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Olga V. Frank-Kamenetskaya
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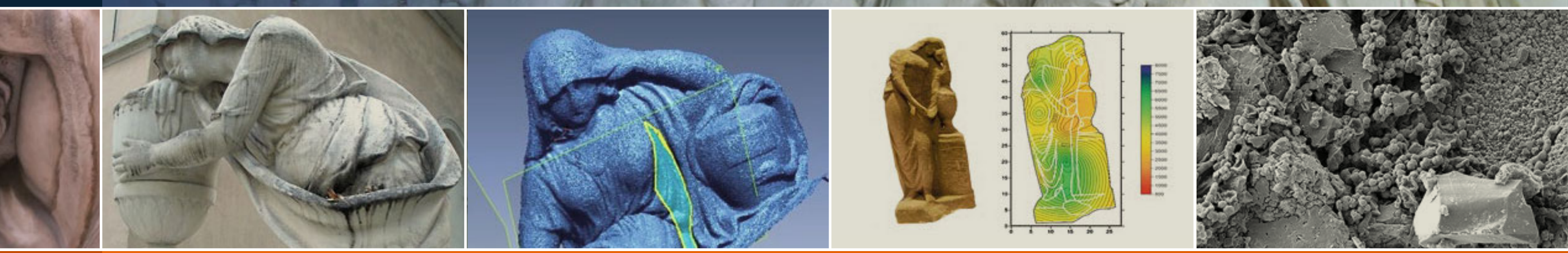

The Effect of the Environment on Saint Petersburg's Cultural Heritage

Results of Monitoring the Historical Necropolis Monuments

Springer

Geoheritage, Geoparks and Geotourism

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Foreword

In this easy-to-read, beautifully designed, and well-conceived book, the results of a long, multifaceted study of the impact of the environment on the state of St. Petersburg monuments in the open air are presented. It is written by a team of different specialists—historians, art historians, museum curators, geologists, biologists, chemists, technologists, engineers, and, of course, restorers. At the same time, the book is excellently illustrated and uniform in style. Its authors are both eminent and young scientists and their undergraduate and postgraduate students, who subordinated their work to the goals seemingly simple but noble and lofty—to preserve the existing monuments of cultural heritage and pass their expertise, methods, ideas onto the others.

The main objects of the research are the monuments in the Necropoleis of the State Museum of Urban Sculpture in St. Petersburg, whose state was assessed over many years of monitoring. The book provides carefully verified facts and observations, presents original genetic models and a system of monitoring, including a numerical estimate of the state of the monuments, and proposes an integrated concept, a strategy for preserving monuments in the open air.

No doubt, the book meets the highest world standards of publications of this kind and will be important for the work of a wide range of expert professionals, first of all, custodians of sculpture and restorers and those in other fields of knowledge (geologists, biologists, chemists, engineers, etc.) dealing with urban ecology and its influence on cultural heritage sites. It is designed in such a way that it is attractive and interesting for everyone who is not indifferent to the history of the world culture and the problems of preserving cultural values.

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Introduction

Preservation of the monuments of cultural heritage is one of the priorities of the modern society. This problem becomes especially acute where the monuments are exhibited in the open air and subjected to destructive effects of the environment. In large cities, such as St. Petersburg, the deterioration of natural stone is notably fast, which is primarily due to the influence of the anthropogenic factor. The book presents the results of a multiyear, comprehensive study of the state of historical monuments of St. Petersburg, which are exposed to the destructive impact of the urban environment. Its authors faced a task to fully describe the main approaches to the monitoring of cultural heritage sites, drawing on the world experience and the data accumulated by the authors. The main specific aspect of this work was the application of an interdisciplinary approach to the tasks.

The basis of this monograph is the book "Monuments of the Museum Necropoleis of St. Petersburg. Conditions of their existence, materials, diagnostics of integrity," published in Russian in 2016 (St. Petersburg, VVM Publishers), which summarizes the results of a long-term monitoring of the monuments in the Necropoleis of the State Museum of Urban Sculpture of St. Petersburg.

The State Museum of City Sculpture is a unique open-air museum. In its charge are collections of St. Petersburg monuments and memorial plaques, works of memorial art of the eighteenth to twentieth centuries, outstanding in their artistic and historical value.

A particular attention is paid to the Necropolis of the eighteenth century, where there are more than a thousand surviving tombstones of the eighteenth century and the first half of the nineteenth century. With a few exceptions, the tombstones are made of stone, primarily marble and limestone—the materials most vulnerable to the destructive influence of the volatile and humid Petersburg's climate and unfavorable ecological situation. The task of preserving this rare, historically formed memorial ensemble presents great difficulties and requires a novel, unconventional approach.

Monitoring of the monuments has been carried out in the Necropolis of the eighteenth century and the Necropolis of Masters of Arts since 1998. In this work, in addition to the museum staff and restorers, scientists, postgraduate students, and students of the St. Petersburg State University, of the Russian A. I. Herzen State Pedagogical University, and of other educational and scientific institutions of the city take part.

The diagnostics of integrity of works of art in the process of monitoring involves the study of the materials from which they are made and the layers (patina) on their surface. The obtained data are of exceptional scientific interest for studying the processes of monuments' deterioration under the impact of the environment.

Preservation of the monuments under the open sky depends not only on climatic conditions and the corrosive activity of the ambient air. The soil characteristics are also important. In addition, in the museum Necropoleis, most of the gravestones are under the trees, and the secretions of the plants (juices) and microorganisms inhabiting the leaves and bark of plants get on their surface. This is why it is so important to monitor the environment and the conditions around an individual monument. With the installation in 2006 of a station for atmospheric air monitoring in the Necropolis of the eighteenth century (made by Russian JSC OPTEK), it became possible to monitor the condition of the air in the museum Necropoleis. In 2007, the soils were studied; in 2013, a geobotanical description of vegetation in the

Necropoleis was made, and biofilms and young soils on the surface of the monuments were examined. On the basis of the obtained results, the impact of the environment on the character of the destruction of the monuments' materials was analyzed.

A specialized database on the state of the sculptural monuments in St. Petersburg was built for storage, structuring, and operational use of the collected information. Currently, the database, which contains the characteristics of more than 600 monuments of the museum Necropoleis and other monuments of the city, is available to all Internet users (http://www.opticalcomponents.ru).

The monitoring showed that many unique works of monumental art were in an unsatisfactory state; in particular, the results of the studies of biogenic damage caused a particular concern, revealing the aggressive role of microorganisms in the processes of stone deterioration. The issue of regular routine care became very pressing. From 2004, the work began on the conservation of the stone monuments in the Necropoleis, on the development of new approaches and methods for their protection against biological and other types of deterioration, including the laboratory tests of new biocides and preservatives, and assessment of their performance in the treatment of monuments. Since 2007, studies have begun to evaluate the effectiveness and safety of laser treatment in the removal of gypsum crust and biofilms from the surface of stone monuments.

The novelty and originality of the book in relation to other similar publications consist in a special strategy of the preservation of cultural monuments, established on an interdisciplinary scientific approach and application of a wide range of the methods of natural science in monitoring and research. The book outlines new approaches that make it possible to significantly expand the informative value of the nondestructive methods of surveillance studies of the state of monuments. The potential of modern computer technologies for mapping the biofouling of monuments and of laser scanning for quantifying the degree of their deterioration are considered. It is especially important to note that all these methodological developments are demonstrated through case histories. All work was performed on historical monuments, many of which are valuable cultural heritage resources of worldwide importance.

The structure of the monograph should be briefly described. The book opens with a historical sketch of the St. Petersburg Necropoleis (Chapter 1), which received a museum status in the first half of the twentieth century, from their inception to the present day, including the information about the nature of the collection of artistic gravestones, a story of its study and restoration. Chapter 2 describes the various stone material of the museum Necropoleis, represented by marbles, limestones, granites, and other rocks; the deposits wherefrom the stone came are discussed. Chapter 3 presents the results of the study of the outdoor environment of the monuments (air, soil, vegetation). The processes of deterioration of stone and bronze monuments as per the results of monitoring are discussed in Chap. 4. Chapter 5 introduces the history of creation and restoration of some outstanding artistic monuments of the museum Necropoleis and the data of monitoring them, wherefrom the changes in the monuments' status over time were traced. Chapters 6 and 7 are devoted to the strategy of monument preservation. In Chap. 6, the methods of and approaches to expert examinations of the state of the monuments are thoroughly reviewed. The experience of the Museum of Urban Sculpture in the protection of stone monuments from biodeterioration and the potential of laser technologies in restoration practice are discussed in Chap. 7.

Check for updates

1 Museum Necropoleis of St. Petersburg. A Brief History

Vladimir N. Timofeev and Yuriy M. Pirjutko

Abstract

The history of the Museum Necropoleis of St. Petersburg is presented from the time when they were created to this day. Their uniqueness as the first open-air museum in Russia is shown. Various periods in the life of the museum are described, alongside with the history of the monuments of exceptional historical and artistic value. The background is provided on architects and sculptors who took part in the erection of artistic gravestones from various materials. Information is given on the current state of the collection, restoration of monuments, the history of their study. The modern period in the history of the Necropoleis, lines of research and practical activities of the Museum of urban sculpture aimed at preservation of the unique collection of artistic gravestones, is described.

Keywords

Museum necropoleis • Museum of Urban Sculpture St. Lazarus cemetery • Necropolis of the 18th Century Tikhvin cemetery • Necropolis of Masters of Arts Artistic gravestones • History • Restoration techniques

The Museum of Urban Sculpture was founded in Leningrad in accordance with the decision of the Presidium of the Leningrad City Council, adopted on July 14, 1939. The most famous memorials and monumental and decorative sculptures of the city were transferred under the purview of the new museum, and nothing of the kind was in existence at the time. Numerous masterpieces of monumental sculpture of St. Petersburg, which with good reason can be called the birthplace of Russian plastic arts, became museum items worthy of safekeeping. The first sculptural monument in Russia, the Bronze Horseman, was inaugurated on the banks of the Neva in 1782.

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The establishment of the Museum of Urban Sculpture was in fact a reorganization, an expansion of the functions of the Necropolis Museum, operating in Leningrad since 1932. It was the first open-air museum in Russia, bringing together the St. Lazarus and Tikhvin cemeteries, St. Lazarus burial vault and that of the Annunciation in the Alexander Nevsky Lavra. In 1935 the Literatorskie Mostki (Literary Boardwalks, part of the Volkovo cemetery) became affiliated to the museum. Thus, the newly formed Museum of Urban Sculpture took custody of not monumental sculpture only, but also of a grand collection of memorial art of exceptional artistic and historical value, including over 1500 grave markers.

As part of the museum, the St. Lazarus cemetery was renamed the Necropolis of the 18th Century, the Tikhvin one —the Necropolis of Masters of Arts. Preservation of the memorial ensembles of these unique Necropoleis is one of the chief priorities of the museum. Preservation of the monument collection of the Necropolis of the 18th century, where there are about 1000 monuments created in the 18th—first half of the 19th century (Figs. 1.1 and 1.2), is a particularly difficult task.

In 2014, it was 300 years since ceremonial funerals began in the Holy Trinity Alexander Nevsky Monastery (on which the title of Lavra was conferred in 1797). In 1714, the Duma nobleman, Prokofy Afanasyevich Ushakov, was buried here, in the presence of Peter I. Five years later, the tsar attended the funeral of his field marshal, hero of the Northern War, Count Boris Petrovich Sheremetev. At the same time, according to Peter's plan, his nearest relatives found rest in the monastery: Tsarevna Natalia Alekseevna, Tsarevich Petr Petrovich, Tsarina Praskovya Feodorovna. This was how the Lavra necropolis began, where the founder of our city wanted to see memorials to his companions who «for fidelity and merit» could rest in peace under the protection of «the hero, Holy Prince Alexander Nevsky».

The first burials were near the wooden church of the Annunciation of the Blessed Virgin Mary, consecrated on March 25, 1713. The church was built on the left bank of the Black River (Monastyrka), nearby were various buildings of

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Fig. 1.1 Necropolis of the 18th Century. Petrovsky path, on the left is the monument to N.M. Yakovlev (unknown master, 1810s)

the Monastery—of rammed earth and wooden (building of stone on the other bank began only in 1717, according to the design by D. Trezzini). Thus, during the initial period of monastic life one cannot speak of a separate cemetery: places for crosses and tombstones were chosen in the monastery courtyard, next to the brethren's cells, houses of worship and service buildings.

In 1717, a small stone church of Righteous Lazarus was built for the burial of Peter's sister, Princess Natalia Alekseyevna, at the altar of the first Annunciation Church. Later, this church was expanded and completely rebuilt, taking the place of the first monastery church torn down in the middle of the 18th century. To the north of St. Lazarus' church in 1756 a new wooden five-domed Church of the Annunciation was built, disassembled at the very end of the 18th century. By that time other buildings of the Monastery on the left bank of the Monastyrka river were also pulled down. In the 1780s, at the time when the stone Gate Church of Joy of All Who Sorrow on top of the gates on Nevsky Prospect side was being built, a stone wall was erected to mark the territory of the St. Lazarus Cemetery. It makes sense to recall these historical facts in order to understand the fate of the oldest graves and monuments of the Lavra necropolis. Most of them were lost during the re-planning of the monastery courtyard during the 18th century; some were later replaced by new monuments; a number of tombstones were covered with earth, and discovered only in 1927–1929 during archaeological research.

The oldest monuments of St. Lazarus cemetery and of the St. Petersburg necropolis in general are the white-stone carved slabs of the Rzhevsky couple, made no later than the end of the 1710s, apparently even during the lifetime of the customers. Stolnik (a courtier lower in rank than a boyar) Ivan Ivanovich Rzhevsky and his spouse Darya Gavrilovna, the "princess-abbess" of Peter's «All-Joking Synod» did not die in Petersburg. On their tombstones, lavishly decorated with carvings of symbolic nature, there are blank spaces in the standard text of the epitaph, where the time of death and the number of years, months and days lived should be. These peculiar cenotaphs were found during excavations near the western wall of St. Lazarus' church on a family plot where in the 1740s the associate of Peter the Great, Count Grigory Petrovich Chernyshev and his wife Avdotya Ivanovna, née Rzhevskaya, were buried.

The Rzhevskys' gravestones cut from light-colored limestone are typologically close to the monuments of the pre-Petrine time, like those which are preserved in the basements of ancient Moscow monasteries.

For the early St. Petersburg period, flat stone slabs are characteristic with a concise text of the epitaph, above which the image of the cross is carved, and in the lower part of the slab there is a skull and bones (the «Adam's death's-head»).

Fig. 1.2 Necropolis of the 18th Century

This symbolic figure will be repeated many times in the future, reminding of the Divine atonement, when the precious blood of the Nailed to the cross was shed on the grave of Adam, buried under Golgotha, as a pledge of Resurrection from the dead and the future life.

In the museum Necropolis, only two stone slabs made in the 1720s remain: that of G.P. Konshin (died in 1725) and T. A. Litvinova (died in 1727). Another type of the commemorative sign was adopted for burials inside the stone Church of Annunciation (1717–1723, architect D. Trezzini, T. Schwertfeger), which was built as a burial vault for the royal family and the highest dignitaries of the state. It was a wall-mounted bronze plaque in the form of a medallion, with a cast epitaph in the ornamental frame. Such plaques were indeed called epitaphs: to Count A.P. Apraksin (died in 1725), Count P.I. Yaguzhinsky (died in 1736). Apparently, no floor ledger stones in the Annunciation burial vault, where there were wooden floors in the 18th century, were installed.

Of the thousand monuments kept in the museum Necropolis of the 18th century, only 116 were made in the 1730s–1790s. Most of the tombstones of this time (along with the stone ones, also cast-iron slabs) became available for study only in the 20th century, thanks to the excavations mentioned above.

In the 1760s new types of tombstones appeared. The first one in the St. Lazarus cemetery was the marble stele of M.V. Lomonosov, made in Carrara by Master F. Medico, according to the design of Academician J. Stäelin sent from St. Petersburg. Eventually, the necropolis was populated with granite and marble sarcophagi, altars, pylons, pyramids, columns and obelisks. Marble sculpture appears, the first of the surviving specimens being the tombstone of A.S. Popov made in 1781 by sculptor J. Semmelhack (since 1955 exhibited in the Annunciation burial vault).

The memorial art in Russia bloomed at the turn of the century (1790–1820s), when the gravestones became a synthesis of the expressive media of sculpture, architecture and poetry (Figs. 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9 and 1.10).

The high ideals of classicism are harmoniously combined in the artistic gravestone with the lyrical mood of sentimentality, which determined the literary genre of epitaph:

Rest, ye sweet ashes, until the joyous morn! (N.M. Karamzin).

