biofilms on the surface of granite, in the places where damage to granite has occurred, and in the primary soil. Dark-coloured micromycetes account for more than 30% of species on the list. *Coniosporium* sp. dominates among microcolonial dark-coloured yeast-like fungi. Its colonies are found everywhere in the micro-cracks and cavities on the granite surface. Moulds often accumulate in places of moss growth, which increases the destruction of the surface layer of the stone. Species of the genera *Penicillium* and *Fusarium* dominate among them.

Table 14. Species composition and occurrence of micromycetes in the samples of damaged granite from the embankments of Saint Petersburg

Species	Occurrence in the samples (%)
Alternaria alternata (Fr.) Keissl.	86.4
Aspergillus niger Tiegh.	18.2
Aureobasidium pullulans (de Bary) G. Arnaud	18.2
Cladosporium cladosporioides (Fresen.) G.A. de Vries	95.5
Cladosporium herbarum (Pers.) Link	22.7
Cladosporium sphaerospermum Penz.	4.5
Coniosporium sp.	59.1
Epicoccum nigrum Link	9.1
Fusarium oxysporum Schltdl.	31.8
Fusarium solani (Mart.) Sacc.	9.1
Fusarium sp.	22.7
Hormonema dematioides Lagerb. & Melin	4.5
Mucor hiemalis Wehmer	13.6
Mucor plumbeus Bonord.	22.7
Mucor racemosus Fresen.	31.8
Paecilomyces lilacinus (Thom) Samson	4.5
Paecilomyces variotii Bainier	13.6
Penicillium brevicompactum Dierckx	22.7
Penicillium chrysogenum Thom	4.5
Penicillium citrinum Thom	13.6
Penicillium decumbens Thom	4.5
Penicillium herquei Bainier & Sartory	9.1
Penicillium purpurogenum Stoll	9.1
Phaeosclera sp.	4.5
Phoma herbarum Westend.	4.5
Rhizopus stolonifer (Ehrenb.) Vuill.	4.5
Scytalidium lignicola Pesante	36.4
Trichoderma koningii Oudem.	9.1
Trichoderma viride Pers.	27.3
Ulocladium chartarum (Preuss) E.G. Simmons	22.7
Mycelia sterilia	4.5

On the contaminated areas of granite, the growth of fungal mycelia and formation of solid biofilms dominated by micromycetes was observed (Figs 54–59). It is noteworthy that the colonization of granite by fungi and crustose lichens is connected with peculiarities of the texture and mineral com-

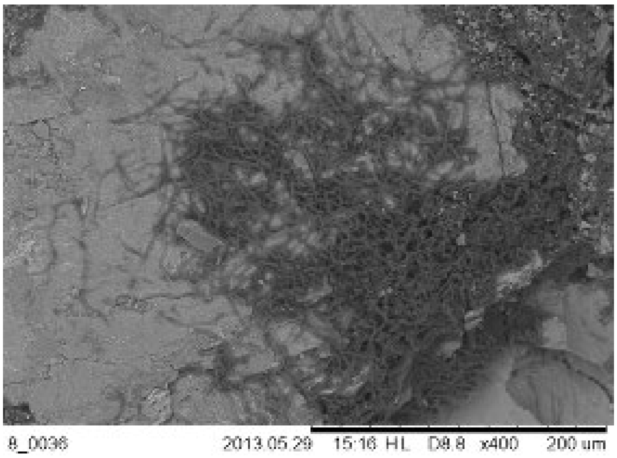


Fig. 59 Development of biofilms dominated by fungi in a zone of granite surface damage. Embankment of Griboedov Canal.

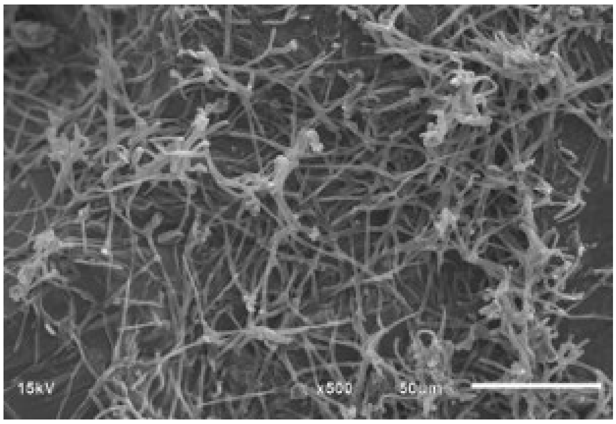


Fig. 60. Mycelium of micromycetes on the surface of granite. Solid biofilm. Robespierre Embankment.

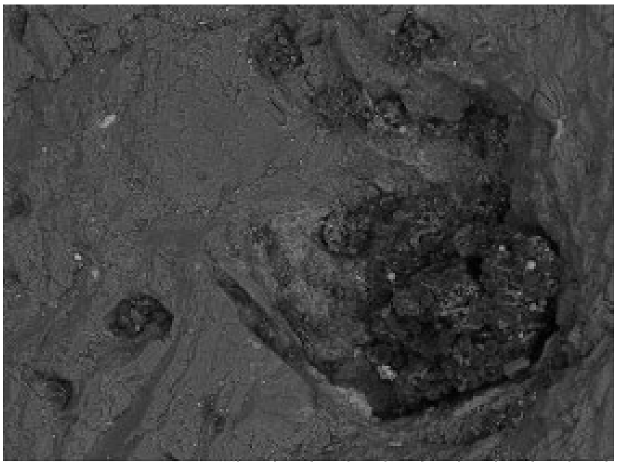


Fig. 61. Microcolonies of fungi in the caverns on the surface of granite. River Karpovka embankment.

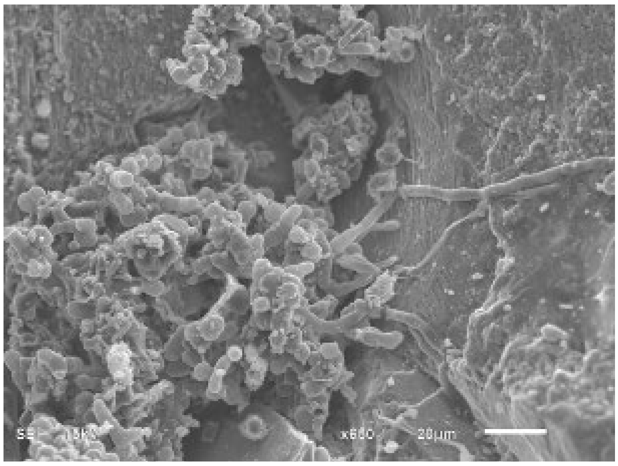


Fig. 62. Microcolonies of fungi with branching and penetrating hyphae in a zone of feldspar destruction. Lieutenant Schmidt embankment.

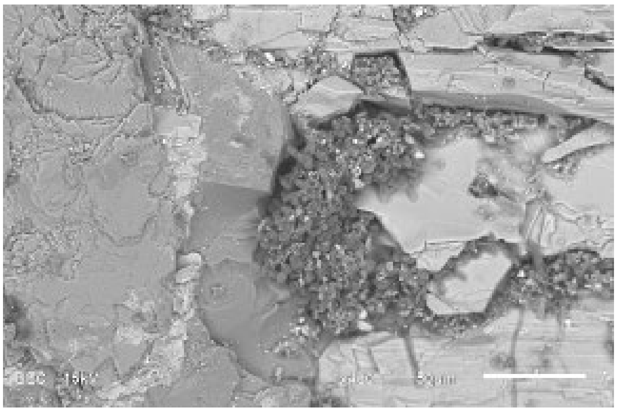


Fig. 63. Microcolony of fungus at the contact between two minerals (feldspar and amphibole). Kryukov canal embankment.

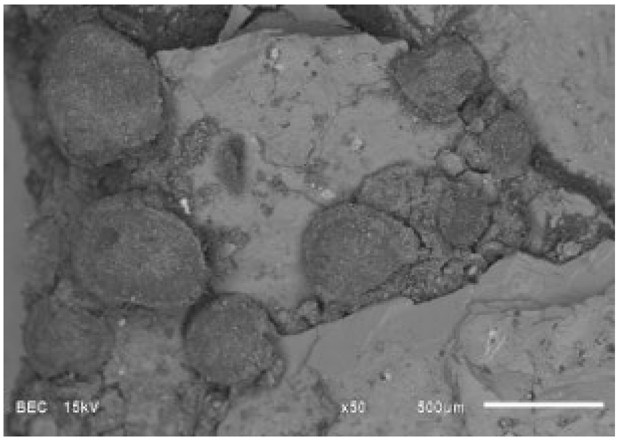


Fig. 64. Apothecia of crustose lichens in microcracks of granite. Robespierre embankment.

position of the rock (Figs 59–64). Hence, colonization of quartz by fungi is mainly observed along micro-cracks. In the process of mica colonization, the hyphae of micromycetes develop between the plates of this mineral. The accumulation of micro-colonies on feldspar is observed in zones of crystal cleavage, where a type of ledges is formed, allowing the fungi to gain a foothold on the surface of the substrate. Colonies are often formed in the contact zones between different minerals with significant heterogeneity of the surface layer and fracturing. Crustose lichens can also develop here, forming apothecia in micro-cracks of the rocks (Fig. 65).

Often crustose and foliose lichens cover a large surface of granite (Figs. 66–70). Lichens often tend to grow in the irregularities on the granite surface, including eroded areas, potholes, cracks and chips, often of anthropogenic origin.

Fig. 65. Fouling of granite by the foliose lichen *Phaeophyscia orbicularis*

Fig. 66. Fouling of granite by the crustose lichen *Candelariella* sp.

Fig. 67. Fouling of granite by the foliose lichen Physcia caesia

Fig. 68. Fouling by the lichens Phaeophyscia orbicularis, Hypogymnia physodes, Xanthoria parietina

Fig. 69 Fouling of granite by the lichen from Physciaceae familiaceae.

Fig. 70. Crustose lichen on the surface of granite

Among the 10 species of lichens found on the embankments of the historical centre of St. Petersburg (determination by D.E. Gimelbrant), 4 species were found on granite, 8 on binding solution and 2 directly on the soil. The species are represented by six genera: *Caloplaca, Candelariella, Lecanora* (2 species), *Phaeophyscia* (2 species), *Physcia* (2 species), *Xanthoria* (2 species). The most common lichen found in the binding solution and granite was *Candelariella aurella* (Hoffm.) Zahlbr.

Spore-bearing (mosses, horsetails, lycopods, ferns) and seed-bearing plants (herbaceous, shrub and woody) take part in the biological colonization of embankments. They develop locally in some areas and form a type of community in others. For plants, embankments are a special habitat, initially devoid of soil and characterized by contrasting conditions: increased evaporation of water and drying action of the wind and the sun, sharp daily temperature fluctuations and direct sunlight. In the spaces between the blocks of granite (slotted ecotopes), the conditions are more stable (Pokhilko & Kozlovski 2006), and this allows the vascular plants to gain a foothold, but they are limited by the edaphic (soil) factor. In terms of the lack of basic nutrients, oligotrophs and plants undemanding of the soil conditions are able to grow here.

A survey of seed and spore plants fouling the granite was carried out on the embankments of the following watercourses in the central part of Saint Petersburg: the Griboedov Canal, Novo-Admiralty and Kryukov Canals, the Rivers Moika, Fontanka, Karpovka and Smolenka, as well as on Neva River (Admiralty, English, University embankments and on Robespierre and Lieutenant Schmidt embankments).

As a result of the research on the granite embankments of the central part of St. Petersburg, 110 species of plants, including 107 species of higher vascular plants (97 of them identified to species and 10 only to genus) and 3 species of mosses, have been detected and identified. The plants mainly occur in the gaps between the granite blocks. Moreover, they are ubiquitous on the protruding parts of the embankments: borders, pedestals and their joints with cast-iron railings, carved ornaments and figure images. Especially active colonization takes place on the elements of embankments that have an economic purpose, such as mooring rings, signs regulating the movement of water transport, waste pipes and cables. The greatest number of species occurs near parks and gardens, which are potential sources of seeds and spores, as well as around bridges. Generally, the diversity of species is higher on the shaded side of embankments.

The vascular plants found on the embankments belong to three orders: Equisetophyta (one species – *Equisetum arvense* L.), Polypodiophyta (2 species – *Dryopteris cristata* (L.) A.Gray and *Athyrium felix-femina* (L.) Roth) and Magnoliophyta. In the order Magnoliophyta there are 15 species from 14 genera and 3 families belonging to the class Liliopsida, and 89 species from 71 genera and 22 families of Magnoliopsida. The list of vascular plants on the embankments in St. Petersburg includes 6 families that in the studied area comprise more than 6 species, 13 families represented by 2–5 species and 8 families represented by one species each. Almost all genera of the plants growing on the embankments are represented by only one species.

Mosses of 3 species are ubiquitous: *Ceratodon purpureus* (Hedw.) Brid., *Pohlia nutans* (Hedw.) Lindb. and *Physcomitrium* sp. (definition by L. E. Kurbatova). They trap moisture and create conditions for the gradual destruction of granite (Figs 71–74). Under the mosses, it is possible to observe the formation of a thin primary layer of soil, which is composed of dead fragments of mosses, particles of damaged granite, as well as sand and dust particles from the external environment. The large number of mica and feldspar particles (granite components) in the samples, which are accumulated in rhizoids, points to the destructive role of mosses.

Fig. 71. The moss *Pohlia nutans* (Hedw.) Lindb. on granite

Fig. 72. The moss *Ceratodon purpureus* (Hedw.) Brid. on granite

Fig. 73. Development of mosses in the joint between granite blocks.

Fig. 74 Caverns in granite visible after removal of the mosses.

Among the identified species of plants, 72% are indigenous (*Phleum pratense* L., *Tussilago farfara* L.) and 28% are alien (*Lycopersicon esculentum* Mill., *Lepidotheca suaveolens* (Pursh) Nutt.). Analysis of the ratio of life forms revealed that herbaceous perennials predominate (50%). In relation to moisture, the mesophytes *Betula pendula* Roth and *Trifolium repens* L. predominate (55%), in relation to the light the heliophytes *Achillea millefolium* L. and *Dactylis glomerata* L. (73%), in relation to eutrophication of the soil the mesotrophs *Potentilla anserina* L. and *Salix caprea* L. (45%), in relation to soil acidity the neutrophils *Amaranthus retroflexus* L. and *Betula pubescens* Ehrh. (86%), in relation to pollination the anemophiles *Alnus incana* (L.) Moench and *Arrhenatherum elatius* (L.) J. et C. Presl (41%), and in relation to seed distribution the anemochores *Sonchus arvensis* L. and *Erigeron acris* L. s. I. (39%).

On the embankments, the plants can grow singly as well as forming communities characterizing the environmental factors that influence their habitats (Figs 75–88). The most common communities on grey granites from Kuznechnoe, which face the embankments of the Rivers Karpovka and Smolenka, are *Polygonum aviculare* L. – *Lepidium ruderale* L. – *Artemisia vulgaris* L. *Pohlia nutans* (Hedw.) Lindb. – *Poa pratensis* L. – *Salix caprea* L. They also occur on rapakivi granites which face the embankments of the Griboedov, Kryukov and New-Admiralty canals, and the embankments of the Rivers Moika, Fontanka and Neva (Admiralty, English and University embankments).

Fig. 75. The plant *Sambuca* sp. on granite

Fig. 76. The plant *Urtica* sp. on granite

Fig. 77. *Polygonum aviculare* L.

Fig. 78. *Lepidium ruderale* L.

Fig. 79. *Chamaenerion angustifolium* (L.) Scop.

Fig. 80. *Epilobium* sp.

Fig. 81. *Artemisia vulgaris* L.

Fig. 82. *Plantago major* L.

Fig. 83. *Lepidotheca suaveolens* (Pursh) Nutt.

Fig. 84 *Taraxacum officinale Wigg.* s. I.

Fig. 85. The herbaceous plant *Poa pratensis* L. on granite

Fig. 86. The herbaceous plant *Carex* sp. on granite

Fig. 87. The woody plant *Populus suaveolens* Fisch. on granite

Fig. 88. The woody plant *Betula* sp. on granite

The investigations carried out have demonstrated that granite embankments in the central part of Saint Petersburg are subjected to considerable biological colonization (macro- and micro-fouling), which induces their gradual destruction. The development of bio-fouling accelerates the processes of physical-chemical destruction of stone caused by fluctuations in temperature and moisture, as well as by the influence of salt removal, which is notable on the vertical walls of the embankments. Rapakivi granite is most strongly subjected to damage, and its colonization is explained by the peculiarities of the mineral composition and texture. Products of stone destruction often remain in biofilms. Some sort of layering is formed on the surface of granite that consists of the cells of living organisms, products of granite destruction and air pollutants.

In general, the diversity of rock fouling in the urban environment is poorer than revealed by similar indicators in natural ecosystems (outcrops, abandoned quarries, and others). In the city, the dominance of the most adapted species, which form the basis of lithobiontic communities, is particularly noticeable. The composition and structure of these communities can be used as a bioindicator of the state of urban ecosystems.

4.3.3 Anthropogenic destruction

Anthropogenic weathering (from the Greek *anthropos* - man) is determined by the human impact on various elements of the environment, including stone. Anthropogenic impacts usually have a destructive character. The combination of anthropogenic impacts on the stone in the urban environment considers several criteria:

- The material-energy nature of the impact: mechanical, physical (thermal, electromagnetic, radiation, radioactive, acoustic), physical-chemical, chemical, biological.
- Categories subjected to the impact: the environment, people.
- Quantitative characteristics of the impact: the spatial scale (local, regional, global), individuality, and plurality of impact, the strength of impact.
- Timing: short term and long term, reversible and irreversible, intentional and unintentional.

Unintentional changes include pollution of the environment, changes in gas composition of the air, changes in the climate, acid rain, accelerated corrosion of metals and the destruction of cultural monuments, the formation of photochemical fogs (smog), violations of the ozone layer, the development of erosive processes, and ecological disasters as a result of major accidents, among others.

Anthropogenic pollution of the environment has recently acquired a global character, which has led to the sharp deterioration of stone in architectural ensembles.

We have distinguished the following types of anthropogenic weathering, which are correlated with the classification by Fitzner where possible (in parentheses): III A Atmospheric mud layers (I-C, Fig. 89); IIIB Cementation of defects in stone (Fig. 90); IIIC Efflorescence (E-C, Fig. 91); IIID Streaks from metal constructions (D-C, Fig. 92); IIIE Deformation (Fig. 93); IIIF Vandalism (aO, aR, aI, Fig. 94); IIIG Catastrophic destruction (Table 14; Fig. 95).