The greatest masters of the Russian sculpture of the classicist epoch paid tribute to the art of memorial plastics:

Fig. 1.3 Necropolis of the 18th Century. Monument to A.A. Chicherin (unknown master, 1809)

Fig. 1.4 Necropolis of the 18th Century. Monument to A.Ya. Okhotnikov (F. Thibaut, 1800s)

M.I. Kozlovsky, I.P. Martos, F.G. Gordeev, V.I. Demut-Malinovsky, P.K. Klodt. At the same time, the contemporaries' did not display any interest in the «churchyard poetry». It suffices to recall the lines by A.S. Pushkin:

The fashionable tombs behind the railing squatting.
Where the great capital's uncounted dead are rotting.
Officials' sepulchers, and merchants', too, all fizzles:
The clumsy products of inexpert, vulgar chisels,
Inscribed in prose and verse with virtues, service, rank,
Outlandish ornaments displayed on either flank;
A widow's fond lament for an old cuckold coffined;
The urns screwed from their posts by thieves…

When, lost in thought, I roam beyond the city's bounds
(English by B. Deutsch)

The poet wanted to flee from such a «public cemetery», to a simple country churchyard, «where the dead sleep in solemn rest», and where, instead of «vain urns and small pyramids, noseless genii, disheveled Charites» the sprawling oak branches rustle above the graves…

Visiting family graves, building tombs and taking care of them have always been considered the sacred duty of the heirs and relatives of the deceased, a family matter that should not concern outsiders. Unfortunately, the «love of forefathers' graves» bequeathed by Pushkin is not shared by all our compatriots. The horrendous condition of many of our modern cemeteries is little different from what the city necropoleis were in the pre-revolutionary years. The places for burial were then paid for depending on the categories into which the land was divided. The sanitary condition of cheap categories, where thousands of people were buried, of course, without any notable monuments, was the cause of deep concern of the city authorities.

However, even the most prestigious, expensive St. Petersburg cemeteries, above all the Lavra ones, where there were no free categories, and where under the magnificent tombstones the cream of the metropolitan high society rested, were a pitiful sight. In the first issue of the *Starye Gody* («Old Years») magazine founded in 1907, an article by Baron N.N. Wrangel appeared, under the telltale title «Forgotten Graves». One of the first students of Russian sculpture, collecting materials for his research, including among tombstones, wrote: «Autumn rains, severe winter frosts—together with our vandals—will finally erase from our memory the names of the deceased and the work of those few Russian sculptors of the 18th century, who have been so little explored. It's dreadful to look at the desolation of St. Petersburg cemeteries, where so many remarkable people are buried, where the monuments by Kozlovsky, Martos, Rachette and Demut are still preserved» (Wrangle 1907).

V.Ya. Kurbatov echoed Wrangle in his famous «review of artistic wealth» of St. Petersburg, published in 1913, writing about the St. Lazarus cemetery: «Almost all of its monuments are remarkable, but, alas, are in a state of decay and gradually vanish» (Kurbatov 1913). True, the Academy of Arts took measures to identify and fix the artistic monuments of the St. Petersburg necropolis. In the spring of 1910, at the request of the Council of the Academy, the St. Lazarus cemetery was inspected by architect V.V. Suslov and sculptor V.V. Beklemishev, who testified: «The condition of the monuments is very poor: some of them (stone and bronze ledgers) have sunk into the ground, are extremely soiled and partly covered with moss and grass, others are half ruined and threaten with falling» (RGIA 1905).

Photographer of the Academy of Arts N.G. Matveev in 1906–1910 took about one hundred and fifty photos of ancient tombstones (Matveev's album is now in the library of the Academy of Arts). In 1912, D.M. Broido's artistic casting workshop made eighteen casts of the most outstanding sculptural monuments of the Lavra necropolis (the replicas made by the workshop of I.P. Martos's work, of the tombstones of E.S. Kurakina and E.I. Gagarina, are now exhibited in the Russian Museum). A remarkable series of 20 etchings depicting the monuments of the St. Lazarus cemetery was created in 1912 by the architect V.N. Taleporovsky.

Fig. 1.5 Necropolis of the 18th Century. In the foreground the monuments of Ya.B. and E.A. Knyazhnins (unknown master, 1832), in the background the monument to E.S. Karneeva (I.P. Martos, 1830s)

On the initiative of the Commission for public education of the City Duma since 1911, funds were allocated from the city budget «to protect the graves of prominent figures in the literary and scholarly fields». The list of such graves, beginning with M.V. Lomonosov's, included about two dozen names, which seemed negligibly short for St. Petersburg cemeteries, where almost all famous Russian scientists, writers, composers, artists of the 18th and early 20th centuries had been laid to rest.

The post-revolutionary years were tragic for the St. Petersburg Necropoleis, when the new government decided to get rid of the ancient problems of urban cemeteries in one fell swoop, simply eliminating them.

In this situation, it would be difficult to find a different way to preserve our historical memory than the one that led to the emergence of the only Museum Necropolis in the country. The St. Lazarus cemetery was already under the supervision of the museum department of Glavnauka from May 1919, and the «Old Petersburg» society, created in the fall of 1921, took the St. Lazarus cemetery in its custody and admitted that a comprehensive study of the monuments of the Lavra necropolis was among its priorities. A full inventory of monuments was completed, sketches were made, measurements and photographs taken.

The first monument of the St. Lazarus necropolis to be restored was the tombstone of «Plenira»—Catherine Yakovlevna, the beloved wife of the great 18th-century poet Gavriil Romanovich Derzhavin. Before the restoration, the marble plates of the pedestal with an allegorical relief of Mnemosyne—the goddess of memory, and the massive urn that crowned the monument, were just a pile of debris.

Unexpected discoveries lay in waiting for the explorers of the Necropolis: when in 1931 the Annunciation Vault was turned over to the museum, a niche was found in its wall, where one of the first sculptural tombstones, made in 1788, was hidden—that to Field Marshal Prince A.M. Golitsyn by F.G. Gordeev. The allegorical composition with the figures of Genii of Glory and Virtue, described by P.P. Chekalevsky in his «Discourse on Free Arts», published in 1792, looked alien in the functioning church, and was immured. At the beginning of the 20th century N.N. Wrangle regretted the loss of this monument.

Fig. 1.6 Necropolis of the 18th Century. In the foreground the monument to A.I. Sushkova (unknown master, 1800s)

An important role in the launch of the museum Necropolis was played by an active member of the «Old Petersburg» society, Nikolai Viktorovich Uspensky, from 1925 till his dying day in 1947 he was the custodian of monuments. For several years he was, in fact, the only research associate of the museum. The «Old Petersburg» society was dissolved in the early 1930s, and the St. Lazarus cemetery, still closed for new burials, was turned over to the «Funeral Service» trust. The artistic and historical significance of the monuments in the Necropoleis did not arouse any interest in communal workers who saw in the old tombstones only a hard-to-find expensive material suitable for reuse. This had a catastrophic effect on the second Lavra cemetery—the Tikhvin one—which in 1935–1937 became the «Necropolis of Remarkable Masters of Arts of the 19th century and Pushkin's companions». At present it is the "Necropolis of Masters of Arts" (Figs. 1.11, 1.12, 1.13, 1.14 and 1.15).

Only in 1938 the Necropolis Museum (officially opened in 1932) was transferred under control of the Department of Arts. One of its areas of focus in the period when «liquidation of dilapidated and orphan monuments in the Leningrad cemeteries» unfolded was the transportation of valuable tombstones in the museum Necropolis «with the transfer of the ashes of famous public figures, writers and artists». In this connection, it was allowed to destroy the «artifacts that are of no artistic importance» and «use the vacated area for the newly delivered monuments».

The monuments were brought in from the cemeteries of the St. Trinity-St. Sergius Monastery, Smolensk, Volkovo, Novodevichy, Mitrofanyevsky, Farforovsky, Malookhtensky, Georgievsky, Vyborg Roman Catholic cemeteries; those of the Annunciation Church on Vasilievsky Island and the Church of Exaltation of the Cross on Ligovka; the Lavra Nikolsky churchyard and from the three demolished churches and vaults: of the Holy Spirit, St. Isidor and St. Theodor. There is no doubt that in the process of the «socialist reconstruction» of the city, none of these monuments would have survived on their historical sites.

The gravestones that have become an integral part of the museum exposition in the open air: of the Pukolovs' with the epitaph «Passer-by, now you are walking, but you'll lie down like me»; of Karneeva with a monumental figure of the Genius of Death, ascribed to I.P. Martos; of the Reisiegs with the famous cast-iron sculpture of a «sleeping officer»; of Kazadayeva, built as a portico, under whose canopy there is a bust, sometimes called the «Queen of Spades»; of Litke

Fig. 1.7 Necropolis of the 18th Century. The sculptural composition of the monument to A.M. Beloselsky-Belozersky (J. Camberlain, 1810)

Fig. 1.8 Necropolis of the 18th Century. The monument to V.Ya. Chichagov (J.-F. Thomas de Thomon, 1810s)

Fig. 1.9 Necropolis of the 18th Century. Monument to P.V. Kindyakov (P. Catozzi, 1828)

—a marble obelisk according to a sketch, allegedly by V. Brenna—all this was rescued by the museum from the wrecked city cemeteries. Just like many tombstones (with «the ashes transferred») of our outstanding architects, sculptors, painters, artists.

>Important observations on the state of the stone and bronze, formation of patina, typology of deterioration and biofouling, cleaning and strengthening of the surface of the sculpture were made during the restoration work that was systematically carried out in the Necropoleis. This work was analyzed and described by the well-known sculptor, a specialist in restoration I.V. Krestovsky in his book «Monumental and decorative sculpture», published in 1949 and for a long time remaining the main textbook on the techniques of manufacturing, maintenance and restoration of monuments.

I.V. Krestovsky wrote about the restoration techniques of the Necropoleis' monuments used in the 1930s: «Moss is removed by layers, while lichens and algae have to be washed away with soap, paintbrushes and bronze wool pads or wire brushes. After washing the sculptures, cracks and crumbling surfaces are filled in either with marmorite (magnesia mass), or with mastic grout (mastic glue with chalk added), or with grout made of zinc white, mixed with a mordant» (Krestovskii 1949). Some of the methods used at the time (like, for example, fluosilicate treatment) are rejected by modern restorers, but their use has to be mentioned as a historical fact.

Fig. 1.10 Necropolis of the 18th Century. Monument to A.I. Vasiliev (I.P. Martos, 1800s)

Fig. 1.11 Necropolis of Masters of Arts. Monument to P.I. Tchaikovsky (I.A. Vsevolozhsky, P.P. Kamensky, 1897)

In the pre-war period, all valuable artistic gravestones in the St. Lazarus cemetery remained in the open air, inevitably exposed to the devastating effect of «autumn rains and severe winter frosts», of which N. N. Wrangel complained. However, it should be noted that as early as in the 1920s the «Old Petersburg» society had a set of wooden covers made, to shield several monuments in wintertime. Before the war, tours of the Necropoleis could be arranged only with prior booking required, so the day-to-day improvement work was not given enough attention. And the staff of the Necropolis Museum at the beginning of 1939 consisted of one gardener, five watchmen and two road sweepers.

Fig. 1.12 Necropolis of Masters of Arts. Monument to A.I. Kuindzhi (A.V. Schusev, V.A. Beklemishev, N.K. Roerich, 1914)

With this kind of maintenance it is difficult to imagine what effort was needed to prepare the museum Necropoleis for the hardships of war. However, it was possible to remove a number of marble and bronze busts and bronze parts from the pedestals and hide them in one of the crypts of the Annunciation burial vault. Masterpieces of I. P. Martos (the gravestones of N.I. Panin and A.I. Lazarev in the Annunciation vault, of E.S. Kurakina in the St. Lazarus cemetery) were covered in the same way as the monuments in the city: with sandbags and wood sheathing. Bigger sculptures (for example, the high relief from V.V. Stasov's tomb) were removed and buried in the ground next to the monument.

Fortunately, large-scale destruction, despite constant bombing, was avoided. Though Sheremetev's tombs in the St. Lazarus vault were strewn with roofing partially caved in because of shelling. In the Necropolis of Masters of Arts, a direct hit broke the tombstone of V.N. Asenkova.

After the war the opening of the museum exposition and the Annunciation burial vault was timed to coincide with the 150th anniversary of A.V. Suvorov's death, whose tombstone was made accessible even in the years of the siege of Leningrad.

The 1950s were an important stage of restoration and conservation work in the Necropoleis. In 1954, the exhibition at the Annunciation burial vault included the marble monuments of E.S. Kurakina, E.A. Kurakina, A.S. Popov, the sculpture of the «Triscorni Mourners» from the gravestone of M.S. Tairova, the bronze statue of E.I. Gagarina transferred from the St. Lazarus cemetery (the Necropolis of the 18th Century). Preservation of these priceless monuments in the museum was necessary in order to protect them

Fig. 1.13 Necropolis of Masters of Arts. On the right is the monument to G.A. Tovstonogov (L.K. Lazarev, 1991) , on the left the monument to N.K. Cherkasov (M.K. Anikushin, 1974)

Fig. 1.14 Necropolis of Masters of Arts. The monument to A.I. Kosikovsky (P. Catozzi, A. I. Terebenev, 1840) on the right; the monument to A.O. Statkovsky (E. M. Tropin, 1830s) on the left

from the dismal St. Petersburg weather. Restoration work on the monument of E.S. Kurakina, the pearl of the museum collection, was done in the 1970s by V.S. Mozgovoy, one of the leading masters of the Leningrad school of restoration.

Many lost sculptural details in the museum Necropoleis were restored from the documentary materials. I.V. Krestovsky recreated in marble the portrait of the Baroness, originally by M.I. Kozlovsky, of which only fragments remained, on S.A. Stroganova's monument, that was badly affected by time. Sculptors N.V. Dydykin, G.D. Yastrebenetsky, V.P. Astapov took part in the sculptural restoration of 1950–1960s.

The unique and singular nature of our St. Petersburg Museum-Necropolis, alongside with its indisputable memorial significance, lies in the fact that it gives an exhaustive picture of all stages in the formation and

Fig. 1.15 Necropolis of Masters of Arts. Monument to F.M. Dostoevsky (H.K. Vasiliev, N.A. Laveretsky, 1883)

development of memorial art in Russia in the 18th and 20th centuries. Various types of tombstones are presented here: from laconic slabs and ledgers to architectural monuments characteristic for the second half of the 19th—early 20th centuries.

The tombstone style developed in the same vein with the monumental sculpture of the time: Baroque, classicism, historicism, search for a national style, modernism, neo-classicism. Suffice it to recall the motifs of the Russian style in the tombstones of M.P. Mussorgsky, A.P. Borodin, V.V. Stasov; the poetic sentiment of the Northern Art Nouveau in the tombs of V.F. Komissarzhevskaya and I.R. Tarkhanov; simple classicism of S.S. Botkin's gravestone. The monument to A.I. Kuindzhi was a true masterpiece of the artistic synthesis, inspiring the artists of the «World of Art» circle. At the turn of the 19th–20th centuries I.P. Ropet, I.Ya. Ginzburg, N.K. Roerich, A.N. Benois, M.L. Dillon, I.A. Fomin, A.V. Schusev worked in the memorial art, who created vivid visual images.

The materials of the museum Necropolis became the subject of a serious study by E.D. Balmazi on the typology of tombstones (in the archives of the State Museum of Urban Sculpture). Old stager of the museum profession in Leningrad G.D. Netunahina, who for some time was the Director of the State Museum of Urban Sculpture, together with V.V. Yermonskaya and T.F. Popova co-authored the first in Russia study of the Russian memorial sculpture, published in 1978. G.N. Shkoda and A.I. Kudryavtsev, authors of the book «Alexander Nevsky Lavra. Architectural Ensemble and Monuments of the Necropoleis» (1986), which contains a serious analysis of the artistic gravestones in the St. Lazarus and Tikhvin Cemeteries (the Necropoleis of the 18th century and of Masters of Arts) worked in the Museum of Urban Sculpture. An original aspect of the research of the monuments in the museum Necropolis was uncovered by N.B. Abakumova in her research paper on the classification of rocks used in the manufacture of tombstones (Abakumova 1975). The restoration practice of the museum was particularly revitalized in the 1970s and 1980s, when an overall restoration of the so-called «background» monuments, which make up the unique environment of the Necropoleis, emphasizing the expressiveness of the masterpieces of the memorial sculpture, was performed. The whole sections of the cemeteries were put in order: in the area of the Betancourt path; near the monument to N.N. Pushkina-Lanskaya; near the path of Masters of Arts the tombstones were straightened, cleaned of the soil, and washed. It must be admitted that the techniques used did not always help to achieve long-term results. Many monuments, restored 30–40 years ago, await another treatment by skilled craftsmen. For various reasons, at the turn of the century the scope of restoration works went down. But at the beginning of the 21st century, the turn has come of large-scale projects, which the museum could not cope with for a long time. Such monuments as the portico of A.I. Kosikovsky in the Necropolis of Masters of Arts; a monument to the young Ponomarevs, returned to its historical site on the Tikhvin Cemetery from the Necropolis of the 18th century; the marble angel of E.A. Kochubey's tombstone made by Florentine master A. Costoli; the romantic grave of A.Ya. Okhotnikov, created by F. Thibaut, are the works that required significant funds and effort of the restorers who did the work at a very high professional level.

The museum, in cooperation with the scholars of the St. Petersburg State University, is now entering a new level of research of the Necropoleis monuments, involving an in-depth analysis of the materials and the effect on them of many factors of a busy urban environment. Much attention is paid to everyday maintenance, which is carried out as part of the annual scientific and practical projects on the conservation of stone monuments of the Necropoleis with protection against biodeterioration: in 2009 the museum received the *Museum Olympus* award for this work.