IIIA Atmospheric mud layers. These are connected with the blackening of stone due to black sooty layers. They cover the stone unevenly, accumulating in caverns and on horizontal parts. Areas of solid film have a rough or smooth surface, and a dull or submetallic lustre. After rubbing, the fingers become blackened. Often, the polluted areas of the stone are colonized by communities of fungi.

IIIB Cementation of defects in stone. The elimination of defects in stone and the healing joints between granite blocks is carried out using cement mortar. This is usually grey, but in the best case, granulated material granite, for example with a pink colour, is added. Recently, red putty has been used.

What happens in the case of such restoration? Cement is a more alkaline medium than granite. Chemical interaction starts at the contact of two different media, causing further destruction. First of all, it occurs because silica in alkaline conditions becomes mobile and destruction of quartz begins. This phenomenon is well known and has been described in connection with the problem of the destruction of dams built from cement with granulated granite material as the filler.

IIIC Efflorescence (E-C). Cement in the space between granite blocks is the cause of efflorescence, which can be easily seen in photos. The carbonate component is leached from the joints forming gypsum (SEM image)

IIID Streaks from metal constructions (D-C). There are two types of such streaks. The most common are streaks with a brownish colour caused by the oxidation of iron constructions and the formation of iron hydroxides on the surface of granite. In the case of copper alloy, secondary copper minerals of a bluish colour appear on the surface of granite.

IIIE Deformations. In the classification by Fitzner, deformations are considered as bending of thin, mainly marble, plates due to their plastic deformation. In the case of granite plates, deformations are connected with the roughness of the base and lifting of the nearby blocks relative to each other. The protruding parts of the plates are most strongly subjected to physical destruction, chipping of large crystals and a gradual increase in the gap between the plates. Such deformations can be seen on the historical embankments of the 18th century and in modern masonry due to the poor quality of work.

IIIF Vandalism (aO, aR, aI). Inscriptions on the stone spoil the exterior of architectural buildings and violate their integrity.

IIIG Catastrophic destruction. Examples of such damage to granite can be seen in the neighbourhood of Kronstad in the Gulf of Finland, on the islands with fortifications that have experienced fires. The laying the fireproof granite plates began in 1846. Granite for fortifications, like the other buildings in Kronstad, was taken from Pyterlahti quarry. As a result of fires, the granite had melted to plagioclase glass, which is clearly seen in the icicles hanging from the vaults and in petrographic thin sections (Fig. 96).

IIIA. Atmospheric pollution

A

B

C

D

E

F

Fig. 89. Anthropogenic weathering. Atmospheric mud layers.

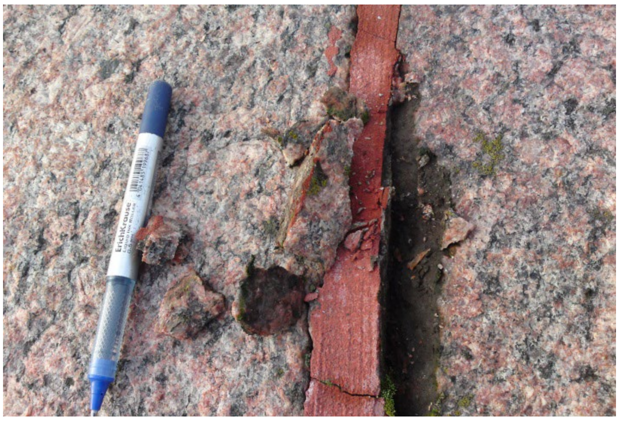
Thus, practically all types of anthropogenic weathering induce mechanical and chemical destruction. Streaks and surface formations create favourable conditions for the penetration of chemical compounds deep into the rocks, deformations of plates accelerate the process of mechanical destruction (splitting, loss of fragments) by several times, and different inscriptions on stone spoil the aesthetic integrity of the architectural object. Possible means of protection could include regular and tight paving, periodic cleaning of the surfaces, thorough individual selection of cement mortars and banning (legislative) of colour inscriptions.

IIIB. Cementation of stone defects

A

B

C



D

E

F

Fig. 90. Continued. Anthropogenic weathering. Cementation of defects in stone.

IIIC. Efflorescence

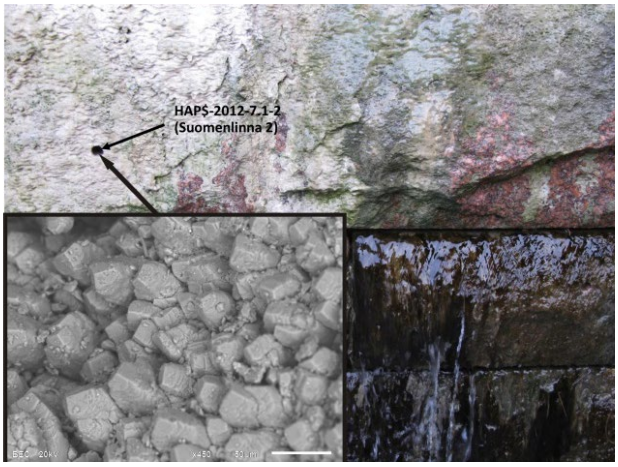
A

B

C

D

E



F

Fig.91. Continued. Anthropogenic weathering. Saline incrustations.

IIID. Streaks from corrosion of metal constructions

A

B

C

D

E

F

Fig. 92. Continued. Anthropogenic weathering. Streaks from metal constructions.

IIIE. Deformations

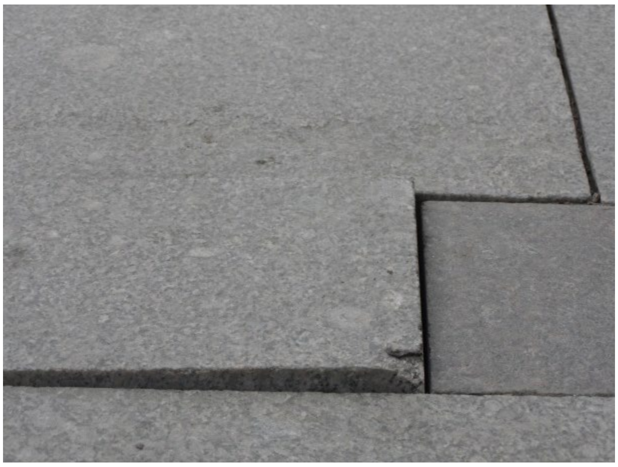
A

B

C

D

E



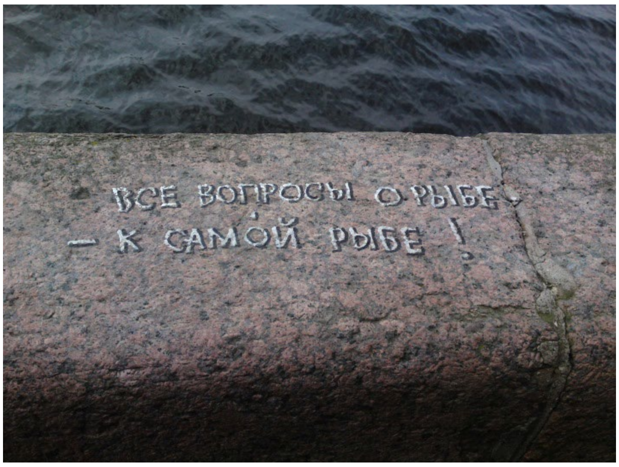
F

Fig. 93. Continued. Anthropogenic weathering. Deformations.

IIIF. Vandalism

A

B



C

D

E

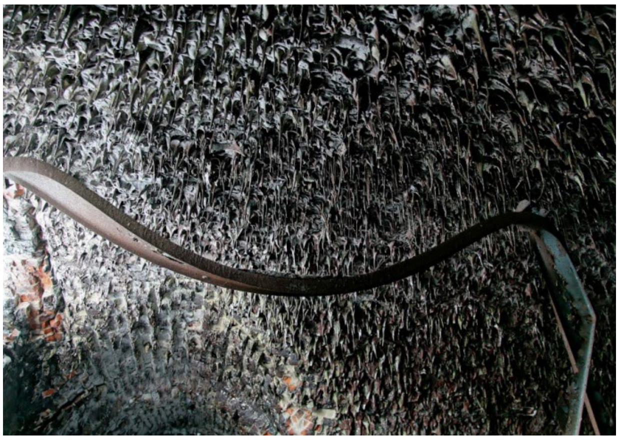
F

Fig. 94. Continued. Anthropogenic weathering. Vandalism.

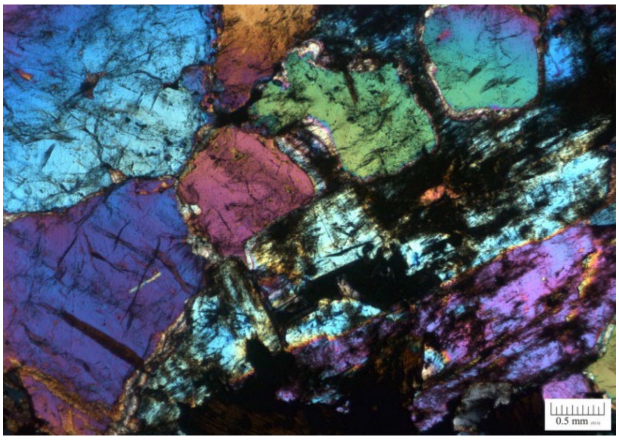
IIIG. Catastrophic destructions

A

B



C



D

Fig. 95. Continued. Anthropogenic weathering. Catastrophic destructions.

CONCLUSIONS

Local natural stone in the area between Helsinki and St. Petersburg was studied from different aspects in the project "Effective use of natural stone in the Leningrad region and Southeast Finland", belonging to the European Neighbourhood and Partnership Instrument (ENPI) of the EU. Local stone, especially rapakivi granite, has been used in the region for construction since the beginning of 18th century. A large number of stone constructions and buildings are still in good condition and represent the cultural heritage of e.g. St Petersburg, Vyborg and Helsinki. The study area belongs to the temperate climate zone with cold humid winters characterized by multiple freezing and thawing cycles per year. Thus, in these conditions, the stone surfaces are exposed to quite significant mechanical and physical weathering processes. However, 300 years of experience of its use in architecture has not made the stone look weathered.

The properties and durability of the local stone used in buildings were studied for weathering resistance, anthropogenic effects, pollution, and aesthetical aspects. Several processes of weathering such as physical, chemical and biological effects were evaluated and described on the local rapakivi granites that have been the most widely used stone types in the above mentioned cities. Generally, physical weathering caused by freezing and thawing opens the structure of stone surfaces providing a base for the accumulation of biological growth and increases chemical reactions between the stone and the atmosphere. It also detaches fine grains and dust particles, which can consists of various sizes and shapes of resistant minerals, such as quartz and feldspar, or metal particles, spherules and ash of technogenic origin.

Physical weathering mainly takes place under the influence of temperature fluctuation, the freezing and thawing of water, the crystallization of de-icing salts contained in the capillary water, the wind, the impact of biotic communities and the root system of plants. The destruction and defects on rapakivi granite were characterized with the common evaluation criteria presented by Fitzner et al. (1995). Many of the features observed, such as breaking of the slab and kerb corners, deformation of the stone structures, etc., can be interpreted as generated by human activities. Fractures, cracks and micro cracks can be observed on the stone surface by visual inspections and optical microscope. The fractured zone in the stone surface is thin however, only few millimetres. In this surface zone also other indications of the mineral disintegration can be observed, including e.g. generation of micro-heterogeneities and micro cracks within the mineral grains.

Chemical weathering is a process of chemical alteration of minerals and stones under the influence of water, oxygen, carbon dioxide, organic acids and biochemical processes. The main general factors affecting the intensity of the chemical weathering are the surface area and particle size, stone type, location, climate and time. Chemical weathering can be observed as a change of colour caused, first of all, by the decomposition of sulphides with the formation of iron hydroxides. The presence of sulphides in granite leads to their oxidation in urban conditions and the appearance of brown spots and stripes on the surface of the stone. This effect can be avoided by the appropriate choice of stone for building, i.e. without sulphides. Water penetrates the cracks and micro-cracks in the stone, creating a favourable environment for chemical reactions. Based on the micro- and macro-element composition of the samples, we can conclude that the crust is depleted for several chemical elements in comparison with the unaltered granite and the crust becomes enriched in elements such as Si, Na, Ca, Sb, As, Pb, Cu and S. The aerosols in the atmosphere carry various chemical elements that also accumulate on the stone surfaces and increase the destruction of the stone. One of the elements carried by the aerosols is mercury that was observed to be concentrated mainly in the oldest parts of the cities. It originates from industry and other human activities. Petrogenic oxides, also transported by the aerosols, have their origin in the traffic and energy production.

Background radioactivity depends on the presence of radioactive minerals in the stone. In General, the level of radioactivity of granites is not dangerous when it is used for facing the buildings, but its application in the internal poorly ventilated indoor spaces may cause accumulation of radon.

Biogenic weathering is connected with the influence of flora and fauna on the stone. The biochemical impact on the stone starts with the colonization of the stone surface by microorganisms, lichen and mosses. The biochemical component has a strong influence on mineral substances. On the one hand, it produces chemically active compounds (organic acids), while on the other hand, it stimulates the extraction of mineral substance from the minerals and contributes to the destruction of the stone. Biotic destruction of stone can consists of various types including the effects of biofilms, lichens, mosses, seed plants and microorganisms. Each form of the biotic weathering agents can be divided into several species, such as algae, bacteria, fungi, etc. The chemical components accumulated on the stone surfaces can influence on the type of biological growth that is favoured. The cracks and micro cracks on the weathered stone surface also provide a basement for the biological growth. The biological growth usually favours sites of high humidity and shadow. It is typically found e.g. on the embankments, basements and old monuments of St Petersburg. It also favours surfaces with microcracks and cavities, irregularities on the surface, eroded areas, potholes, cracks and chips, often of anthropogenic origin. Biological growth can also be attached on the cleavage planes of minerals and open spaces of the mineral structure. As the result of the research on the granite embankments of the central part of St. Petersburg, 110 species of plants, including 107 species of higher vascular plants (97 of them identified to species and 10 only to genus), 3 species of mosses and 10 species of lichens have been detected and identified.

Anthropogenic effects on stone are caused by human activities. They can be connected to initial construction process, renovation and maintenance of the buildings and structures as well as effects given by other construction materials, e.g. metal structures. Typical damages caused by maintenance work are physical breaking of stone elements by de-icing and snow clearance machinery. The combination of anthropogenic impacts on the stone in the urban environment considers several criteria, such as the material-energy nature of the impact: mechanical, physical (thermal, electromagnetic, radiation, radioactive, acoustic), physical-chemical, chemical, biological, categories subjected to the impact (the environment, people), quantitative characteristics of the impact and timing (short term and long term, reversible and irreversible, intentional and unintentional). Unintentional changes include pollution of the environment, changes in gas composition of the air, changes in the climate, acid rain, accelerated corrosion of metals and the destruction of cultural monuments, the formation of photochemical fogs (smog), violations of the ozone layer, the development of erosive processes, and ecological disasters as a result of major accidents, among others. The deformation due to movements of the stone mounting basement can be found especially in the historical areas. Vandalism and catastrophic damages, such as graffiti, changing the stone visual appearance, and fires affecting the mineral structure, both increase the weathering.

As a summary of the results of this study can be concluded that the weathering in granite and rapakivi granite elements in particular, is prominent in the depth of few millimetres on the stone surface. The combined effect of physical, chemical and biological weathering causes the mineral structure on stone surface to disintegrate, which provides conditions for freezing and thawing of water, crystallization of de-icing salts and settlement of biological growth. The effect is mostly aesthetical and doesn't have impact on the strength and durability of the elements. Anthropogenic weathering can affect the durability of the stone elements through defects caused in the construction phase, during the maintenance or in restoration works. Typical examples are movements of the mounting basement and broken corners or open joints in the stone elements.

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APPENDIX 1.

The qualimetric evaluation of a construction

Suppose, it is necessary to estimate the condition of the south façade of the main building of the Russian Academy of Science in Saint Petersburg which overlooks the Neva River (Fig.1).

The building was designed by the architect Giacomo Quarenghi in 1783–1789. Like any object of art, the building is characterized as a whole, and none of its elements can be separated from each other. However, to estimate the general condition of the façade before restoration and the necessary restoration works, it is convenient to subdivide the façade into several parts. For example, it is possible to distinguish the following parts: the granite podium of the building, the octastyle with a fronton on the jutting basement with two granite side staircases, the walls of the middle part of the building and side avant-corpses with window apertures and cornices. This corresponds to the first detailing level of subdivision of the façade. At the second level of detailing, each element is divided into certain parts, while on the third level, each of these parts is further divided into smaller parts, and so on more to more minute scales. Hence, it is possible to characterize the condition of the façade in general as well as in parts, such as decorative and constructive elements.

Poly-level model. Next, we develop a modelsubdividing the object into elements. Obviously, the model is a poly-level one: at first, the object is studied in its large elements (parts, details), and then each of them is subdivided into smaller details. This idea of consecutive detailing of the object could be described as a tree and its root system at several levels (Fig. 14). The number of detailing levels depends on the requirement for expertise. Creation of the model is the most important initial step in the procedure for estimating the condition of an architectural monument, and it should be the result of the collaborative work of architects, engineers, art historians and restorers.

Two parts of the poly-level model. Hierarchical levels in the scheme are marked from 1+ to n+ (upwards) and from 1- to m- (downwards). The higher (lower) we ascend (descend) along these hierarchical levels relative to the zero level, the more minutely we estimate the condition of the object. In general, there could be any number of levels.

Fig 1. The Russian Academy of Science in Saint Petersburg.

The upper part of the model (tree) considers purely the technical characteristics of the object. It is used to estimate the condition of the material of the monument (e.g. stone, bronze, stucco, concrete) under the influence of chemical and physical weathering, microbial contamination, vandalism and other factors. The types of damage to the materials should be classified in accordance with the international photographic atlas by B. Fitzner and K. Heinrichs (http://www.stone.rwth-aachen.de). These scientists have worked out the methods for the instrumental identification of categories and intensities of damage to materials and constructions (Expertise 2005). This system has been tested on many monuments of global importance that are protected by UNESCO.

The lower part of the model includes the artistic value of the object, the aesthetic impression and the rate of divergence of the present condition from the original idea.

Weight coefficients. Furthermore, we should evaluate the weight coefficient αi for each particular (local) index. This coefficient reflects the influence of qi index on the general condition of the monument. It is noteworthy that the coefficient αi has values in the range from 0 to 1. This is why all intermediate calculations in qualimetry are carried out with numbers in fractions of one. The results could be presented in other numbers, for example on a five-point rating scale.