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2 Stone Materials of the Necropoleis Monuments

Olga V. Frank-Kamenetskaya, Evgeniya I. Polyanskaya, and Vera V. Manurtdinova

Abstract

Based on the results of many years of monitoring, the unique stone material of tombstones in the historical Necropoleis of the Museum of City Sculpture is described, represented by marbles, limestones, granites and other rocks. The most probable locations of deposits of the used decorative facing stone were in most cases identified with the help of archival data and other literature. It is shown that the diversity of stone in the Necropoleis is as great as in downtown St. Petersburg. There are also unique monuments (to N.A. Rimsky Korsakov, I.R. Tarkhanov, etc.), whose stone material has not yet been found elsewhere. The stone was delivered mainly from Italy and the vicinity of St. Petersburg (from the territories of the present Leningrad region, Karelia and Finland).

Keywords

Historical Necropoleis • Artistic gravestones Tombstones • Marble • Limestone • Granite Deposits of decorative facing stone

The collection of artistic gravestones in the historical Necropoleis of the Museum of Urban Sculpture is a unique collection of decorative and facing stone: marbles, limestones, granites and a number of other rocks.

The first description of marble of the Necropoleis tombstones was performed by N.B. Abakumova in 1975 (Abakumova 1975). A systematic study of the stone material of the museum Necropoleis has been under way since 1998 (Mironova 2000; Lepeshkina 2004; Esipova 2006, Kuruleva et al. 2012; Kompleksnyi monitoring 2011, 2013). Based on the results obtained, the diagnosis of the stone is made and, in most cases, a reasoned conclusion is given about the site where it was quarried.

2.1 Marble

Memorials of marble are, undoubtedly, the treasures of the Necropoleis. The most common is *milky white homogeneous fine- and medium-grained (grain size < 1 mm) marble* (Fig. 2.1). Such marble often has a cloudy pattern (indistinct spots and/or bands) (Fig. 2.2), as, for example, on the gravestones of A.N. and A.P. Mordvinovs, Y.G. Bryansky, M.P. and A.M. Kolychevs, E.A. Rantsova. White homogeneous marble was widely used for manufacturing various ornamental parts of monuments: sculptures, reliefs, vase lamps, urns. Monuments made of this stone are often characterized by a complex shape and have a unique artistic value. These include the tombstones of A.I. Kosikovsky (sculptor P. Catozzi), E.A. and V.N. Kochubeys (sculptor A. Costoli), A.Y. Okhotnikov (sculptor F. Thibaut), Z.A. Khitrovo (sculptor P. Triscorni) and others.

The results of field observations and laboratory studies (polarization microscopy, X-ray phase analysis) showed that the rock is composed of isometric grains of carbonates (calcite, less often together with dolomite), 0.05–1.00 mm (mostly 0.3–0.6 mm) in size (Fig. 2.3). Mosaic structure of the marble is typical for rocks of uniform composition and formation conditions. Quartz is found among impurity minerals.

The mineralogical and petrographic characteristics of the marble in question and the archives of the Museum of Urban Sculpture (Timofeev et al. 2006) indicate that this is the famous Italian Carrara marble, called Statuario (statuary) marble (Shuman 1986). The Carrara marble is a collective name for marbles in northern Italy, near the town of Carrara in the province of Tuscany, at the foot of the Apuan Alps

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Fig. 2.1 Monument to A.N. Esipova from white Italian marble in the Necropolis of Masters of Arts

(Fig. 2.4). It was quarried in the days of ancient Rome and is still quarried to the present day. The Carrara marble has served as a material for many masterpieces of world sculpture. In St. Petersburg, sculptures in the Summer Garden were made of this marble (now they are replaced with replicas) and other sculptural compositions (Bulakh and Abakumova 1987, 1993).

Light gray (sometimes pearlescent) homogeneous fine- and medium-grained marble, often with indistinct banding can also be found in the Necropoleis (Figs. 2.5a, 2.6). Marble was used, mainly, for pedestals and decorative elements (tombstones of N. Buturlin, P.Ya. Dubyansky, A.K. Imeretinsky, M.M. Golitsyn). The P.V. Sheremetev's funerary memorial is entirely made of this marble (Fig. 2.6).

The results of laboratory studies of the marble of A. Imeretinsky's gravestone showed that in terms of its mineralogical and petrographic characteristics, light gray homogeneous marble is very close to the Carrara white marble described above. The rock is composed of isometric calcite grains 0.1–0.9 mm in size, with the size of 0.3–0.6 mm prevailing. Coal dust is registered at the grains boundaries (Fig. 2.7).

Visually the light gray marble from the museum Necropoleis is very similar to the bardiglio marble from the Carrara Quarries, which was mined near Serravezza (Tuscany, Italy) (Fig. 2.5b). This marble was used in the first restoration of the outer facing of the walls of St. Isaac's Cathedral (1870–1890) (Bulakh and Abakumova 1987).

Quite often in the museum Necropoleis monuments of *white, mostly coarse-grained* (*predominant grain size* > 1 mm) *marble* can be found (Fig. 2.8).

Such marble was used in the manufacture of semi-columns and supports for them, large vase lamps, urns. It is from this marble that the monuments to A.I. Jendre, A.N., A.P. and A.K. Mordvinovs, S.A. Tishevsky, E.I. Neklyudova are carved.

The results of field observations and laboratory studies of marble have shown that this is an inequigranular rock composed of calcite, or calcite and dolomite grains (dolomite

(a) (b)

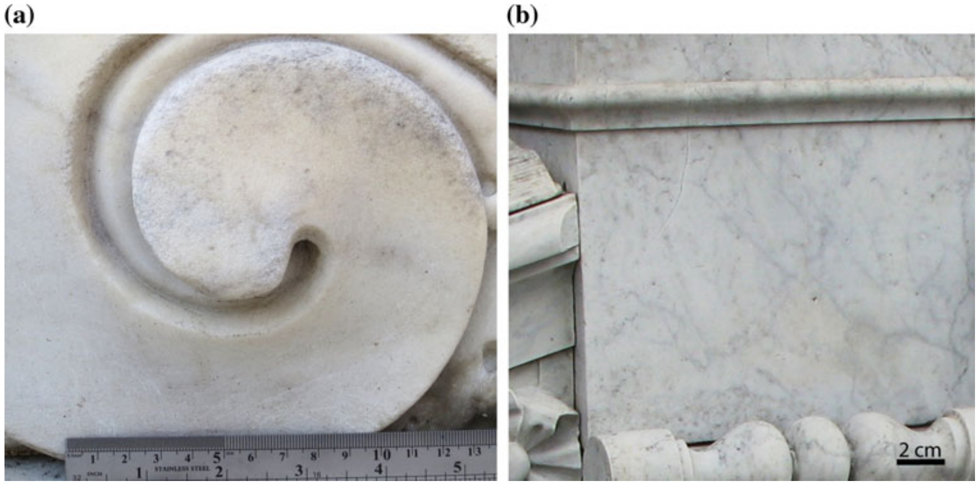

Fig. 2.2 White homogeneous marble with a cloud pattern. Monuments: **a** to E.A. Rantsova, **b** to A.N. and A.P. Mordvinov (Necropolis of the 18th century)

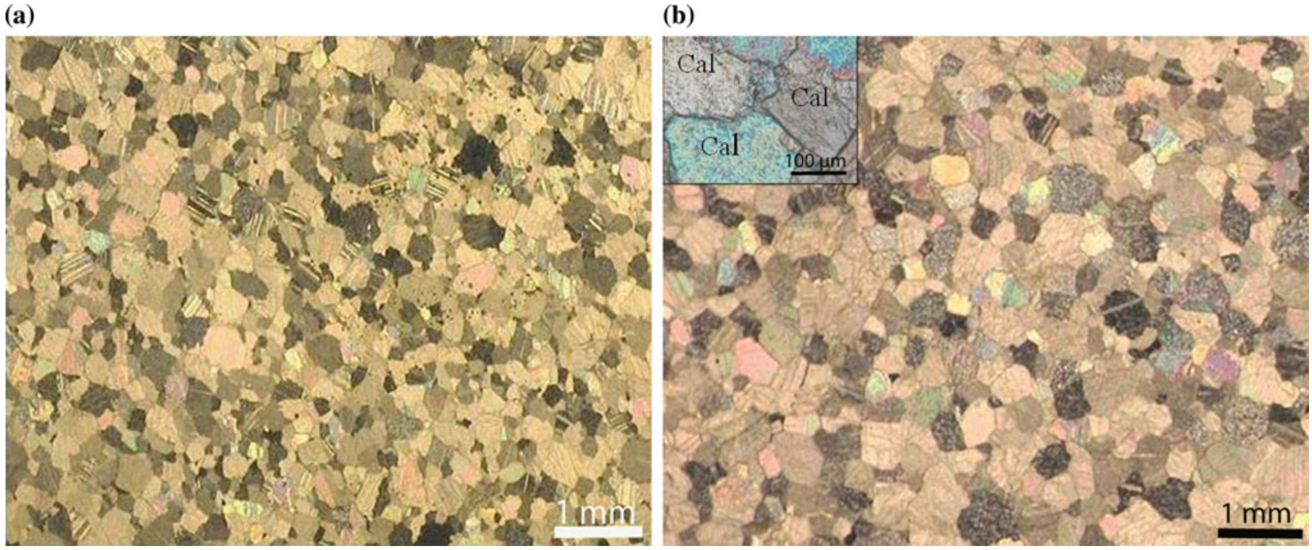

Fig. 2.3 Light microscope images (XPL) of the thin sections of white small- and medium-grained calcite marble: **a** the monument to F.V. Zakurin (Necropolis of the XVIII century), **b** Carrara deposit (Italy). Here and below: XPL—cross—polarized light, Cal—calcite

Fig. 2.4 Carrara quarries (https://limanskaia.tourister.ru/excursions/6436)

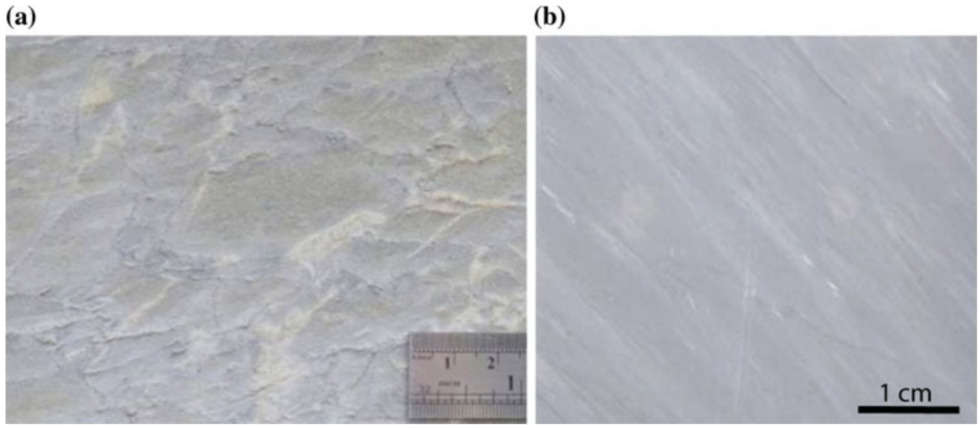

Fig. 2.5 Light gray homogeneous marble: **a** the monument to P.V. Sheremetev, **b** "bardiglio" from the Carrara deposit, Italy

Fig. 2.6 Monument to P. Sheremetev from light gray homogeneous marble in the Necropolis of the 18th century

Fig. 2.7 Light microscope image (PPL) of the thin section of light gray homogeneous calcite marble (the monument to A.K. Imeretinsky) Here and below: PPL—plane—polarized light

in a subordinate amount). The grain sizes vary from 0.1 to 7 mm. Grains larger than 1 mm predominate (Figs. 2.8, 2.9). Quartz is found among impurity minerals.

Visually, this rock is very similar to the marble used by A. Rinaldi in the construction of the Marble Palace in St. Petersburg (the decor of the windows, the main staircase and the marble hall).

It is known that marble for the Marble Palace was brought from the Urals (Ukhnalev 2002). The mineralogical and petrographic studies of this marble made by the experts of the *Spetsproektrestavratsiya* R&D Institute (Mamonov and Haryuzov 2003) showed that the stone was most likely brought from the quarry of the State Polevskoy factory located in the present Sverdlovsk Region. Thus, the Ural marble from this field may have been used in the manufacture of the Necropolis monuments.

The next most common after the white homogeneous Italian marble is *gray banded, heterogeneous inequigranular marble*. Dark gray and light gray bands vary considerably in width and can be very contrasting (Fig. 2.10). Often there are agglomerates of green grains, which can form bands and spots (Fig. 2.11). Such marble was widely used for monuments and individual details (semicolumns, pedestals, vase lamps). Gravestones of S.K. Münnich, E.A. Demidova, E.M. Konstantinova, P.P. Bakunin, E.A. Rummel were made of it.

The results of field observations and laboratory studies have shown that in addition to carbonates (calcite and dolomite occurring in different ratios), there are quartz,

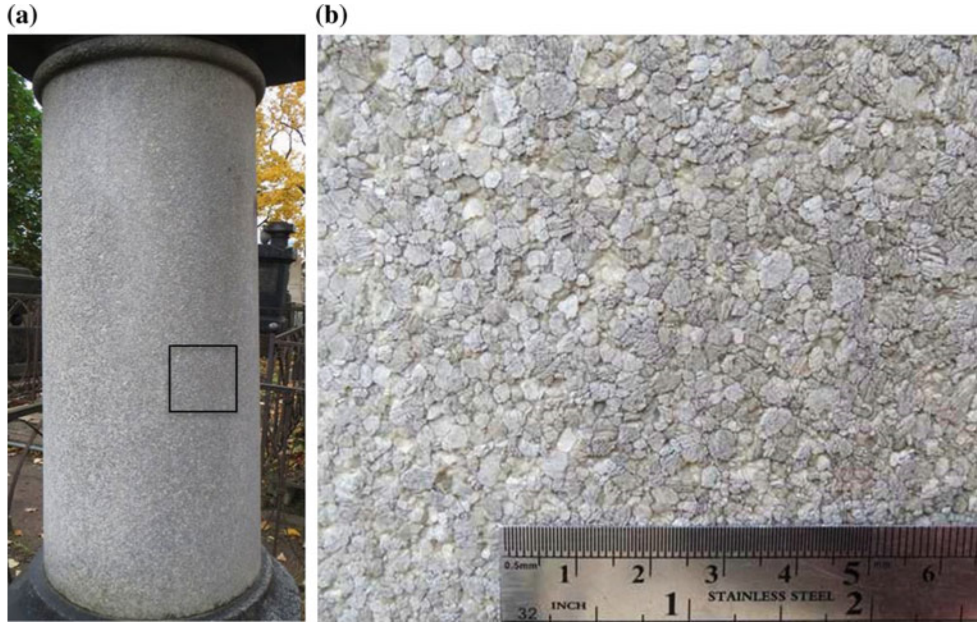

Fig. 2.8 Pillar of white, mostly coarse-grained marble of the monument to A.I. Jendre (Necropolis of the 18th century): **a** general view, **b** fragment of the rock. (field 1 in Fig. 2.8**a**)

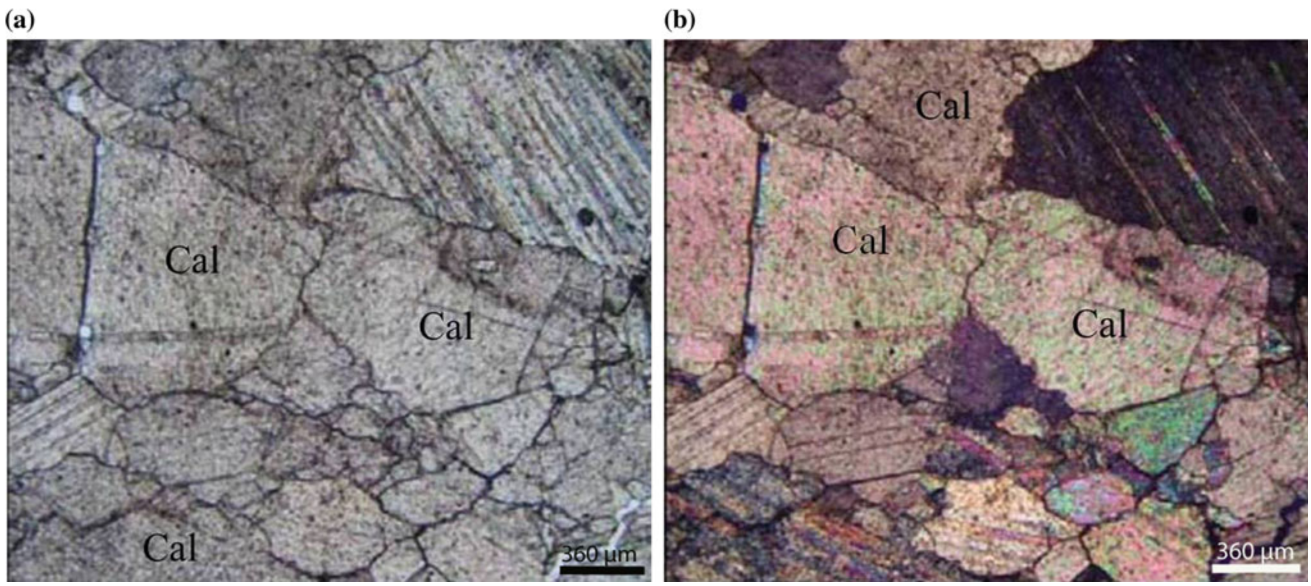

Fig. 2.9 Light microscope images of the thin section of white, mostly coarse-grained marble of the monument to the Unknown (N-18 No. 592) (Hereinafter, the numbers of the Unknown monuments are given according to the "Database on the state of sculptural monuments of St. Petersburg". The cipher N-18 indicates to the location of the monument in the Necropolis of the 18th century.): **a** PPL, **b** XPL. There is banding due to polysynthetic twinning

amphiboles (tremolite, hornblende), pyroxenes (diopside), talc, chlorites, mica (phlogopite) and feldspars (microcline) present in the rock. The content of silicate minerals may be comparable with the content of carbonate ones. The carbonate grain size (of isometric and irregular forms) vary substantially (from 0.1 to 6 mm). Dark gray, sometimes wavy, bands are due to the presence of dark-colored minerals and finely-dispersed carbonaceous substance. Green amphibole crystals sometimes form radiate aggregates.