Integral estimations. To calculate the integral estimations q of monument condition by n particular values of qi and αi, the formulas for weighted geometric and arithmetic average values are applied:

$$q = \begin{cases} \prod\limits^{N} q_i^{\alpha i}; \\ \sum\limits^{N} \alpha_i q_i \,. \end{cases}$$

N = number of particular indices at the same detailing level.

Limitation for the weight coefficients:

$$\sum^{N} \alpha_i = 1.$$

The theoretical basis of the calculations is presented elsewhere (Marygin & Azgaldov 2008 2010), while their application to some architectural monuments is described and summarized in a special publication (Bulakh & Marigin 2009). In practice, the following equation is used to estimate the condition of the object:

$$q = \alpha_1 q_1 + \alpha_2 q_2.$$

The first member of this equation corresponds to the artistic characteristics of the object, the second member – to technical characteristics. For architectural and sculptural monuments: α1 = 0,8 and α2 = 0,2.

For example, for four monuments of architecture and sculpture (Bulakh & Marugin 2013), the following values of q were obtained: 0.81, 0.72, 0.85 and 0.69. The values characterize the general condition of the objects as a number and will help in prioritising the necessary restoration and repair work.

Summarized index q_r of the efficiency of restoration work for objects of art (*r* means "resultant") is the difference between two numbers. The formula is obvious:

$$q_r = q_a - q_b.$$

To calculate the values of q_a и q_b, the following equations are used:

condition before restoration

$q_b = 0.8c + 0.2a$ (1)

condition after restoration

- $q_a = 0.8d + 0.2b.$ (2)

For example, it has been calculated for an architectural monument that $q_b = 0.68$, $q_a = 0.85$. This means that the quality increase resulting from restoration could be characterized by the value +0.17. The figures could help to analyse the results of restoration and the efficiency of the expenditures.

Architectural ensembles. Qualimetric methods could be applied to more complicated objects, such as architectural ensembles. It is possible to estimate their current condition taking into account seismic stability and other peculiarities of the site.

Work procedures of experts and supervisors. As an example, we shall take the Count Kushelev-Bezborodko mansion (Fig. 15). This construction is simple but at the same time complicated. Marble and granite are its decorative materials. The palace was built in 1857–1862 by the architect E. Schmidt. Its first owner was Count Nicolas Kushelev-Bezborodko, but it later belonged to Princess E. Yur'evskaya. In 1924 it housed ballet classes, and in 1927 the All-Union Scientific Research Institute of Labour Protection. It is now the location of the European University in Saint Petersburg.

The expert's work consists of the following: 1) ranking of the architectural elements, 2) ranking of the artistic characteristics, 3) making estimations. All the following calculations are organized by the leader of expertise.

<u>Step one:</u> all experts are given the same sets of Tables 5–8, which have been prepared by the leader of expertise. The leader only fills column 1. The experts rank the architectural elements of the façade according their importance and put the marks in column 2. This is complicated and crucial task and requires a high level of qualification and experience. The results are presented in Table 5. Its upper and lower parts differ in the level of detailing of the same elements of the façade. Below, the table is carefully examined.

Upper part of Table 1.

Column 1. The most important architectural elements of the façade are listed here. Their number (n) is equivalent to the number of lines in column 1, i.e. there are seven elements and seven lines.

Column 2. The expert defines the place (rank) for each architectural element according its importance relative to the other elements of the façade. The number of places (ranks) is equivalent to n (in this case there are 7). There could be ranks, such as 1–2, 5–6, and so on; 1 is the most important placing (first), while 7 is the lowest place (last).

Thus, in column 2, each element is allocated its place (rank) and it is quite obvious that different experts rank the same elements differently. However, even one expert can mark a strong or weak difference between the first and second places. Thus, a more accurate method of ranking in per cent is used. This method is not discussed here.

Lower part of Table 1.
Column 1. Here, each position (line) of the upper part of the table is divided into sub-positions, and the number of sub-positions can be different in each position.

Column 2. For each sub-position, the expert defines its place (rank). If there are 2 sub-positions, the ranks would be 1 and 2, while if there are 6 sub-positions, the ranks would be 1, 2, 3, 4, 5 and 6, and so on. Ranks such as 1–2, 5–6, etc. are also possible.

Column 3. It is noteworthy that the sums of weight coefficients of sub-positions are equivalent to the weight coefficient of the corresponding position in the upper part of the table.

<u>Step two:</u> the experts rank the artistic features of the façade. The procedure is the same as in step 1. The data are presented in Table 2. "Emotional impression" in its lower part corresponds to the first impression of the expert, while "aesthetic impression" mainly depends on the rationale and the taste of the expert in evaluating the artistic peculiarities of the façade.

Table 1. Ranks for architectural elements of the façade (mansion of Count Kushelev-Bezborodko, Gagarinskaya st., 3)

Number and the name of architectural element	**Rank (place)**	**Weight coefficient**
	First level of detailing	
1 – Finishing of the basement storey and walls	2	0.215
2 – Architectural appearance of terraces	5–7	0.072
3 – Spatial plastic forms	5–7	0.072
4 – Architectural decoration	3–4	0.161
5 – Architectural decoration of window. door and driveway apertures	1	0.250
6 – Architectural decoration of the roof. superstructure and spillway	3–4	0.161
7 – Blind area	5–7	0.072
		For the first level $\sum =$ **1.000**

Table 1. Cont.

Number and the name of architectural element	**Rank (place)**	**Weight coefficient**
	Second level of detailing	
1/1 – Basement facing	1	0.072
1/2 – Wall facing	2	0.057
1/3 – Cornice (including frieze) facing	3–4	0.036
1/4 – Rib and mould facing	3–4	0.036
1/5 – Contraction joint facing	5	0.014
		∑ = **0.215**
2/1 – Terrace railing (balustrade)	1	0.048
2/2 – Terrace walls. including those with entrance apertures	2	0.024
		∑ = **0.072**
3/1 – Mascarones	1	0.048
3/2 – Sculpture	2	0.024
		∑ = **0.072**
4/1 – Pilasters	1	0.108
4–/2 – Decorative stone carving	2	0.053
		∑ = **0.161**
5/1 – Outdoor stairs	8	0.008
5/2 – Entrance hall	1–6	0.038
5/3 – Door frames	1–6	0.038
5/4 – Door leaves	1–6	0.038
5/5 – Window frames	1–6	0.038
5/6 – Window sashes and glazing	7	0.014
5/7 – Driveway frame	1–6	0.038
5/8 – Gates	1–6	0.038
		∑ = **0.250**
6/1 – Roofing	2	0.042
6/2 – Chimneys	3–5	0.022
6/3 – Spillway pipes	3–5	0.022
6/4 – Attic trap door	3–5	0.022
6/5 – Superstructure	1	0.053
		∑ = **0.161**
7/1 – Pavement and wall jointing	1–2	0.036
7/2 – Pavement	1–2	0.036
		∑ = 0.072
		Summary for the second level ∑= **1.000**

Table 2. Ranks of the artistic characteristics of the façade

(mansion of the Count Kushelev-Bezborodko, Gagarinskaya Saint, 3)

Number and the name of the characteristic	Rank (place)	Weight coefficient
First level of detailing		
1 – Preservation of the original design	1	0.666
2 – Visual impression	2	0.333
		∑ = **1.000**
Second level of detailing		
1/1 – Originality of materials	1	0.222
1/2 – Preservation of proportions	4–5	0.066
1/3 – Preservation of colour and pattern	2	0.178
1/4 – Preservation of facing (stonework)	4–5	0.066
1/5 – Conformity with the original purpose of the building	3	0.134
		∑ = **0.666**
2/1 – Emotional impression	1	0.222
2/2 – Aesthetic impression	2	0.111
		∑ = **0.333**
		∑ = **1.000**

Step three: experts estimate the condition of the elements of the object using a five-point rating system (columns 3 in Tables 3 and 4). The highest mark is 5, and fractional values of the points are possible. All the other columns are filled by the leader of the expertise.

Step four: the experts fix in their reports of observations, special remarks, ideas and recommendations about the object in general and its parts in particular.

Table 3. Technical indices of the condition of the façade before and after restoration
(mansion of Count Kushelev-Bezborodko, Gagarinskaya st., 3)

Number and name of the architectural element	**Weight coefficient**	**Before restoration**			**After restoration**		
		Index of condition		**Balanced index of condition (2)·(4)**	**Index of condition**		**Balanced index of condition (2)·(7)**
		Points	**Fractions of 1**		**Points**	**Fractions of 1**	
1	2	3	4	5	6		8
First level of detailing							
1 – Finishing of basement storey and walls	0.215	3.0	0.50	0.108	4.0	0.75	0.161
2 – Terraces architectural appearance	0.072	3.0	0.50	0.036	4.0	0.75	0.054
3 – Spatial plastic forms	0.072	2.0	0.25	0.018	5.0	1.00	0.072
4 – Architectural decoration	0.161	2.0	0.25	0.040	5.0	1.00	0.161
5 – Architectural decoration of window. door and driveway apertures	0.250	2.0	0.25	0.063	3.0	0.50	0.125
6 – Architectural decoration of the roof. superstructure and spillway	0.161	2.0	0.25	0.040	3.0	0.50	0.080
7 – Blind area	0.072	1.0	0.00	0.000	1.0	0.00	0.000
∑	**1.000**			**0.305**			**0.653**
Second level of detailing							
1/1 – Basement facing	0.072	3.0	0.50	0.036	4.0	0.75	0.054
1/2 – Wall facing	0.057	3.0	0.50	0.028	4.0	0.75	0.043
1/3– Cornice (including frieze) facing	0.036	3.0	0.50	0.018	4.0	0.75	0.027
1/4 – Rib and mould facing	0.036	3.0	0.50	0.018	4.0	0.75	0.027
1/5 – Contraction joint facing	0.014	3.0	0.50	0.007	2.0	0.25	0.004
∑	**0.215**			**0.108**			**0.155**
2/1 – Terrace railing (balustrade)	0.048	3.0	0.50	0.024	4.0	0.75	0.036
2/2 – Terrace walls. including those with Entrance apertures	0.024	3.0	0.50	0.012	4.0	0.75	0.018
∑	**0.072**			**0.036**			**0.054**
3/1 – Mascarones	0.048	2.0	0.25	0.012	5.0	1.00	0.048
3/2 – Sculpture	0.024	2.0	0.25	0.006	5.0	1.00	0.024
∑	**0.072**			**0.018**			**0.072**
4/1 – Pilasters	0.108	2.0	0.25	0.027	5.0	1.00	0.108
4/2 – Decorative stone carving	0.053	2.0	0.25	0.013	5.0	1.00	0.053
∑	**0.161**			**0.040**			**0.161**
5/1 – Outdoor stairs	0.008	1.0	0.00	0.000	2.0	0.25	0.002
5/2 – Entrance hall	0.038	2.0	0.25	0.009	4.0	0.75	0.029
5/3 – Door frames	0.038	3.0	0.50	0.019	4.0	0.75	0.029
5/4 – Door leaves	0.038	2.0	0.25	0.009	3.0	0.50	0.019
5/5 – Window frames	0.038	3.0	0.50	0.019	4.0	0.75	0.029
5/6 – Window sashes and glazing	0.014	1.0	0.00	0.000	4.0	0.75	0.011
5/7 – Driveway frame	0.038	2.0	0.25	0.009	2.0	0.25	0.010

Table 3. Cont.

Number and name of the architectural element	Weight coefficient	Before restoration			After restoration		
		Index of condition		Balanced index of condition (2)·(4)	Index of condition		Balanced index of condition (2)·(7)
		Points	Fractions of 1		Points	Fractions of 1	
1	2	3	4	5	6		8
5/8 – Gates	0.038	1.0	0.00	0.000	1.0	0.00	0.000
∑	**0.250**			**0.066**			**0.129**
6/1 – Roofing	0.042	2.0	0.25	0.009	4.0	0.75	0.032
6/2 – Chimneys	0.022	2.0	0.25	0.006	2.0	0.50	0.011
6/3 – Spillway pipes	0.022	1.0	0.00	0.000	3.0	0.50	0.011
6/4 – Attic trap door	0.022	2.0	0.25	0.005	4.0	0.75	0.017
6/5 – Superstructure	0.053	2.0	0.25	0.013	2.0	0.25	0.013
∑	**0.161**			**0.033**			**0.084**
7/1 – Pavement and wall jointing	0.036	1.0	0.00	0.000	1.0	0.00	0.000
7/2 – Pavement	0.036	1.0	0.00	0.000	1.0	0.00	0.000
∑	**0.072**			**0.000**			**0.000**
∑	**1.000**			**0.301**			**0.654**

Table 4. Indices of the artistic characteristics of the façade before and after restoration (mansion of Count Kushelev-Bezborodko, Gagarinskaya Saint, 3)

Level of detailing. number and name of the characteristic	Weight coefficient	Before restoration			After restoration		
		Index of condition		Balanced index of condition (2)·(4)	Index of condition		Balanced index of condition (2)·(7)
		Points	Fractions of 1				
1	2	3	4	5	6	7	8
First level of detailing							
1 – Preservation of the original design	0.666	3.5	0.625	0.416	4.0	0.750	0.500
2 – Visual impression	0.333	3.5	0.625	0.208	4.0	0.750	0.250
∑	**1.000**			**0.624**			**0.750**
Second level of detailing							
1/1 – Originality of materials	0.222	5.0	1.000	0.222	5.0	1.000	0.222
1/2 – Preservation of proportions	0.066	3.0	0.500	0.033	3.0	0.500	0.033
1/3 – Preservation of colour and pattern	0.178	3.0	0.500	0.089	4.0	0.750	0.133
1/4 – Preservation of facing (stonework)	0.066	3.0	0.500	0.033	4.0	0.750	0.050
1/5 –1/5 - Conformity with the original purpo-se of the building		1.0	0.000	0.000	1.0		0.000 0.000
∑				**0.410**			**0.438**
2/2/12/1 – Emotional impression		4.0	0.750	0.167	5.0	1.000	0.222
2/2 – Aesthetic impression		3.0	0.500	0.056	3.0	0.500	0.056
∑	**0.333**			**0.223**			**0.278**
∑	**1.000**			**0.633**			**0.716**

The work of the leader of the expertise. The leader organizes all calculations (see the next chapter). It is necessary to point out that all calculations are carried out according to algorithms using special software, but in the next section the calculations are carried out manually from the methodological point of view with detailed explanations. As the result, the leader of the expertise prepares a review of the experts' reports and summarizes the remarks, opinions, observations and recommendations for the object in general and for its parts.

The results. Based on calculations using equations (1) and (2), the leader of the expertise obtained the following results:

- before restoration q_b = 0.561, or 3.3 points;
- after restoration q_a = 0.717, or 3.9 points;
- as a result of restoration, q_r in points is 0.6;
- the absolute increase in quality is +15.4%, which is calculated from the ideal condition: (0.717 – 0.563)•100% / 1 = 15.4;
- the increase in quality in relative per cent is +27.4 rel.%, which is calculated relative to the starting condition: (0.717 – 0.563)•100% / 0.563 = 27.4.

Thus, the summarized index for the condition of the façade has increased by 0.6 points. Experience indicates that this is a large improvement in the condition of the facade after restoration, and that the expenditures were not in vain.

Examples of calculations

Below are detailed explanations for the calculations in Tables 1–4.

1. Calculations of weight coefficients αi. Calculations of α_i were carried out according the formula $\alpha_i = A_i / \Sigma A_i$ (Qualimetric expertise 2008), where A_i is rank position, ΣA_i – the sum of rank positions. The procedure is similar to the sequencing described in "Qualimetric expertise" 2008 (p.108–109).

Table 1, upper part, column 3. There are seven places in the example, so:

$\Sigma A = 1 + 2 + 3 + 4 + 5 + 6 + 7 = 28; \alpha_1 = 7/28 = 0.250$,
$\alpha_2 = 6/28 = 0.214$,
$\alpha_3 = 5/28 = 0.179$,
$\alpha_4 = 4/28 = 0.143$,
$\alpha_5 = 3/28 = 0.107$,
$\alpha_6 = 2/28 = 0.071$,
$\alpha_7 = 1/28 = 0.036$.

Checking: $\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + \alpha_5 + \alpha_6 + \alpha_7 = 1.00$, i.e. the calculations are correct.

Values of α_1 and α_2 for the first and second ranges are put into corresponding lines of column 3, and for intermediate places these values are average. For example, for the rank 3–4 we have (0.179 + 0.143):2 = 0.161; for the rank 5–7: (0.106 + 0.071 + 0.036):3 = 0.071.

Table 5, lower part, column 3. In the upper part of the table there are 7 positions, each one of which is divided into sub-positions (correspondingly 5, 2, 2, 2, 8, 5 and 2 sub-positions). For each position, the values of αi are calculated separately. For example, the first line is divided into 5 lines, so:

$\Sigma A_i = 1 + 2 + 3 + 4 + 5 = 15$;

$\alpha_1 = 5/15 = 0.333$, $\alpha_4 = 2/15 = 0.133$,
$\alpha_2 = 4/15 = 0.266$, $\alpha_{3–4} = 0.167$.
$\alpha_3 = 3/15 = 0.200$, $\alpha_5 = 1/15 = 0.067$.

The sum of all αi for positions 1, 2, 3, 3–4, (original 1-2, 3–4) 5 is 1.00 (0.334 + 0.267 + 0.167 + 0.167 + 0.067), but it should be equal to α on the first level of the table (0.215). Hence, all αi values should be multiplied by 0.215 (this procedure is called the balancing of weight coefficients). Thus:

$\alpha_1 = 0.334·0.215 = 0.072$,
$\alpha_2 = 0.267·0.215 = 0.057$,
$\alpha_3 = 0.200·0.215 = 0.043$,
$\alpha_{3–4} = 0.167·0.215 = 0.036$,
$\alpha_5 = 0067·0.215 = 0.014$.

These values are placed in column 3. Their sum is 0.215.

Calculation of the values of αi in Table 6 is carried out as in Table 5. Values of α_i in Table 6 are calculated in the same way as in Table 5.

Following this: (fraction of one) = (ball – 1)/4. For example, for ball 2: (2 – 1)/4 = 0.25. For whole points, the ratios are the following: 5 balls correspond to 1.0, 4 balls to 0.75, 3 balls to 0.50, 2 balls to 0.25, and 1 ball to -0. The results are entered in columns 4 and 7 of Tables 7 and 8.