In the thin section of the marble from E.A. Rummel's memorial (Fig. 2.12a), it is easy to see different-sized, generally isometric, carbonate grains. The groundmass of the rock is composed of 0.6–4 mm grains. In some areas their size is 0.1–0.3 mm. Between large grains of carbonates, chain aggregates of smaller ones are often observed. Amphibole (tremolite) is present in the form of columnar crystals and their aggregates and is confined, for the most part, to the fine-grained component of the rock. In

Fig. 2.10 Monument to S.K. Münnich from gray banded marble (Necropolis of the 18th century)

intergrowth with amphibole, small lamellar crystals of weakly pleochroic mica are found. A few small grains of quartz can be seen.

Mineralogical and petrographic characteristics of the silicate-carbonate rock under investigation are typical for the Ruskeala marble field (Fig. 2.12b) (Kitsul 1963; Bulakh 2005). This deposit, which is located in the area north of Lake Ladoga near the village of Ruskola (Ruskeala) near the town of Sortavala (Karelia), has been under development since the middle of the 18th century. At present, on the basis of the Ruskeala open casts, where marble was quarried to face the walls of St. Isaac's Cathedral, the Natural Park of Ruskeala operates (Fig. 2.13), which annually hosts thousands of tourists from different countries (Borisov 2008a).

In the Necropolis of the 18th century there is also gray, gray-white wide-banded marble (Fig. 2.14). In appearance, this marble is very similar to that from Ruskeala and differs from it only in the greater width of the bands and their more intense colour. Marble was used in the manufacture of sarcophagi and individual decorative elements. Memorial monuments of D. Frederiks, P.A. Polyansky, A.A. Polyanskaya, V.D. Smirnov are made of this marble.

The results of field and laboratory studies of the wide-banded marble of the tombstone of D. Frederiks (Fig. 2.15a) confirmed the similarity of this rock to the Ruskeala marble. The size of the carbonate grains (mainly calcite, and dolomite—to a much lesser extent) varies from fractions of a millimetre to 7 mm. Mica (mainly phlogopite) forms monomineral aggregates. There are areas of weak brecciation, where among the abraded mineral mass grains of carbonates are found (up to 1.5 mm). The colour of dark bands is due to the presence of dark-coloured minerals and finely dispersed carbonaceous matter.

The examined silicate-carbonate rock, both in appearance and in its mineralogical and petrographic characteristics is close to the marble that was mined in the northern Ladoga area on the island of Uven (Fig. 2.15b).

This coastal island (Fig. 2.16) (150 m long and 80 m wide) is located off the village of Läskelä, close enough to the village of Ruskeala. The Uven marble belongs to the complex of carbonate and silicate-carbonate rocks of the Ruskeala deposit. The Uven pits were in operation from 1769 till the early 19th century, and abandoned because of tough mining conditions (Borisov 2008a). This marble was used in the external and internal decoration of the Marble Palace (Ukhnalev 2002) and other architectural structures of St. Petersburg (Bulakh and Abakumova 1987, 1993; Bulakh 2005, 2012).

One of the most beautiful marbles of the Necropoleis is the pink veined inequigranular marble (Fig. 2.17). It is diverse in colour patterns (from pink, gray-pink, white-pink to crimson and violet). The colour of the rock is unevenly distributed and is determined to a large extent by the quantitative ratios of oxides and hydroxides of iron. Marble can be uniform, banded, brecciated, which is often emphasized by different shades of colour (Fig. 2.18). It contains veins of calcite and quartz. Of this marble, pedestals and semicolumns were usually made: the gravestones of L.I. Kusheleva, V.N. Bibikova, S.A. Balakshin, A.D. Litke, and A.V. Khrapovitsky.

The results of field observations and laboratory studies of pink marble have shown that the rock is composed of isometric grains of carbonates (calcite and dolomite in different ratios). The size of the grains varies from 0.05 to 1.2 mm. There are also large (up to 5 mm) dolomite grains of diamond shape. Quartz is present in the form of isolated grains and their small aggregates (Fig. 2.19a).

According to its appearance and mineralogical and petrographic features, the examined carbonate rock is similar to

(a) (b)

Fig. 2.11 Monument to E.A. Rummel from gray heterogeneous marble: **a** general view, **b** fragment of the rock. Gray-green stripes and spots can be seen

(a) (b)

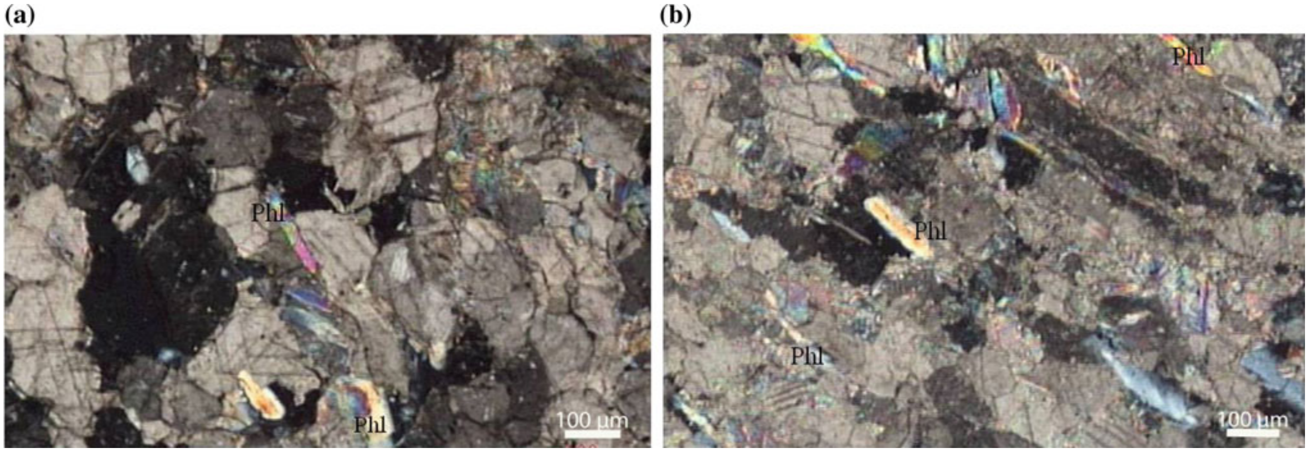

Fig. 2.12 Light microscope images (XPL) of the thin sections of gray heterogeneous banded marble: **a** the monument to E.A. Rummel, **b** Ruskeala deposit (Karelia) . In the mass of carbonate grains, lamellar crystals of mica (phlogopite—Phl) can be seen

the Belogorsky (Tivdiysky, Olonetsky) marble (Fig. 2.19b). This marble was quarried in Lake Onega area from the 18th century. It is usually called the Tivdiysky (after the name of the village—Tivdiya), or Belogorsky (by the place of the main open casts near the village of Belaya Gora), or Olonetsky (according to the ancient name of the land). The Belogorsky open cast is one of the largest mining and geological sites of Karelia, interesting for the variety and artistic value of its marbles (Fig. 2.20).

The Tivdiysky marble adorns the facade of the Marble Palace (pilasters, columns, insets above the windows, the frieze, attic, tower) and interiors of many other palaces and cathedrals in St. Petersburg (Bulakh and Abakumova 1987, 1993).

In the Necropolis of the 18th century there are also very unusual, picturesque breccia and breccia-like marbles.

Variegated breccia marble (Fig. 2.21). The rock consists of cemented blocks of various sizes (from 0.8 mm to 5 cm)

Fig. 2.13 Marble quarries of Ruskeala (Karelia). Photos by Dmitry Yu. Vlasov, 2008

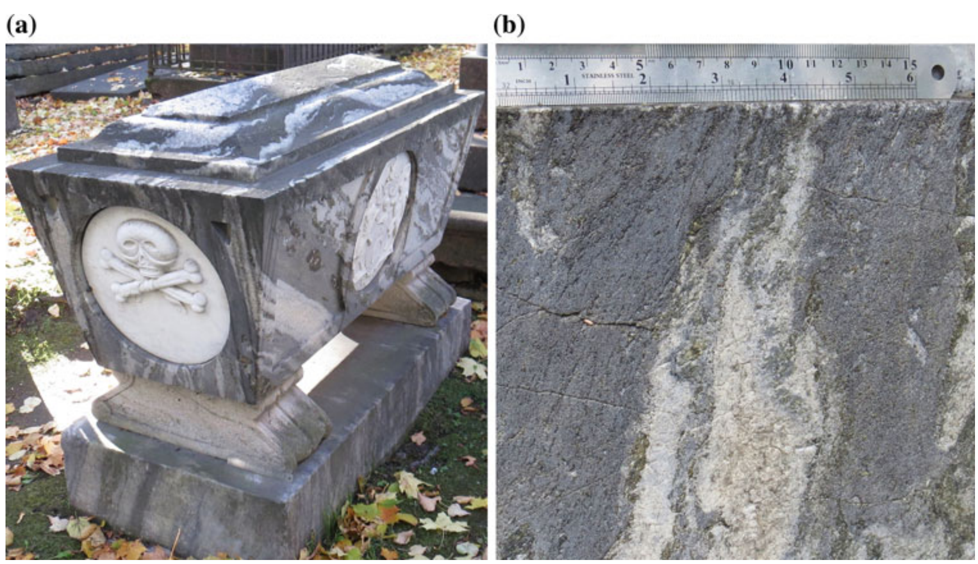

Fig. 2.14 Monument to A.A. Polyanskaya from gray-white wide-banded marble: **a** general view, **b** fragment of the rock. The width of the bands reaches 10 cm

and colours (from light yellow and white to pink and even violet). This marble can be seen in the Necropolis of the 18th century only on three tombs, of Georgian princess Maria Alexandrovna (née Khilkova), A.P. Berilova, E.I. Kokoshkina.

The study of the marble of A.P. Berilova's tomb showed that the rock is a fine-crystalline aggregate of mostly calcite and dolomite (with grain size of 0.05–0.1 mm) (Fig. 2.22). It contains segregations of up to 9 mm, made of large (up to 1.5 mm) carbonate crystals. In the marble of the monument

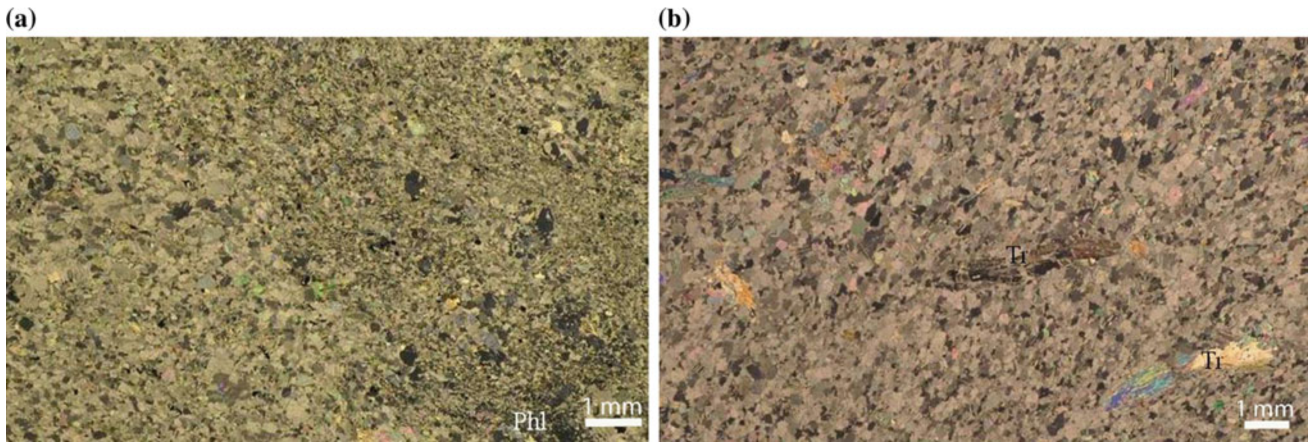

Fig. 2.15 Light microscope images (XPL) of the thin sections of gray-white wide-banded marble: **a** the monument to D. Frederiks, **b** the Uven field (Island of Uven). In the fine-grained carbonate mass, grains of silicate minerals are visible: mica (phlogopite—Phl) and amphibole (tremolite—Tr)

Fig. 2.16 Island of Uven (Karelia) . Photos by Dmitry Yu. Vlasov, 2008

to Maria Alexandrovna in addition to calcite, calcium silicate larnite was found.

According to the archive of the State Museum of Urban Sculpture the marble for Maria Alexandrovna's memorial was imported from Italy (Artistic Tombstone 2006). It is known that deposits of colourful varieties of marble with angular clasts are found in Italy near the cities of Verona and Carrara (Shuman 1986). Vases of amazing beauty made from Italian breccia marbles of different colours can be seen in the State Hermitage.

Gray-white spotted brecciated marble (Figs. 2.23, 2.24). The rock is very heterogeneous. The breccia-like look is due to unevenly distributed patchy colouration and numerous multidirectional veins of calcite of varying length and

Fig. 2.17 Monument to V.N. Bibikova from pink patterned marble (Necropolis of the 18th century)

thickness. Calcite veins have greater resistance to the impact of the environment, and therefore a web of bulging segregations is formed on the rock surface.

Gray-white spotted brecciated marble is more common in the Necropolis of the 18th century than the motley one. It was used in the manufacture of various parts of gravestones—pedestals, semicolumns, etc. (monuments to N.A. Mordvinov, E.A. Kurakina, A.P. Berilova, E.I. Kozitskaya).

The laboratory studies of the rock showed that it is dominated by fine-grained calcite aggregate and dolomite. Quartz, diopside, larnite, and mica are present as impurities. In the marble of N.A. Mordvinov's gravestone there is a small area of calcite grains of 0.05–0.20 mm in size. In the marble of the monument to A.P. Berilova (Fig. 2.25), a section is composed of isometric carbonate grains 0.1–1.0 mm in size, with a predominant size of 0.3–0.6 mm. Among these grains, numerous lamellar crystals of mica of roughly the same size and individual grains of pyroxene are evenly distributed. The fine- and medium-grained area is replaced by a coarse-grained section of large (up to 2.5 mm) calcite grains with serrated edges. On the whole, it can be seen that the carbonate rock under investigation is a limestone where, as a result of repeated non-uniform recrystallization, marmorized sections were formed.

It is known that the white marble for the sarcophagus of the monument to N.A. Mordvinov was mined in Carrara after the model of the "famous sarcophagus in Rome" (Artistic tombstone 2006), which suggests that the gray-white brecciated marble (marmorized limestone) for this and other monuments was imported from Italy. According to the Italian geologist Lorenzo Lazzarini, the rock looks like Portoro limestone, quarried in the province of La Spezia.

White with a yellowish tinge, slightly brecciated marble. This marble was used for the monument to N.A. Rimsky-Korsakov (Fig. 2.26) in the Necropolis of the Masters of the Arts. The monument was carved according to the sketch by N.K. Roerich and has a high artistic value. It is known that the authors sought to age the stone artificially and for this purpose they gave it a light yellow shade (http://lomonosov.org).