3. Calculation of particular indices. Multiplications of figures are calculated in columns 2 and 4, and 2 and 7. The values are placed in columns 5 and 8, respectively, in Tables 7 and 8.

4. Calculations of *a, b, c, d.* The values *a, b, c* and *d* are the members of the following equations:

$$q_a = 0.8d + 0.2b, \quad (1)$$

$$q_b = 0.8c + 0.2a. \quad (2)$$

a = the sum of numbers in column 5, Table 7. It is an average for two detailing levels: (0.305 + 0.301)/2 = 0.303.
b = the sum of numbers in column 8, Table 7. It is an average for two detailing levels: (0.653 + 0.654)/2 = 0.654.
c = the sum of numbers in column 5, Table 8. It is an average for two detailing levels: (0.624 + 0.633)/2 = 0.629.
d = the sum of numbers in column 8, Table 8. It is an average for two detailing levels: (0.750 + 0.716)/2 = 0.733.

5. Final calculations are carried out in the following way:

1. We apply equation (1): $q_b = 0.8c + 0.2a$.

Thus, before restoration, $q_b = 0.8 \bullet 0.6285 + 0.2 \bullet 0.3030 = 0.5028 + 0.0606 = 0.563$. In points – 3.3.

2. We apply equation (2): $q_a = 0.8d + 0.2b$.

Thus, after restoration, $qa = 0.8 \cdot 0.733 + 0.2 \cdot 0.654 = 0.586 + 0.131 = 0.717$. In points – 3.9.

3. Calculation of the general index for the efficiency of the work carried out:

$$q_r = q_b – q_a = 0.717 – 0.563 = 0.154.$$

The condition of the façade has improved by 0.6 points (3.9 - 3.3).

4. Calculation of quality increase in absolute per cent:

$$(q_r \cdot 100) / 1.000 = 0.154 \cdot 100 = 15.4.$$

5. Calculation of the quality increase in relative per cent:

$$(q_r \cdot 100) / q_b = (0.154 \cdot 100) / 0.564 = 27. 4.$$

Comparison of indices

What estimation indices could be obtained after the restoration of architectural monuments? In the case of our example, the final estimation for the efficiency of restoration of the façade of Count Kushelev-Bezborodko's mansion increased by 0.6 balls. This is a considerable increase, although there are no statistics for such estimations. However, it is impossible to reach the original condition. Why? No restorer is the architect of the monument. No one can repeat the unique combination of the architect's ideas and the aesthetic trends of the epoch. Also, it is not always possible to use original material and technology in restoration.

The results of restoration for four sites on St. Petersburg are compared in Table 5.

Table 5. Condition of some objects after restoration.

Object	Address	Increase/loss Rel.. %
Sphinxes (eastern and western)	University emb.	+15 +19
Kushelev-Bezborodko mansion	Gagarinskaya st., 3	+27.4
Russian Bank for Foreign trade	Bolshaya Morskaya st., 32	-20.6
Palace of the Great Prince Mikhail Mikhailovitch	Admiralty emb., 8	-14.6
Kazansky Cathedral	Kazanskaya sq., 2	-18.0

The results of qualimetry are exceptional: the effect of restoration could be negative. This problem has been discussed elsewhere (Bulakh & Marugin 2013).

APPENDIX 2.

Characteristic of the main groups of microorganisms – destructors of granite

As a rule, heterotrophic microorganisms are as described as potential destructors of granite (Hutchens 2003). However, biodestructors can be chemolithotrophic microorganisms, such as thiobacteria, nitrifying bacteria and iron bacteria (Dierck et al. 1991, Gusev 2008). The following groups of microorganisms are abundant and often described in the literature as destructors of granite.

Silicate bacteria are a weakly studied group of bacteria. There is an assumption that these microorganisms can grow on silicate rocks, contributing to their destruction. They can dissolve silicates and aluminosilicates. Silicate bacteria were observed on quartz, feldspar and clay minerals. This group includes bacteria of the genus *Bacillus*: *B. siliceous* and *B. mucilaginosus* (Nyanikova & Vinogradov 2000).

Actinomycetales (actinobacteria) are heterotrophic bacteria that have the ability to form a dendritic mycelium at some stages of development. Most actinomycetales are aerobes; facultative anaerobes are found among the actinomycetales with a short mycelium stage. Soil is the main habitat for actinimycetales (Saiz-Jimenez 1999). Actinomycetales are abundant on the surface of facing materials (Pessi et al. 2002). Their influence on granite is discussed later.

Photoautotrophic organisms, for example, microscopic green algae and cyanobacteria, are often considered the pioneers of the colonization of rocks in the open air, because they are not dependent on the presence of organic matter (Warscheid 2000). Algae are able to excrete into the environment various products of assimilation, including amino acids, sugars, growth substances and antibiotics. These substances are often a source of nutrition for chemoorganotrophic bacteria and fungi and can have a significant impact on the substrate. Algae can form biofilms (usually green). Among algae dominating on the surface of granite are representatives of the division Chlorophyta (green algae) (Karaca et al. 2011).

Microscopic fungi (micromycetes) are heterotrophic microorganisms that use various organic substances from the substrate or from the external environment as a source of energy for growth and development. Metabolites or residues of algae, lichens and bacteria can serve as a source of nutrition for the fungi. The destructive activity of micromycetes is caused by their chemical and mechanical (physical) influence on the substrate (Silverman 1979, Berthelin 1983). The main damaging factors in the growth of micromycetes on the surface of granite are the excretion of aggressive metabolites (primarily organic acids and enzymes), as well as the ability to mechanically penetrate into the thickness of the substrate along microcracks (Walsh 2001). The most common fungi on rocks are soil fungi of the genera *Penicillium*, *Aspergillus*, *Cladosporium* and *Fusarium*. Some scientists consider these fungi as the most harmful group of organisms settling on the facades of buildings in the urban environment (Krumbein 1988). They are able to utilize a wide range of nutrients. Even trace amounts of organic matter can stimulate their growth and be used as a source of energy.

The visual impact of fungi on rock can be manifested in both the destruction of the stone and in the formation of black spots on the surface of the substrate. Fungal hyphae are found at a depth of several millimetres from the surface of the stone. Fungi inside cracks form complexes with biomineral formations of calcium oxalate and calcite. This layer of microbial communities and mineral formations creates internal pressure and leads to exfoliation of the rock (Bennett 2001).

The above-discussed microorganisms form microbial communities that often cover granite in natural outcrops and in the urban environment. Microbial damage of stone enhances and accelerates the process of weathering, resulting in the crumbling of the surface layer of the stone, and the formation of recesses (an uneven surface) or surface sediments (crusts).

Environmental conditions are crucial for colonization of the stone substrate by microorganisms. In many cases, the composition of microbial communities is determined by the substances deposited from the atmosphere or deposited on the stone surface in other ways. The main sources of these substances may be rain and groundwater, soil and the atmosphere, as well as the surrounding flora and fauna. External conditions determine the accumulation on the surface and inside the rocks of organic matter differing in chemical origin, including cellulose, pectin, starch, proteins, organic compounds of alcohols, fats and aldehydes. All of these can be utilized by heterotrophic organisms of the microbial community forming on the surface of the stone. High amounts of heavy metal salts, aliphatic and aromatic hydrocarbons, sulphur, phosphorus, chlorine, nitrogen, carbon and other elements are deposited in industrially polluted areas on the surface of granite as a result of gravitational forces and precipitation. On the one hand, depositing substances can serve as a source of nutrition for heterotrophic organisms in the urban environment. On the other hand, toxic components of precipitation are able to inhibit the development of surface microbiota (Saiz-Jimenez 1997).

Biofilms represent communities of microorganisms attached to a substrate. They consist of representatives of one or several different species of microbes. The cells of microorganisms in the biofilm are immersed into an organic matrix of microbial origin, which is composed of polymeric substances: polysaccharides, lipopolysaccharides, proteins, glycoproteins, lipids, glycolipids, fatty acids and enzymes. It plays an integrating role and stimulates adhesion (attachment) to the substrate. The metabolic products of microorganisms (mucus and other extracellular polymeric substances, the remains of the dead cells and thalli) can stick together with mineral particles forming a kind of "biomineral" surface layer. The size and texture of such films in many respects are determined by the properties of the substrate and a combination of external factors (Mitchell & Gu 2000).

In biofilms bacteria are tightly attached to the substrate and they extract inorganic compounds from the mineral matrix and organic compounds necessary for life (Frey et al. 2010). The appearance of biofilms on granite is stimulated by accumulation of contaminants on the surface of the substrate. The development of biofilms can lead to changes in the hydrothermal characteristics of the material (Urzi et al. 1993, Dornieden et al. 2000, Warscheid 2000). The change in porosity is accompanied by disruption of the circulation of moisture within the material. Exsopolymers cause water retention in pores, increasing the pressure. Biofilms reduce evaporation from the surface of the stone.

The formation of biofilms starts with changes in the colour of the substrate surface caused by the accumulation of organic pigments (chlorophyll, melanin, carotinoids and others). Often, these are partly composed of mineralized chlorophyll of cyanobacterial origin or the pigments of green algae. They are complemented by coloured iron and manganese oxides, which are formed under the influence of fungi. Coloured primary biofilms can be subdivided into the following: dark coloured biofilms due to the presence of melanin, melanoides, products of chlorophyll degradation, iron and manganese minerals; green and greenish biofilms due to photosynthetic pigments of algae and cyanobacteria; yellow-orange-brown biofilms (caratini, carotenoids, products of chlorophyll decomposition, such as ficobiliproteins); and bright orange, pink and reddish biofilms due to the presence of pigments of chemoorganotrophic (halophilic) bacteria, as well as products of cyanobacterial and algal degradation, which are rich in iron (Urzi et al. 1993). The formation of biofilms can be considered as the initial biophysical effect on the surface of granite.