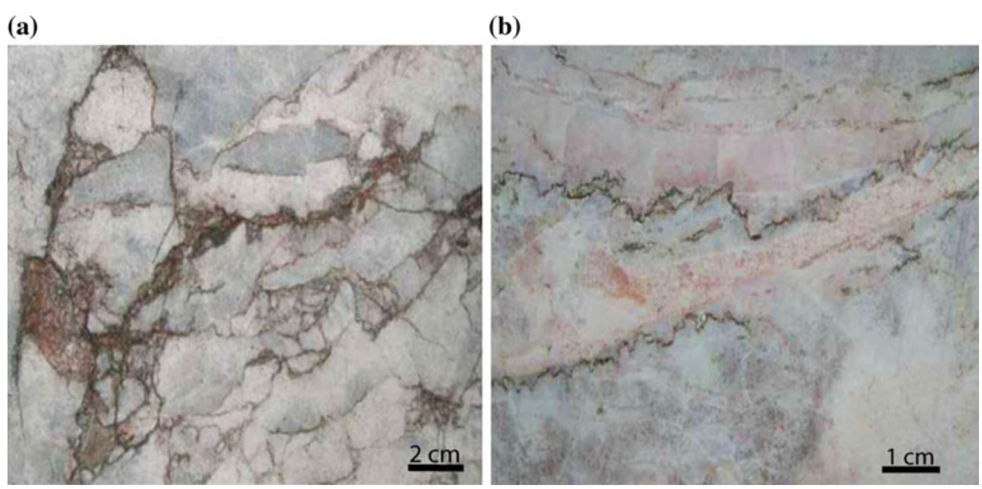

Fig. 2.18 Pink patterned marble: **a** brecciated (the monument to L. I. Kusheleva), **b** banded (the monument to V.N. Bibikova) (Esipova 2006)

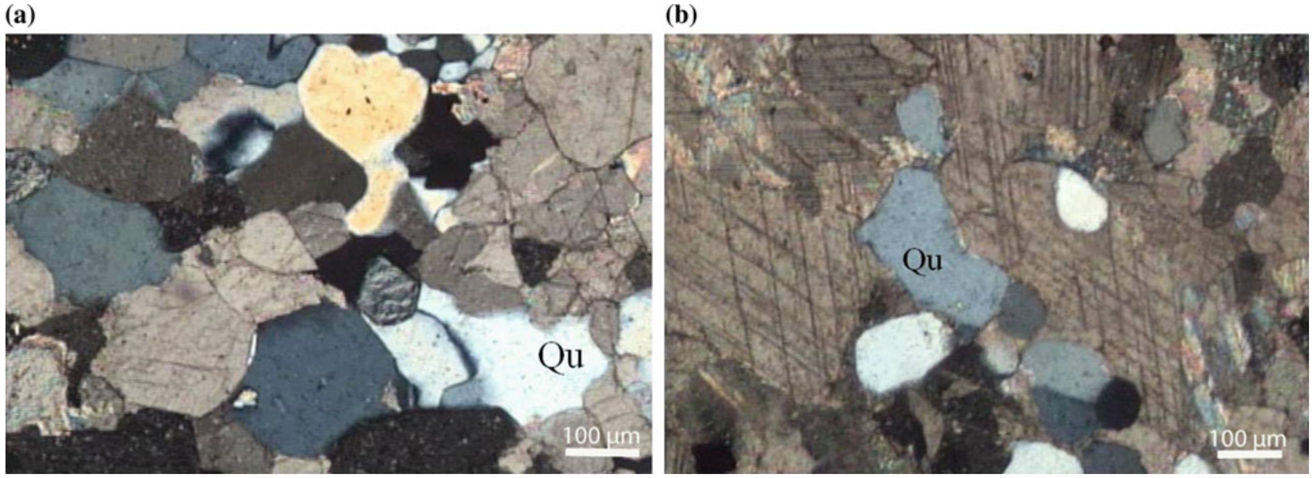

Fig. 2.19 Light microscope images (XPL) of the thin sections of pink patterned marble: **a** the monument to the Unknown (N-18 No. 699), **b** the Belogorsky deposit. Among the carbonate grains, quartz grains (Qu) can be seen (Esipova 2006)

Fig. 2.20 Tivdiysky stone quarry (http://regionavtica.ru)

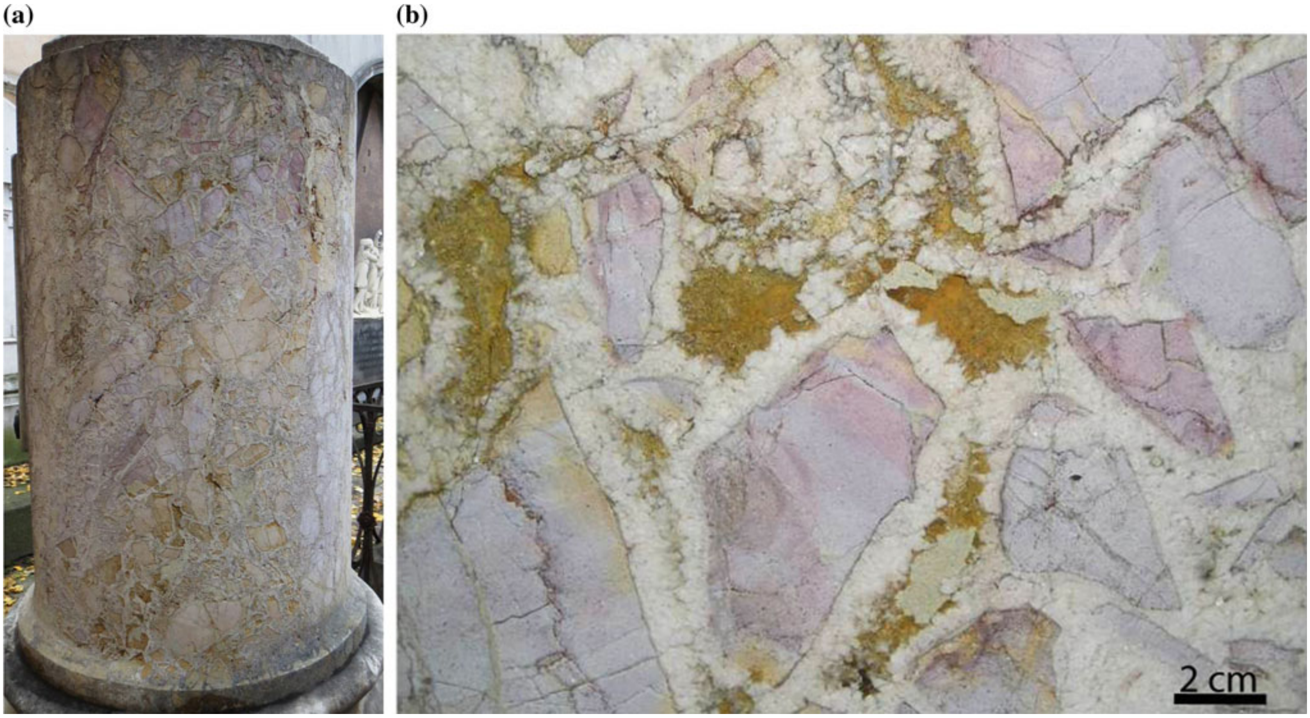

Fig. 2.21 Pillar of the monument to the Georgian princess Maria Alexandrovna (née Khilkova) from the mottled breccia marble (Necropolis of the 18th century): **a** general view, **b** fragment of the rock

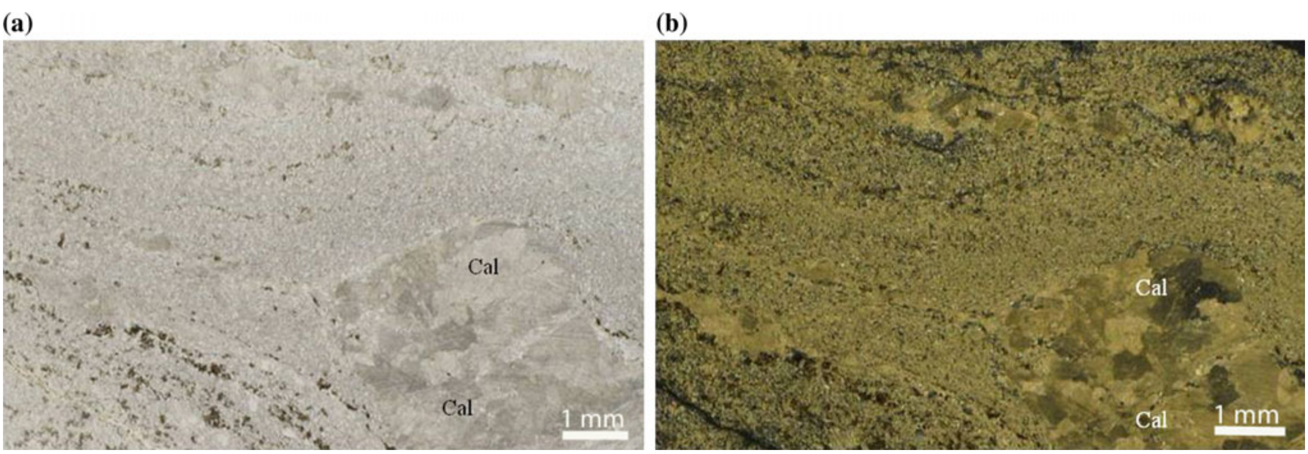

Fig. 2.22 Light microscope images of the thin section of mottled brecciated marble of the monument of A.P. Berilova: **a** PPL, **b** XPL. In the fine-grained carbonate mass clusters of coarse calcite grains can be seen

The laboratory study of the marble showed that in a small- and medium-grained calcite aggregate there are areas of coarse-grained aggregation and those of columnar crystals (Fig. 2.27). In addition, lamellar crystals of biotite are present, almost completely replaced by fine flaky aggregates of light mica. Grains of quartz are observed mainly in the fine-grained part of the rock. Where the marble for N.A. Rimsky-Korsakov's tomb was brought from remains unknown.

2.2 Limestone

Carbonate rocks of the Necropolis are represented not only by marbles, but also by various limestones.

The most common of these is *multicolored flaglike limestone* (Fig. 2.28). Its clearly manifested stratification is emphasized by the presence of thin clay partings and different colour layers, whose thickness is usually 5–20 cm. Gray,

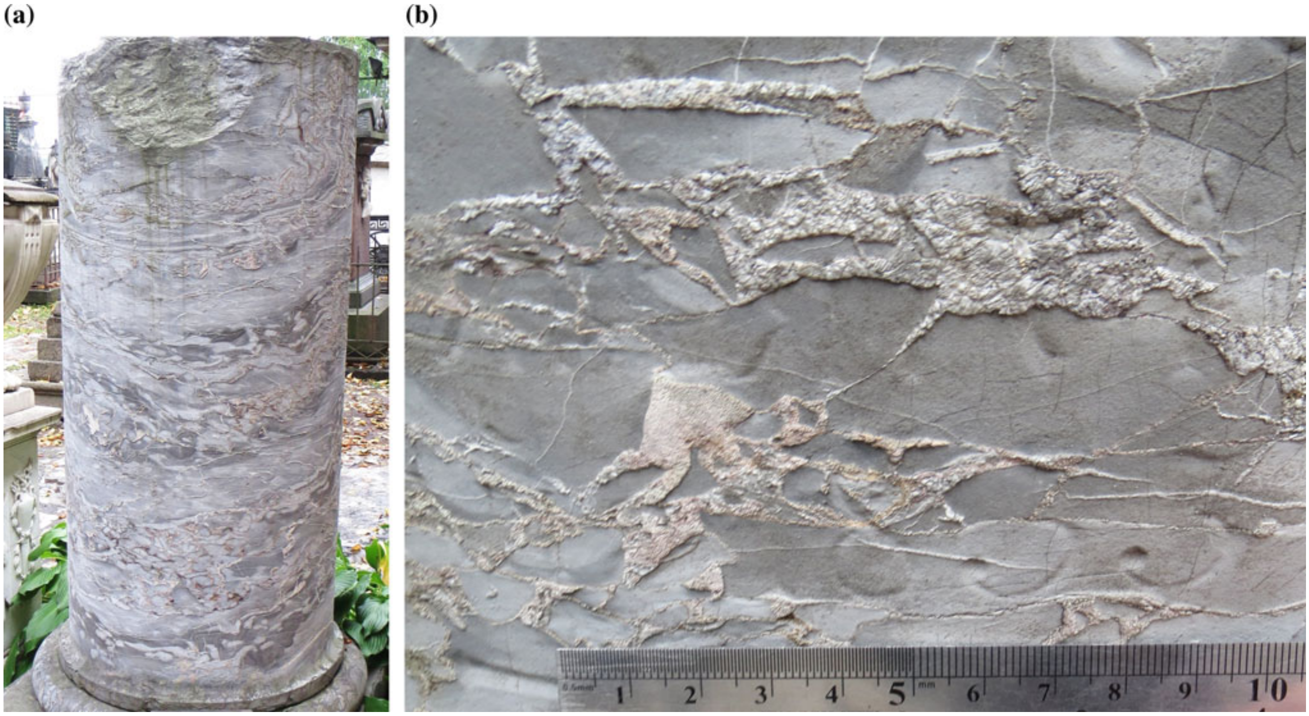

Fig. 2.23 Monument to E.I. Kozitskaya from gray-white brecciated marble: **a** – broken column, **b** fragment of the rock

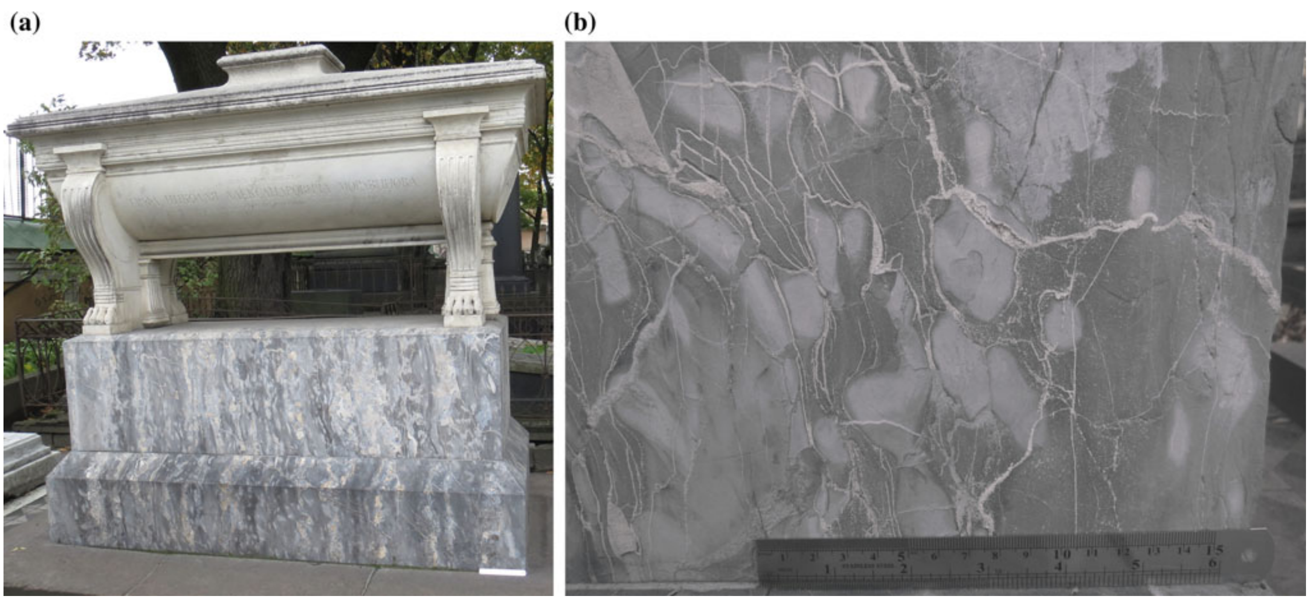

Fig. 2.24 Monument to N.A. Mordvinov from gray-white brecciated marble: **a** general view, **b** fragment of the rock. Color spots are visible

yellowish-gray dense limestone, often with brown spots is the most common in the Necropolis (Fig. 2.29). There are also grayish-green, gray-pink, rusty-yellow (ochre-coloured), brownish-red, pink-violet varieties. Numerous fossils can be seen. Foundations of most of the memorials in the Necropolis are made of such limestone. For the manufacture of semi-columns, sarcophagi, tomb canopies it was used more seldom (monuments of A.Y. Potemkina, F.I. Ivanov, Y.B. Knyazhnin, S.I. Lavrov, I.I. Cherkasov, I.I. Arbenev).

The laboratory studies have shown that the flaglike stratified limestone of the Necropolis monuments is predominantly a fine-grained dolomitized carbonate rock (Fig. 2.30a, b). The main rock-forming mineral is calcite. Areas of recrystallization with coarser grains are observed.

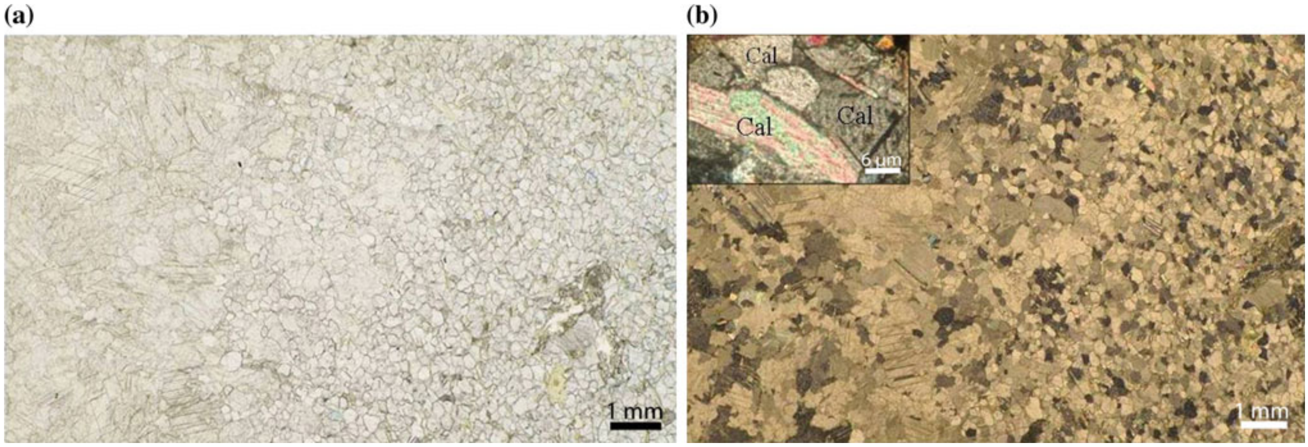

Fig. 2.25 Light microscope images of the thin section of gray-white spotted brecciated marble of the monument to A.P. Berilova: **a** PPL, **b** XPL

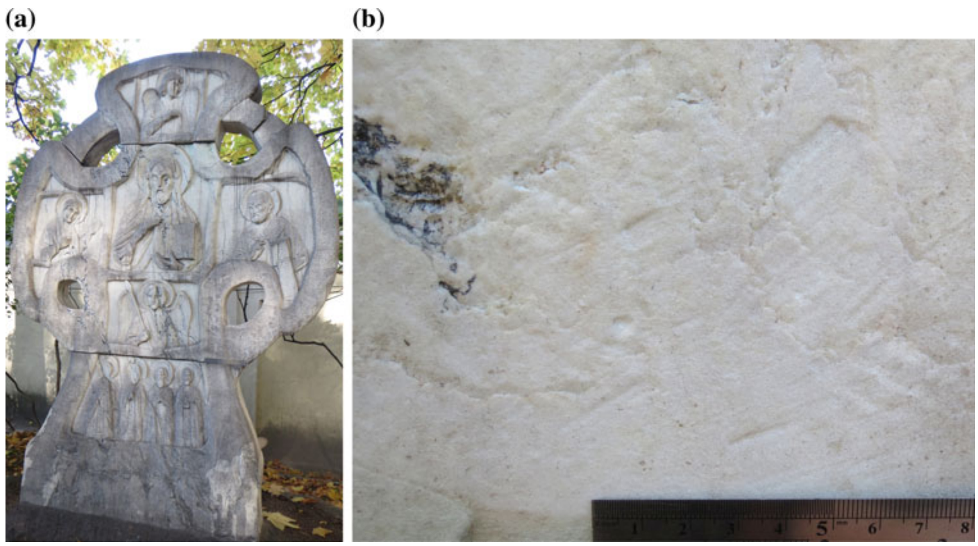

Fig. 2.26 Monument to N.A. Rimsky-Korsakov from white-and-yellowish marble: **a** general view, **b** fragment of the rock with traces of secondary changes

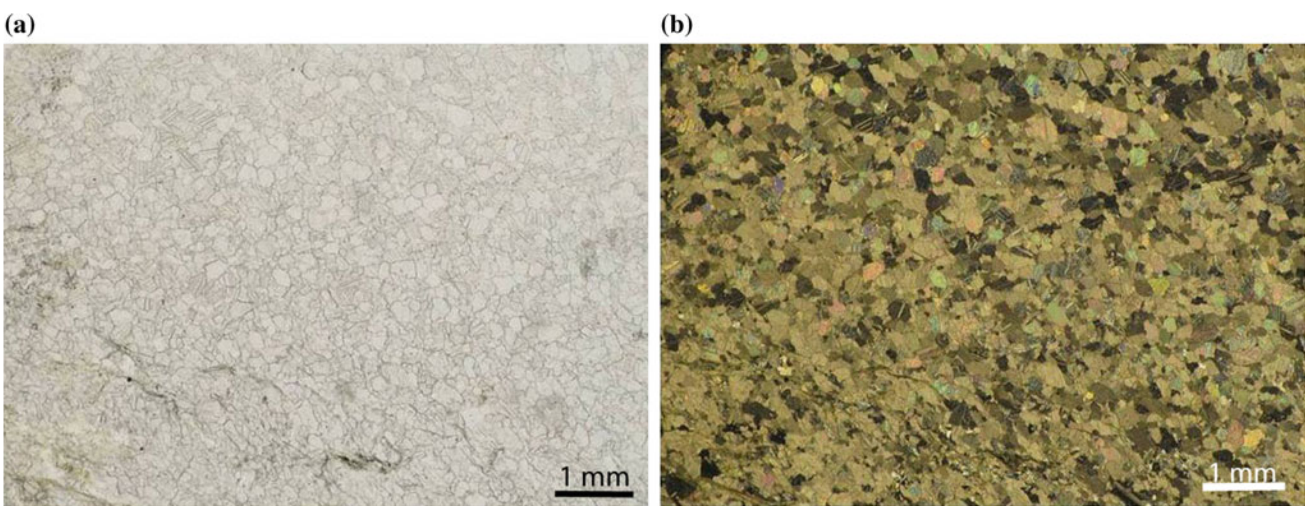

Fig. 2.27 Light microscope images of the thin section of white, slightly brecciated, yellowish-tinged calcite marble of the monument to N.A. Rimsky-Korsakov (thin section): **a** PPL, **b** XPL

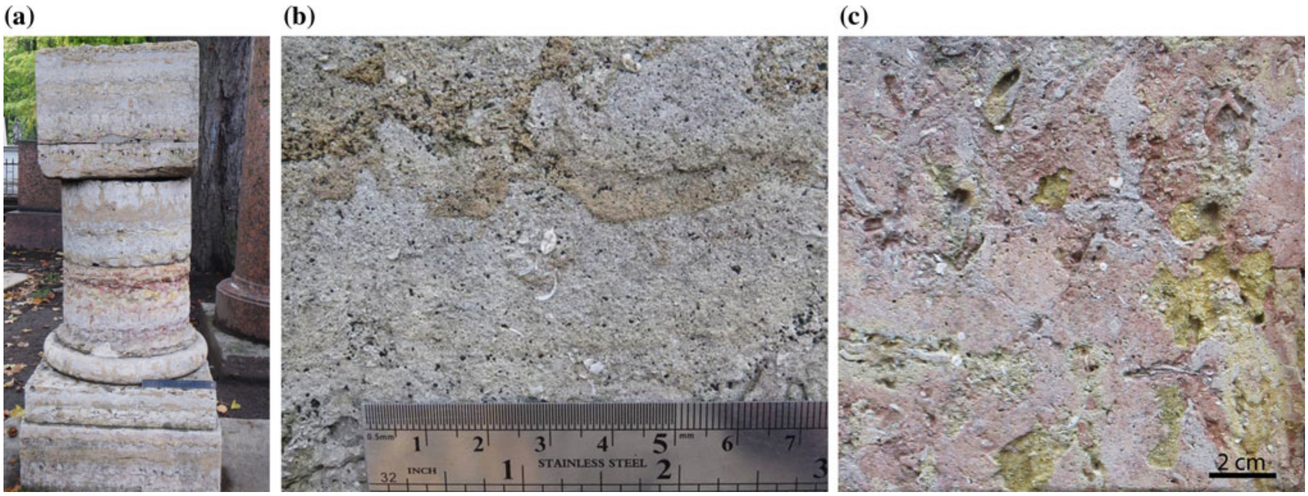

Fig. 2.28 Monument to Ya.B. Knyazhnin from the variegated flaglike limestone: **a** general view of the monument from the east; **b** gray part of the rock, traces of ferruginization; **c** pink-violet part of the rock, green speckles are visible

Fig. 2.29 Gray flaglike limestone with yellow-brown interlayers

There are large diamond-shaped crystals of dolomite. The limestone contains a great amount of faunal organic remains. This determines the bioclastic structure of the rock. A characteristic feature of flaglike limestone is the presence of green mineral grains—those of glauconite (iron potassium phyllosilicate). In addition, there is quartz.

The structure of the rock, its mineral composition and abundance of organic remains are characteristic of the limestones from the Putilovo deposit (Fig. 2.30c, d). The deposit of Putilovo stone is located in the Leningrad region (near the village of Putilovo) (Fig. 2.31). Flaglike limestone was mined there from the early 18th century and was one of the main materials used in the construction of St. Petersburg. The main areas where it was quarried were the southern coast of Ladoga Lake, lower reaches of the Volkhov River, the basins of the Syas River, and of the Tosna and Sablinka rivers. Currently, there are only two quarries located in the areas where Putilovo limestones were originally excavated—Babino Seltso and Putilovsky (Harjuzov et al. 2012).

In the Necropolis of the 18th century there is also *gray dense limestone* (Fig. 2.32). The colour of the rock varies from light gray to grayish black. The rock is full of small fossilized fauna. Such limestone was usually used for pedestals, stands for vases and various decorative elements. From it, details of the monuments to S.N. Marin, Ketavana Konstantinovna (née Bagration-Mukhrani), A.G. Kusheleva, A.S. Belavina, and others were made.

The results of the study of the gray limestone of A.G. Kusheleva's tomb showed that this was a fine-grained crystalline carbonate rock composed of calcite, to a much lesser extent of dolomite, with an admixture of clayey material (Fig. 2.33). Numerous faunal remains can be seen. Quartz and clayey minerals are found as impurities.

It is known that gray, dense, fossil-containing marmorized limestone is mined in Germany (Bavaria). This is so-called Jurassic marble, which was mined as early as in the Middle Ages (Shuman 1986) . It is possible that it was this limestone that was used for the Necropolis monuments.

Porous, spongy, gray or yellowish-gray limestone—travertine is much rarer in the Necropolis of the 18th century (Fig. 2.34). There are portions of brown or yellowish-brown colour, stained by oxides and hydroxides of iron (Fig. 2.35). Such limestone, which is often called calcareous tufa, was used in the manufacture of canopies, grottoes, pyramids (memorials of N.S. Bem, P.A. Golitsyna, V.I. Potemkina, and others).

The results of laboratory studies of the travertine of the monument to the Unknown (N-18 No. 901) in the Necropolis of the 18th century showed that the examined limestone is a highly porous rock composed of fine crystalline or

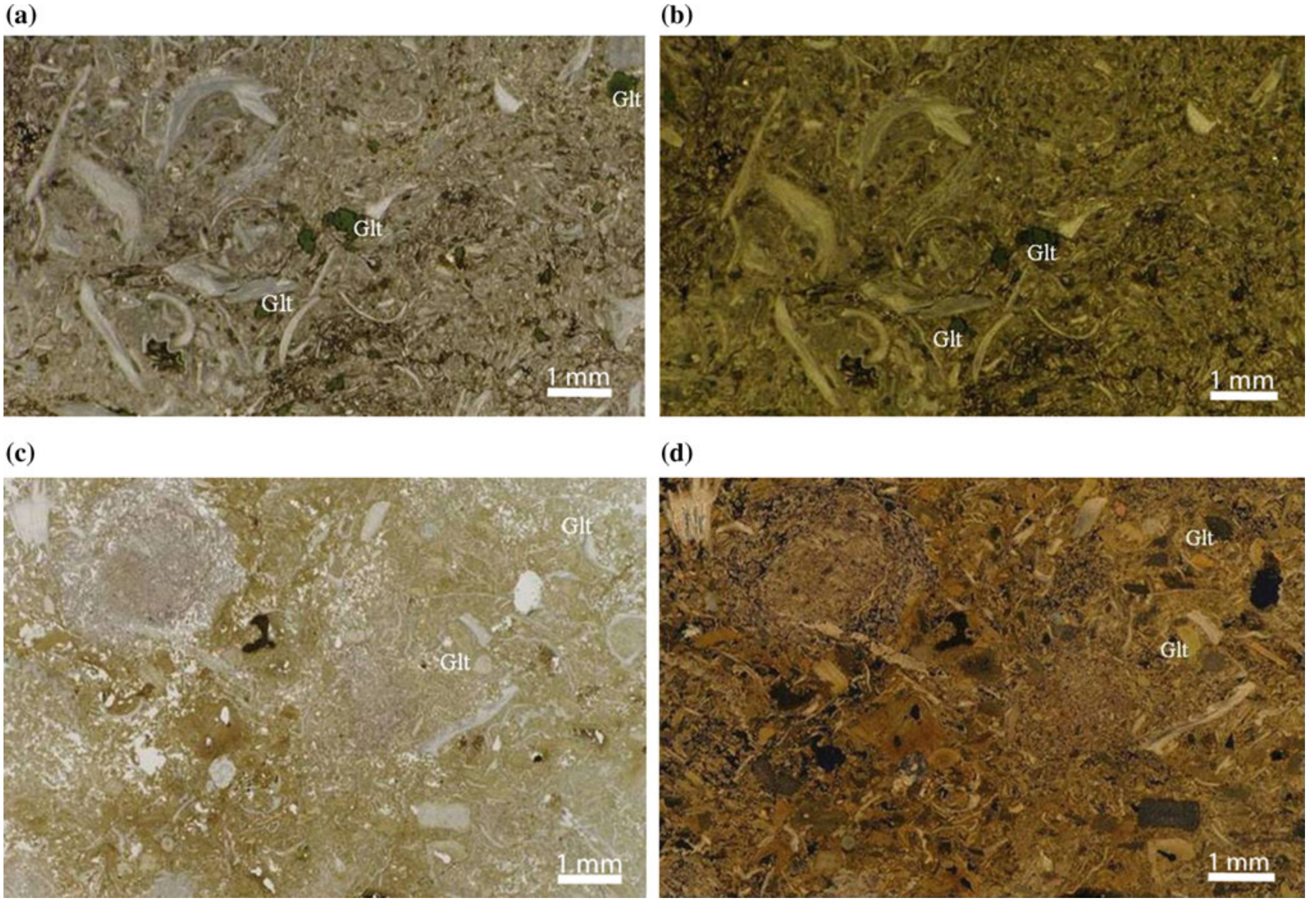

Fig. 2.30 Light microscope images of the thin sections of the flaglike limestone of the monument to the Unknown (N-18 No. 160) in the Necropolis of the 18th century (**a**, **b**) and from the Putilovsky deposit (**c**, **d**): **a**, **c** PPL, **b**, **d** XPL. There are numerous fragments of shells and green grains of glauconite (Glt)

Fig. 2.31 Putilovsky deposit. Photo by Aleksandr M. Marugin, 2007

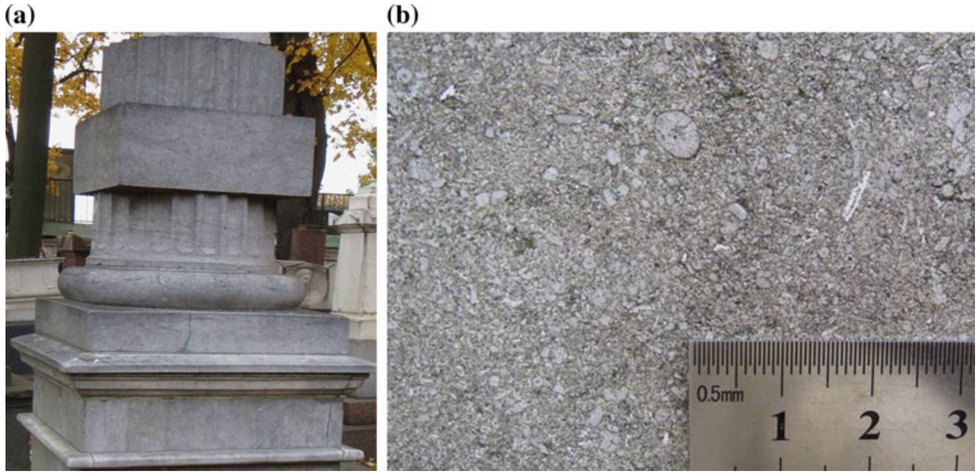

Fig. 2.32 The pedestal of the monument to S.N. Marin from gray dense limestone: **a** general view, **b** fragment of the rock

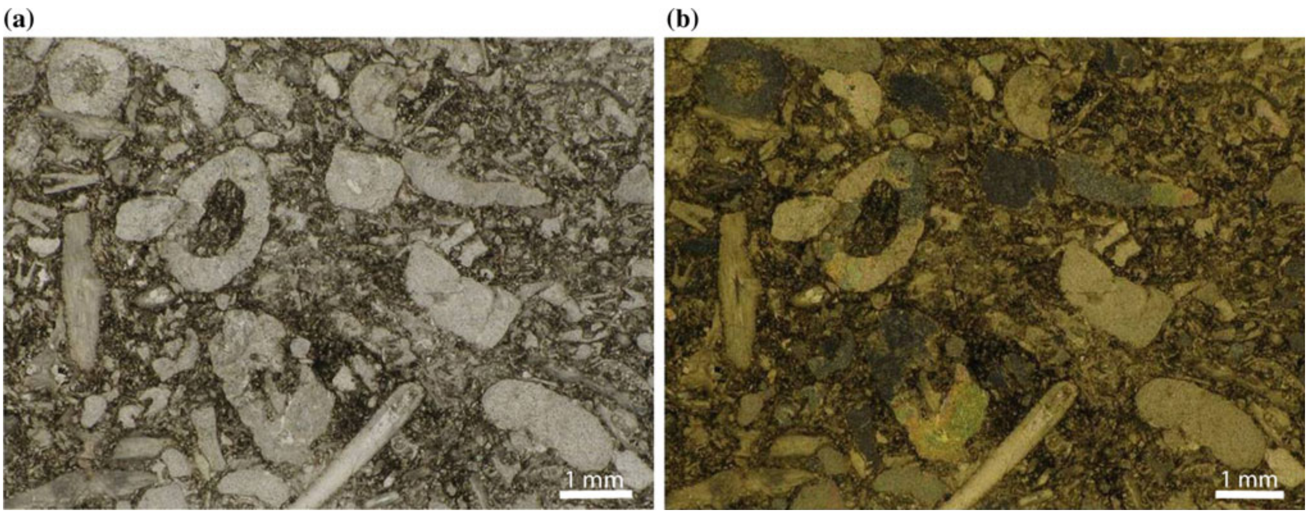

Fig. 2.33 Light microscope images of the thin section of gray limestone of the monument to A.G. Kusheleva: **a** PPL, **b** XPL. Numerous fragments of fossilized fauna are visible

cryptocrystalline carbonate (mainly calcite, rarely dolomite) (Fig. 2.36). Quartz is found as an impurity.