Excretion of organic acids is one of the important causes of microorganism impact on mineral substrates. While excreting these acids, the microorganisms have a direct chemical effect on the processes leading to alteration of the mineral composition of rock, especially at the site of attachment to the substrate. Organic acids react with silicate minerals and leach metals, forming complexes of oxalate, including complexes with aluminium and iron (Griffin et al. 1991, Welch, McPhail 2002).

Some scientists have pointed out that in the formation and distribution of lithobiontic films, external environmental factors play a greater role than the properties of the stone (Sanjurjo-Sánchez et al. 2012).

Here are presented some examples of the impact of bacteria on granite. In particular, it has been demonstrated that actinobacteria stimulate the destruction of rapakivi granite. The dominant genera of actinomycetes extracted from damaged granite in our study were *Nocardia* and *Streptomyces*. Actinobacteria are able to form dendritic threads and thus to gain a foothold on the substrate and accelerate mechanical and chemical weathering of the rock. It is necessary to mention the possible biotechnological impact of actinomycetes on granite. They are able to take part in bioremediation (biological treatment) of the surface of stone contaminated with metals. Some actinobacteria can precipitate such metals as copper, iron, zinc, cadmium and silver (Hesham 2009).

Some bacteria (such as species of the genera *Arthrobacter*, *Janthinobacterium*, *Leifsonia* and *Polaromonas*) can produce hydrocyanic acid (HCN).

It has been experimentally demonstrated that the simultaneous excretion of hydrocyanic and oxalic acids by bacteria increases the solubility of K, Ca, Fe, Na and Mg (Frey et al. 2010).

Spore-forming bacteria of the genus *Bacillus* are often found on granites. Bacteria of this genus are able to withstand unfavourable conditions on the stone surface due to the formation of spores. The participation of bacteria of the genus *Bacillus* in the weathering of granite has been noted. It has been experimentally demonstrated that *Bacillus subtilus*, as a result of its impact on granite, forms caverns. Bacteria are selectively attached to minerals and "consume" important elements from them. Plagioclase is more exposed to the impact than biotite (Song et al. 2007). In general, it is noteworthy that many microorganisms selectively colonize minerals. For example, on quartz there are more simple communities in comparison with the other minerals. The chemical formula of quartz is simple, SiO_2, and it limits the nutrition of bacteria to a greater extent than other minerals. However, surface contamination can change the number and variety of microorganisms (Gleeson et al. 2005).

Some studies on the impact of *Pseudomonas aeruginosa* on rapakivi granite have been carried out by Vuorinen et al. (1981). They observed higher concentrations of Na, Ca, K, Fe and Mg in the culture solution after incubation. The elements were mainly leached from feldspar ovoids, and iron was leached from biotite. During this, the microorganisms colonized the substrate step by step, changing their number and variety (Bennett et al. 2001).

In general, the processes of destruction are complex, involving inorganic (hydrolysis of minerals) and organic (biocolonization) phenomena. Both of these effects intensify in their combined (synergistic) impact on the rock. For example, the weathering of mica stimulates the adsorption of water and biocolonization, and fungal colonies retain water, leading to hydrolysis and destruction along the weaker sites on the rock (Blazquez et al. 1997).

APPENDIX 3.

Lichen – destructors of granite

Lichens, which represent a symbiosis of two organisms, a fungus and algae, are perfectly adapted to life on rocky substrates. They actively develop on carbonate and silicate rocks, concrete, tile and other materials and stimulate the accumulation of moisture and organic matter on the surface layer of stone (Edwards & Perez 1999). Among lichens living on silicate rocks, some settle mainly on acid (porphyry, granite) rocks and others mainly on basic (basalt, diabase) rocks. Lichens of rocky substrates are divided into epilithes living on the surface of the substrate and endolithes that penetrate into the rocky substrate. Endolithes, in turn, are subdivided according to the degree of penetration into the stone:

cryptoendolithes – colonize structural cavities within porous rocks;
chasmoendolithes – colonize fissures and cracks in the rock;
euendolithes – actively penetrate into the interior of rocks

Some scientists consider the physical impact of lichen as the main impact type (Carballal et al. 2001). However, it should be noted that weathering of granite under the influence of lichen is a complicated physical-chemical process.

Lichens produce organic acids with chelating activity, which can dissolve minerals and form complexes with metal cations. One of the most studied acids exuded by lichens is oxalic acid. Some types of crustal lichens can produce more than 50% of their total weight in oxalic acid. Metabolites of lichens cause changes in the surface layer of the stone directly under the structure of the lichen. As a result, the main chemical elements of stone are released (Al, Mg, Mn, Zn, Si, Ca, K, Fe) and some of them also accumulate (Adamo & Violante 2000).

Lichens stimulate the precipitation of iron oxides and the formation of secondary clay minerals and crystals of metals oxalates. Crystallization of salts of biogenic and abiogenic origin in the pores and cracks of stone produces sufficient pressure on individual minerals or fragments of stone. Secondary salts, formed as a result of the interaction of organic and inorganic acids with the mineral substrate, cause the disaggregation of minerals. Oxalates are an example of secondary salts (Chen et al. 2000).

When lichen dies it leaves signs of spotty corrosion due to metabolic activity and the inclusion of mineral fragments in the thallus. In some cases, the crust of lichen can protect the substrate from destructive agents (Tiano 2002).

At the initial colonization of granite by lichen, they use all the weathered sites, boundaries between grains and tiny cracks in the rocks where the fungal hyphae can better penetrate. (http://www.ecosystema.ru/08nature/lich/i04.htm) As a result of hyphal penetration into stone, surface water can reach a considerable depth. When water freezes, splitting takes place caused by the expansion and swelling of the thallus. This mechanism of destruction (freezing – thawing) influences the strength of granite, especially in cold regions. Lichens also cause the disintegration of grains on the surface of the stone and capture mineral particles using the thallus. The release of rock elements primarily depends on the sensitivity of minerals to weathering. In granite, calcium and sodium are easily released from plagioclase and potassium is released to a lesser extent, as it occurs in stronger minerals such as K-feldspar and muscovite (Silva et al. 1999).

Petrographic and electron-microscopic studies have demonstrated that hyphae penetrate into the stone mainly through inter-crystalline spaces, but in some cases along the cleavage surfaces of mica and feldspar. The depth of penetration can be more than 4 mm. The growth of hyphae takes place in a different direction and traces the pores of the rock. Hyphal penetration causes disintegration, the destruction of grains and inclusion of grains in the thallus. Mica is broken down into small crystals, and quartz and feldspars into larger grains (Carballal et al. 2001).

It was observed that in many solid rocks, hyphae of endolithic lichens penetrate into the stone in the areas occupied by mica and develop further due to the chemical destruction of the rock. Hyphae destroy layered crystals of mica rather rapidly. Here, they are branched and push plates of mica apart from one another. As they slowly grow and branch, hyphae form fungus plectania, or a false fabric of fungi, through the intertwining of hyphae. The algal cells then penetrate into this plectania, where they multiply and twine, pushing separate pieces of mica away. Thus, in granite, mica is the mineral that is most exposed to physical (penetration of hyphae) and chemical (exposure to organic acids) impacts (Favero-Longo et al. 2005, Chen et al. 2000).

Through the destruction of solid rocks, turning them into a granular mass, endolithic lichens act as the pioneers of vegetation. They prepare the surface of rocks for colonization by other organisms, including foliose and bushy lichens, mosses and flowers.

APPENDIX 4.

Mosses and seed plants, colonizing the stone in urban environment

Embryophytes often develop on the rocky substrate in the urban environment. Basements of historical and modern buildings and monuments colonized by mosses and herbaceous plants are such examples. It is known that the appearance of plants on the rocky substrate leads to its destruction (Pope et al. 2010). Monuments constructed of both carbonate and silicate rocks suffer in the same way. The structure of granite and the presence of cavities and cracks are often additional factors in biological colonization. The appearance of moss, grass and even woody plants most often occurs in places where there is noticeable destruction of the stone. Organic matter and the ever-present moisture accumulate in the forming cavities and cracks, which creates favourable conditions for plant development. Moreover, seed and spore plants can colonize large spaces between blocks of stone. The destructive effect is expressed both in the immediate physical impact of plants on the stone and in creating conditions for the development of an aggressive microbial community.

In general, all types of weathering are closely interrelated and interdependent. Physical weathering causes the mechanical disintegration of granite and rock forming minerals, creating favourable conditions for chemical and biological weathering, and these, in turn, increase physical destruction. The destruction of stone in the urban environment increases under the influence of anthropogenic factors and agents.

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Natural stone is a traditional material that has been used for construction throughout human history. It has usually been quarried from areas close to where buildings have been constructed. On the eastern coast of the Baltic Sea, local rapakivi granite was easily available and the most commonly used stone during the construction of St. Petersburg, Helsinki and Vyborg. Other local stones have also been used in smaller amounts. This study describes the durability of local stones in the city environment from the beginning of the 18th century until today. It deals with biological, chemical and physical weathering processes and destruction characteristics, and also discusses the research methods and their suitability for evaluating the weathering and durability of natural stone.

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