Textural and structural features of the travertine are characteristic for the biochemical limestones of the Pudost deposit (Fig. 2.36) located in the Leningrad region in the valley of the Izhora River, near the village of Bolshaya Pudost (Fig. 2.37). The first deliveries of calcareous tufa to St. Petersburg began in 1706–1713 when fountains and grottos were built in the Summer Garden in the Western fashion (Bulakh 2012). One of the last references to the use of Pudost stone dates back to 1965–1969, when it was quarried for the restoration work on the Kazan Cathedral (Gavrilenko 2007; Bulakh 2012).

For the tombs of F.P. and A.I. Tolstoys in the Necropolis of the 18th century, *gray-white spotted brecciated limestone* was used (Fig. 2.38).

The limestone is rich in fossilized fauna. The blotchy colour of the rock makes it look brecciated.

By its gray-white colour scheme, patchy, sometimes banded, colour distribution the rock is close to gray-white marmorized limestone (brecciated marble) described in Sect. 2.1. Its main difference is the abundance of fossilized fauna. It can be assumed that the compared rocks belong to a single geological structure, and brecciated organic limestone was also imported from Italy.

2.3 Granite and Other Hard Rocks

Many monuments of the Necropoleis are made of granites and other hard rocks. The most common is pink, red-pink, brownish-pink porphyritic, often ovoid, granite (Fig. 2.39).

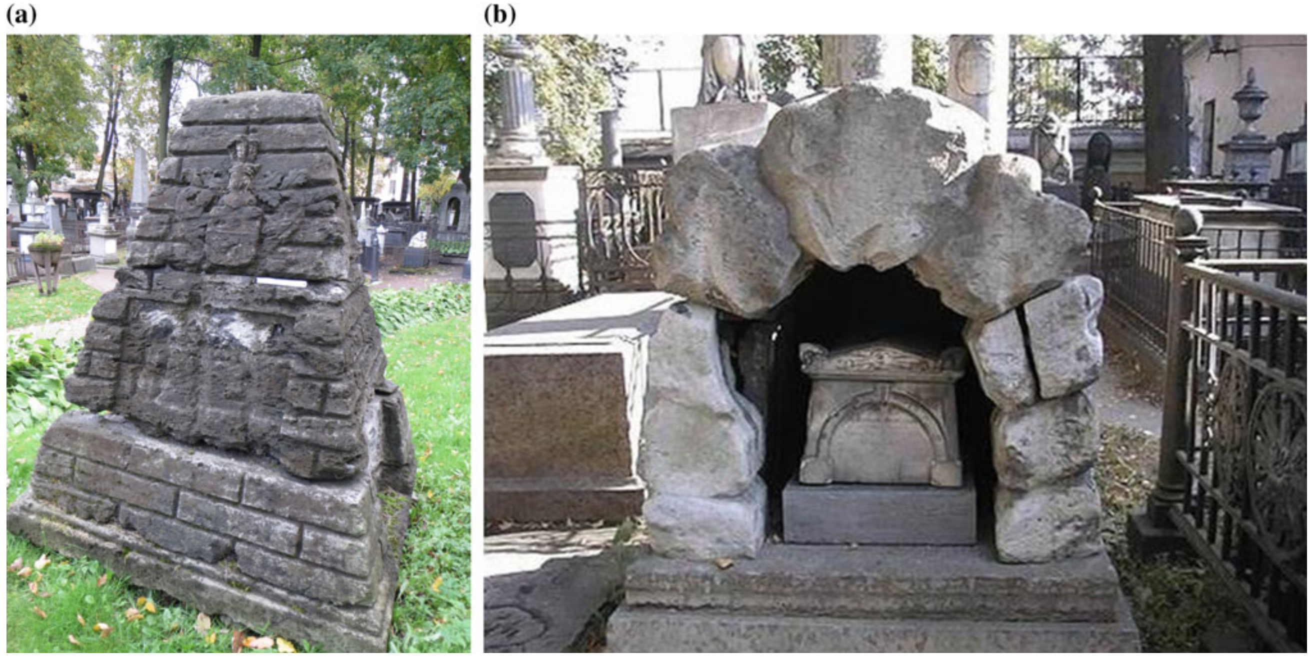

Fig. 2.34 Monuments from travertine: **a** to the Unknown (N-18 No. 901), **b** to P.A. Golitsyna

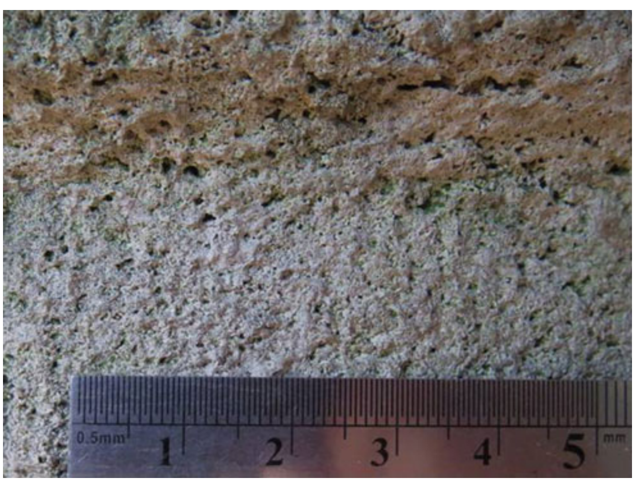

Fig. 2.35 Gray porous travertine with traces of ferruginization

Such material was mainly used for the foundations of monuments, pedestals, columns, semicolumns, steles. Memorials of V.V. Stasov, L. Euler, I.P. Martos, I.V., V.G., N.V. Kusovs and others were made from it.

On the surface of the granite of V.V. Stasov's tomb there are large (up to 8 cm) tabular crystals of potassium feldspar (microcline) immersed in the ground mass of the rock, composed of smaller quartz, feldspar and dark-coloured mineral crystals (Fig. 2.39b). In the thin sections it can be seen that microcline forms large (up to 13 mm) tabular crystals containing numerous intergrowths of plagioclase (Fig. 2.40a, b). Plagioclase (albite, oligoclase) is also present in the form of regular tabular crystals (0.3–0.5 mm), and quartz—in the form of separate isometric and angular grains and their clusters. Biotite and amphibole are found in the form of rare small intergrowths.

By its mineralogical and petrographic characteristics, the granite of V.V. Stasov's tomb (Fig. 2.40a, b) is similar to the porphyritic granite from the Montferrand quarry (Fig. 2.40 c), which is located in the South-East of Finland. From this granite the columns of St. Isaac's Cathedral and the Alexander Column in the Palace Square were carved.

Ovoid phenocrysts of pink feldspar (microcline, orthoclase) in porphyritic granite can reach 10 cm in diameter. Zonality is often manifested, formed by chains of inclusions of dark-coloured minerals (Fig. 2.41).

By their mineralogical and petrographic characteristics, pink, pink-red porphyritic ovoid granites of the Necropolis monuments are similar to rapakivi granites of the Vyborg massif. In St. Petersburg rapakivi granites and other pink porphyritic granites were supplied from the territories of the modern Leningrad region, Karelia and Finland (Ziskind 1989).

Brown-red equigranular granite (fine- and medium-grained or medium- and coarse-grained) is found in the Necropoleis much more rarely. In the Necropolis of the Masters of Art the pedestal of A.I. Kuindzhi's tomb (Fig. 2.42), and the gravestones of A.K. Glazunov, I.A. Melnikov, F.I. Stravinsky are made of this granite. It is known that this equigranular granite, called the Valaam

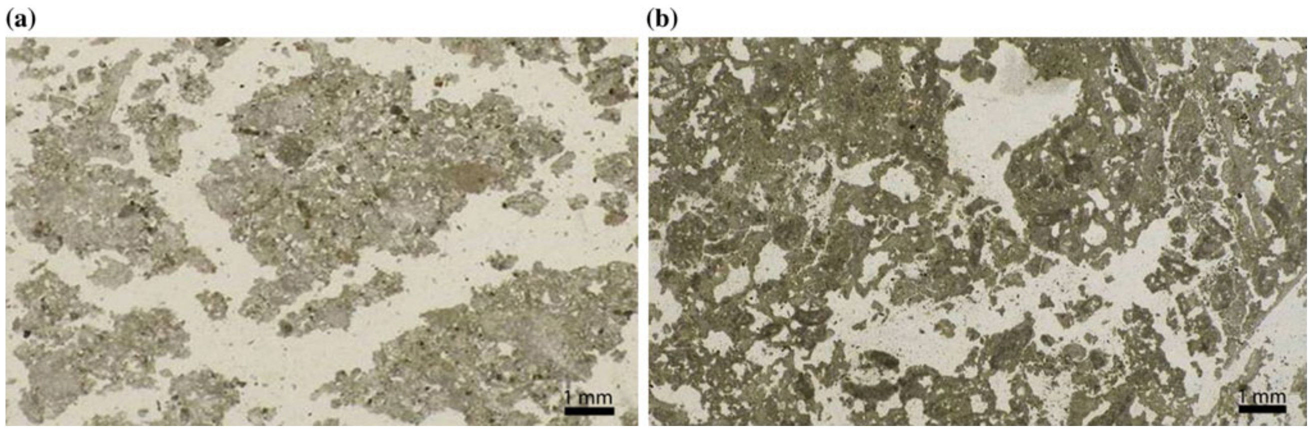

Fig. 2.36 Light microscope images (PPL) of the thin sections of highly porous travertines: **a** monument to the Unknown (N-18 No. 901), **b** pudost deposit

Fig. 2.37 Pudostsky quarry. Photo by Vera V. Manurtdinova, 2009

granite, is mined to date on Syskyjansaari Peninsula, located in the Ladoga Lake and connected to the mainland by a dam (Ziskind 1989). The similarity of rocks is manifest in their colour, structural features, qualitative and quantitative ratio of light-coloured and dark-coloured minerals (Fig. 2.43). The Valaam granite is often found in the decor of old and modern buildings in St. Petersburg.

The gravestone of G.A. Senyavin in the Necropolis of Masters of Art (Fig. 2.44) is close to Valaam granite in colour and mineral composition, but differs in its clearly manifested breccia texture and erratic distribution of rock-forming minerals and their aggregates. Where the rock was brought from is not established.

In the manufacture of the Necropolis monuments, gray, grayish-white, grayish-pink ovoid granite was also used. This is a medium-grained rock with large rounded feldspar inclusions (Fig. 2.45).

Gray rapakivi granites of the Vyborg Massif are known (Ziskind 1989); today quarries of this granite are near Vyborg and in Finland (south of Lappeenranta) (Bulakh 2012).

Gray ovoid granite was used in St. Petersburg from the end of the 19th century, for example, for the podium of the Stock Exchange and the pedestals of the Rostral columns. The obelisk “To Leningrad, the Hero-City” on Vosstaniya Square is made from it.

(a) (b)

Fig. 2.38 Cross on the pedestal of the monument to F.P. Tolstoy from light gray spotted brecciated limestone: **a** general view, **b** fragment of the rock

(a) (b)

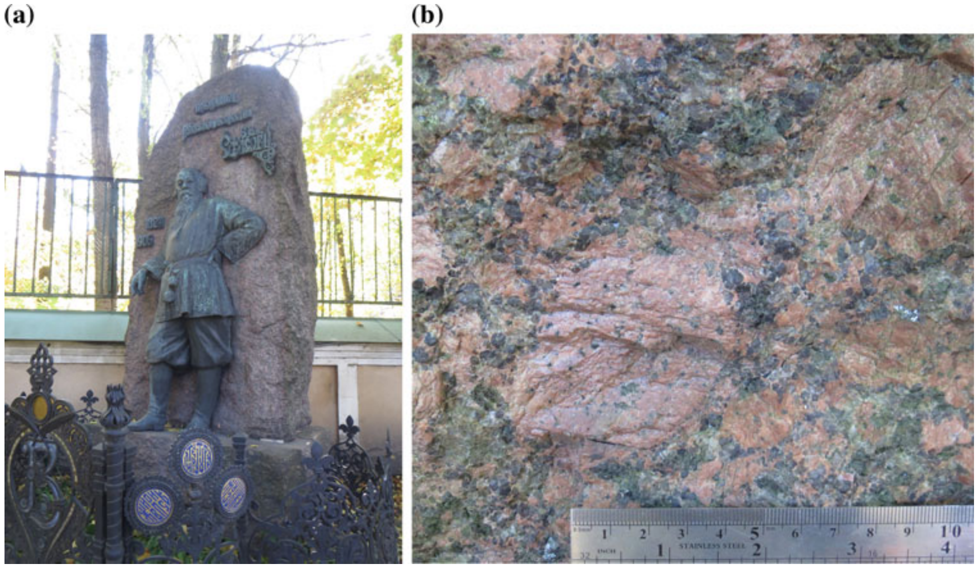

Fig. 2.39 Bronze portrait of V.V. Stasov against a block of pink coarse-grained granite: **a** general view of the monument, **b** fragment of the rock

(a) (b) (c)

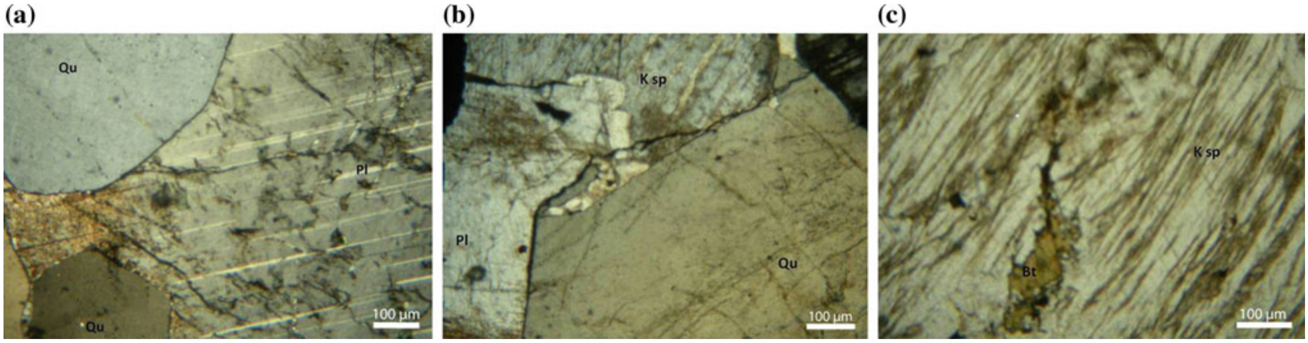

Fig. 2.40 Light microscope images (XPL) of the thin sections of pink porphyritic granite: **a**, **b** monument to V.V. Stasov, **c** Piterlaks (Piuterlahti) deposit, Montferrand's quarry. Legend: plagioclase—Pl, potassium feldspar (microcline—Mi), mica (biotite—Bt), quartz—Qu

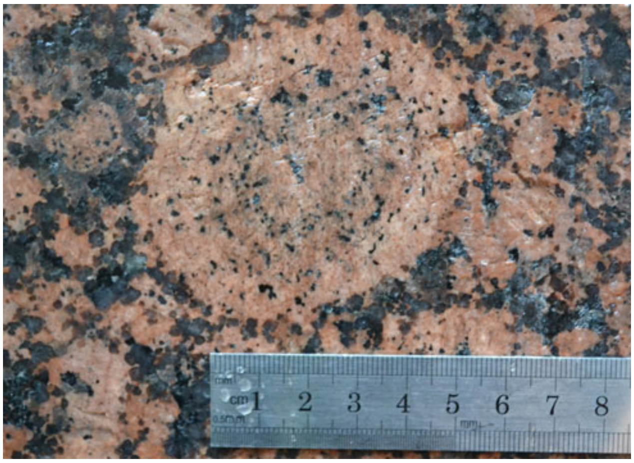

Fig. 2.41 Porphyritic granite with ovoids (monument to I.V., V.G., N. V. Kusovs in the Necropolis of the 18th century)

Tombs of gray, fairly homogeneous fine- and medium-grained, medium- and coarse-grained rocks are very common in the museum Necropoleis (Fig. 2.46). They often demonstrate a banded texture, which is manifested in the alternation of strips and lenses of different mineral composition and structure. The rocks look very much alike from the outside. The research identified granites, gneiss-granites, granite-gneisses, diorites and gabbros among them.

Mineralogical and petrographic study of F.A. Vlasova's gravestone showed that the rock consists of feldspars (predominantly), quartz and mica (Fig. 2.47). There are slightly elongated tabular crystals of acid plagioclase 0.2–0.8 mm, sometimes up to 1.5 mm in size. Quartz is represented by isometric grains of 0.1–0.5 mm in size, rarely—up to 2 mm, mica (biotite)—by subparallel lamellar crystals of 0.1–0.8 mm in size. According to the results obtained, the examined gray

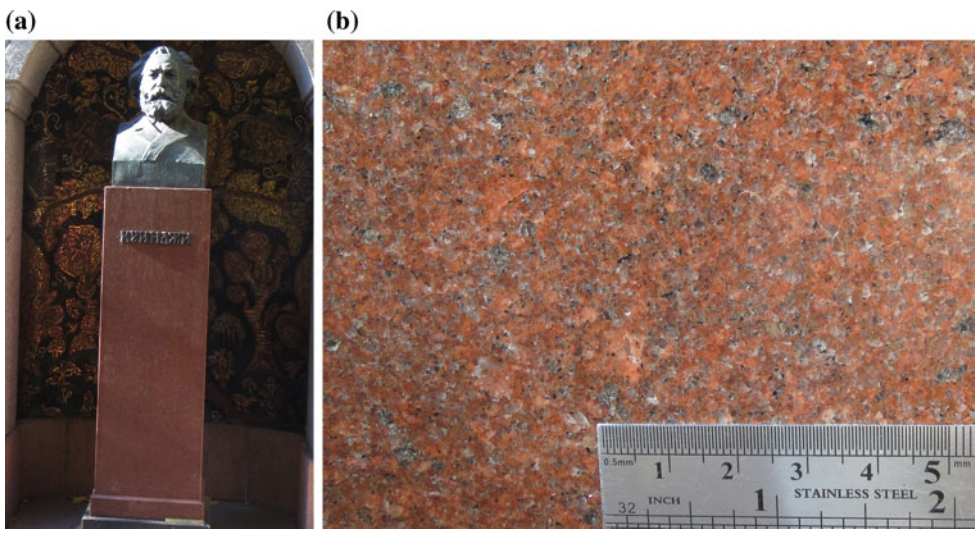

Fig. 2.42 Monument to A.I. Kuindzhi with a pedestal of brown-red fine- and medium-grained granite: **a** general view of the monument, **b** fragment of the rock

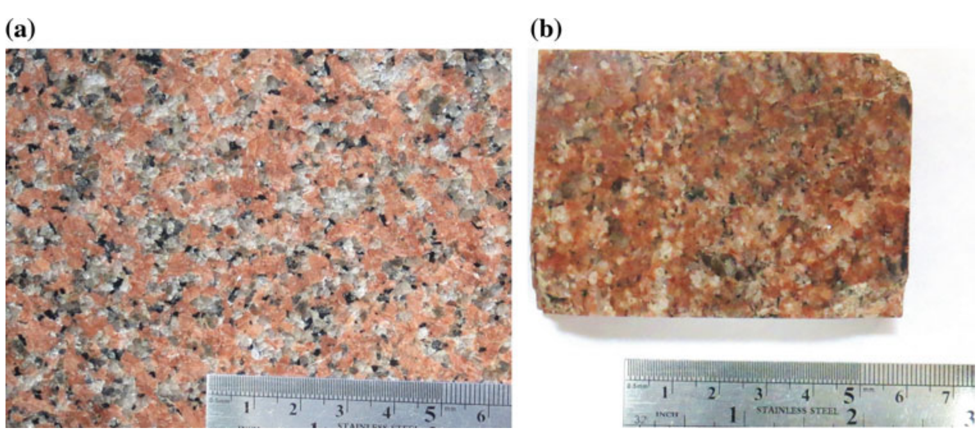

Fig. 2.43 Brown-red medium- and coarse-grained granite: **a** monument to I.A. Melnikov in the Necropolis of Masters of Arts, **b** the deposit (Island of Syskyjansaari)

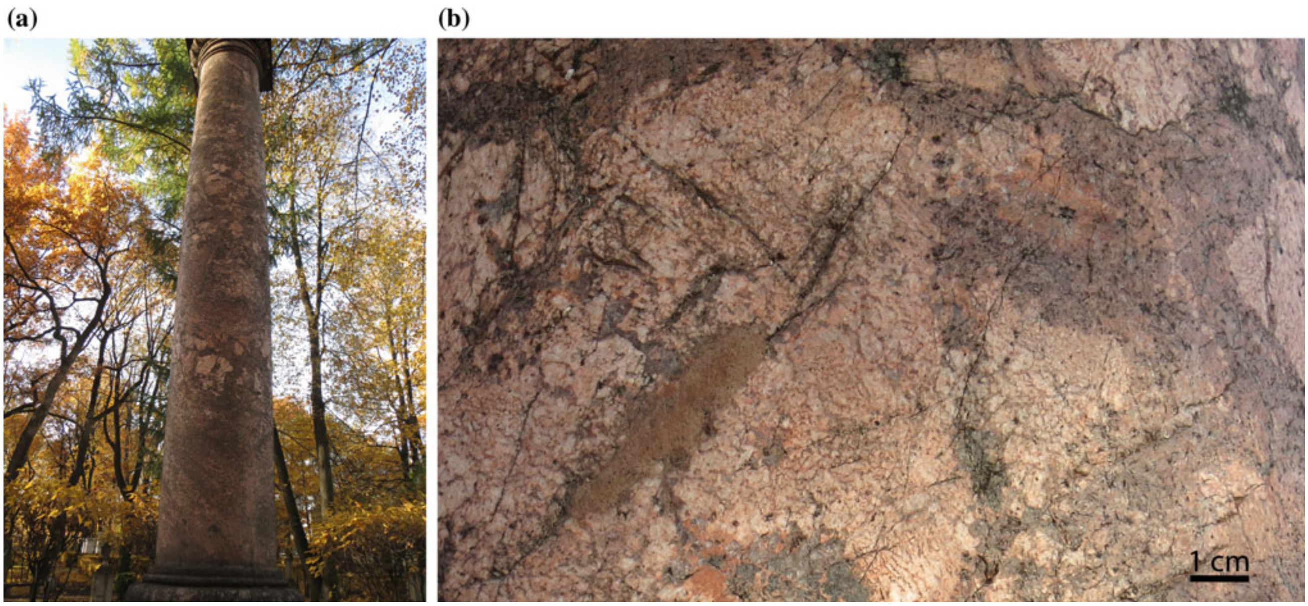

Fig. 2.44 G.A. Senyavin's column from brecciated granite: **a** general view, **b** fragment of the rock

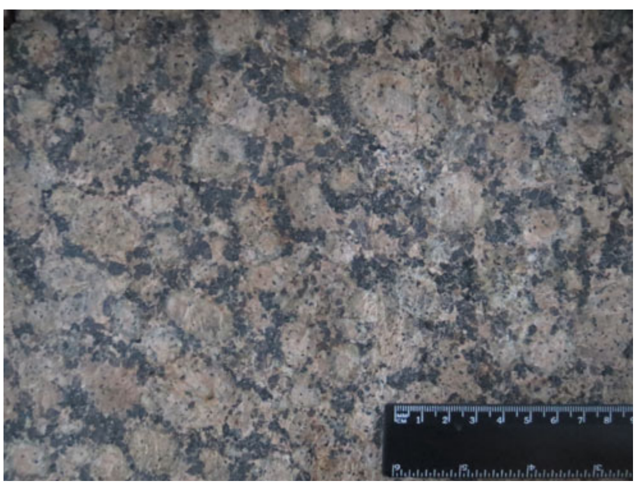

Fig. 2.45 Grayish pink ovoid granite (monument to M.I. Petipa)

Fig. 2.46 Gray homogeneous gneiss granite (monument to F.A. Vlasova)

fine- and medium-grained rock is gneiss-granite and, in its mineralogical and petrographic characteristics, is close to gneiss from the deposit near the village of Nukuttalahti and the town of Sortavala (Fig. 2.47b).

The results of the laboratory study of A.G. Kusheleva's and A.E. Egorov's gravestones showed that they are close to each other in terms of the mineral composition and structural features (Fig. 2.48).

Both are made up of fine- and medium-grained, sometimes porphyritic rocks, composed mainly of feldspar (basic plagioclase), pyroxene—to a lesser extent, also amphibole and mica. Plagioclase is represented by tabular, elongated crystals of 0.3–2.0 mm, sometimes up to 3 mm. Pyroxenes (diopside-augite) are represented by small isometric grains up to 1.5 mm, rimmed with amphibole (hornblende) and mica (biotite). In A.E. Egorov's gravestone microcline and quartz are present in very small amounts. In conformity with these data, the monuments to A.G. Kusheleva and A.E. Egorov are made of light-coloured gabbro.

Looking very much alike, these homogeneous, fine- and medium-grained rocks (gneisses, granites, granite gneisses, light-coloured varieties of gabbro), mined in Karelia near Sortavala (formerly called Serdobol), belong to the

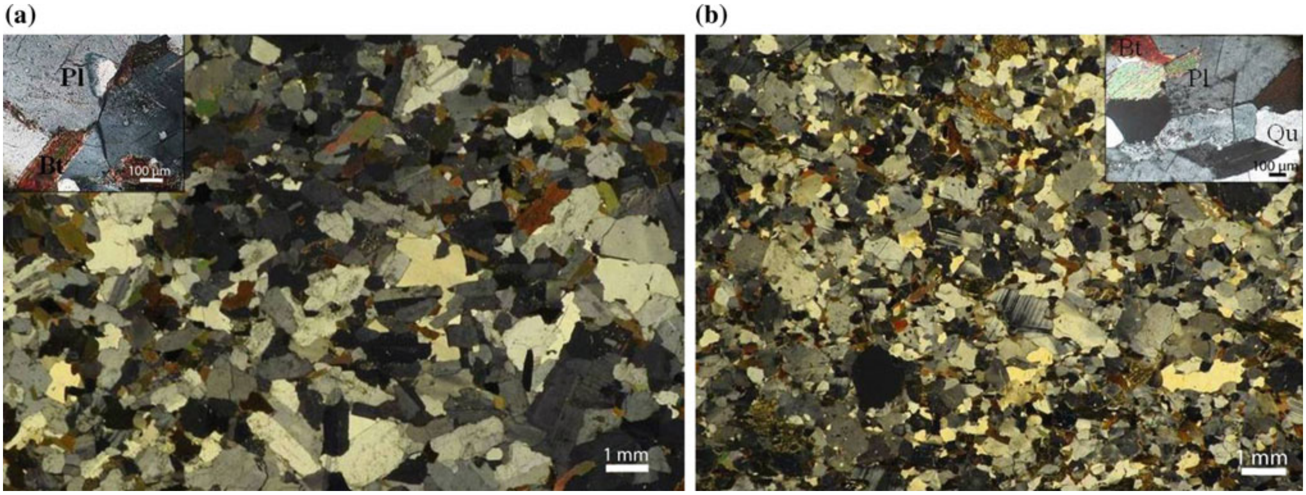

Fig. 2.47 Light microscope images (XPL) of the thin sections of gray gneiss-granite: **a** monument to F.A. Vlasova, **b** the deposit (Karelia, village of Nukkatalahti). Legend: plagioclase—Pl, mica (biotite)—Bt, quartz—Qu

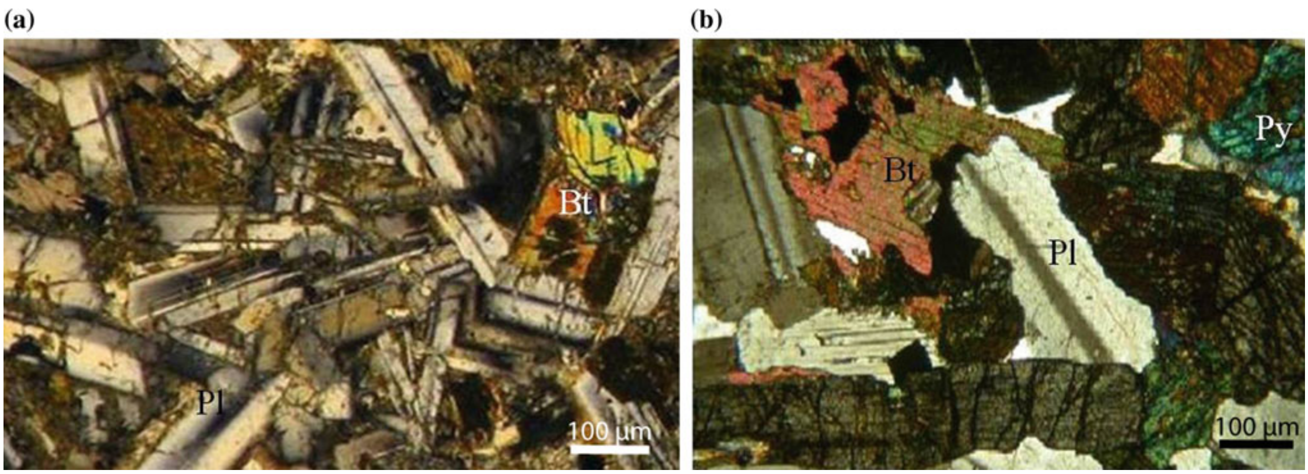

Fig. 2.48 Light microscope images (XPL) of the thin sections of light gabbro of the monuments: **a** to A.E. Egorov, **b** to A.G. Kusheleva. Legend: mica (biotite—Bt), plagioclase—Pl, pyroxene—Py

Impiniemi-Lavuatsaari complex (Geologiya 2000). Historically, these rocks are commonly called «Serdobol granites» (Borisov 2008b). They were quarried on the islands of Lake Ladoga. It is known that Serdobol granites were widely used in the construction of St. Petersburg. Probably, the stone for most of the tombs of the Necropolis of gray uniform fine- and medium-grained rocks was mined in the quarries in the Sortavala area.

Much less common in the Necropolis are dark-colored (when polished—black or dark gray) rocks of gabbro type, from which the memorials to I. Musin-Pushkin, L.I. Shestakova, M.I. Glinka, M.A. Balakirev are carved (Fig. 2.49). It is known that these are equigranular fine crystalline rocks consisting of basic plagioclase and pyroxene (Ziskind 1989). The gabbro type rock is quarried in Karelia near Sortavala, and in the Leningrad Region.

The tomb of N.I. Utkin in the Necropolis of Masters of Art is made of *dark gray-green dense, fine- and medium-grained silicate rock with poorly manifested banding* (Fig. 2.50).

The laboratory study showed that the rock is mainly composed of amphibole, feldspars and quartz (in a subordinate amount) (Fig. 2.51a). Amphibole is represented by tabular and isometric crystals of hornblende. The grain size varies from 0.5 to 2 mm, sometimes reaching 3 mm. In the intergrowth with hornblende, relicts of pyroxene grains and chain sphene grains are observed. Plagioclase (andesine) is present in the form of tabular and isometric crystals

Fig. 2.49 Monument to I. Musin-Pushkin from gabbro-type rock

0.2–0.4 mm in size, quartz—as small xenomorphic grains and ingrowths in hornblende. According to the results of the study, it was established that the rock is amphibolite, similar in mineralogical and petrographic features to the amphibolite from the quarry on the island of Syskyjansaari (Karelia) (Fig. 2.51). Further research should answer the question whether there are other monuments of amphibolite in the museum Necropoleis.

Amphibolites are widespread in Karelia, in particular in the Sortavala area, where Serdobol granite is mined (Borisov 2008b). Usually they do not form large deposits. There are cases when amphibolite was mistaken for a darker variety of Serdobol granites.

Monuments made of *garnetiferous gneiss—a mottled rock with various phenocrysts (up to 10 cm in diameter) of crimson garnets—almandines* make the Necropoleis look very graceful (Fig. 2.52). Segregated banding of dark-colored minerals and garnets is clearly visible (Fig. 2.53). Garnetiferous gneiss was used for the monument to S.S. Botkin, as well as for pedestals of the monuments to P.V. Kindyakov, P. I. and E.S. Meshcherskys, P.I. Shubin and others.

The petrographic research of the material of S.S. Botkin's monument showed that this medium- and coarse-grained rock is a quartz-feldspar aggregate containing a substantial amount of mica (biotite). Garnet grains, intergrown with quartz, reach 3 mm in diameter in the thin section. Feldspar is represented by acid plagioclase (Fig. 2.54). Most likely, the stone was brought from the Ladoga area, where the outcrops of this rock are found (Borisov 2007; Baltybaev et al. 2009).

A notable place in the Necropolis of Masters of Art is occupied by the monument to I.R. Tarkhanov, sculpted to the design made by his wife E.P. Tarkhanova-Antokolskaya. The stone material of the monument is a very beautiful *greenish-gray medium- and coarse-grained porphyritic rock with large lathlike crystals of feldspar* (Fig. 2.55).

(a) (b)

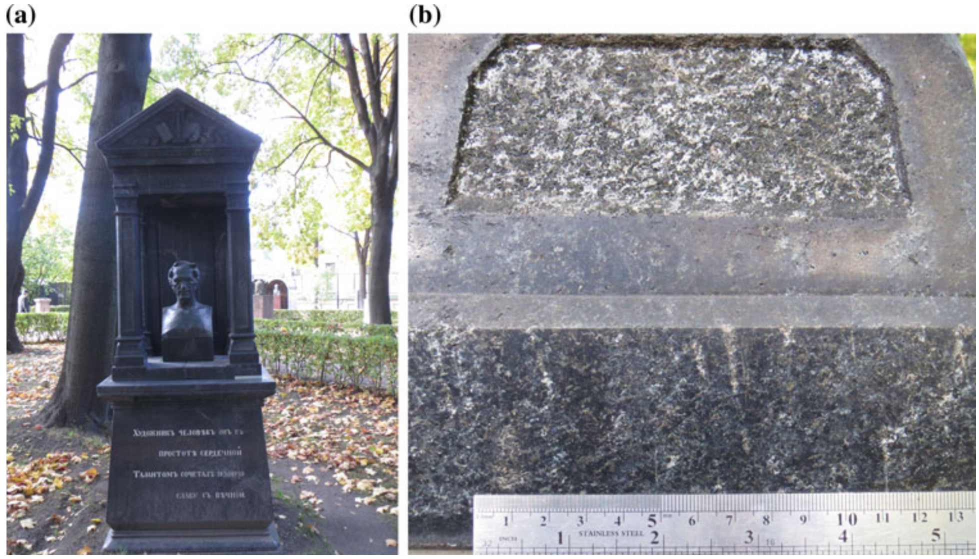

Fig. 2.50 Monument to N.I. Utkin from amphibolite: **a** general view of the monument, **b** fragment of the rock

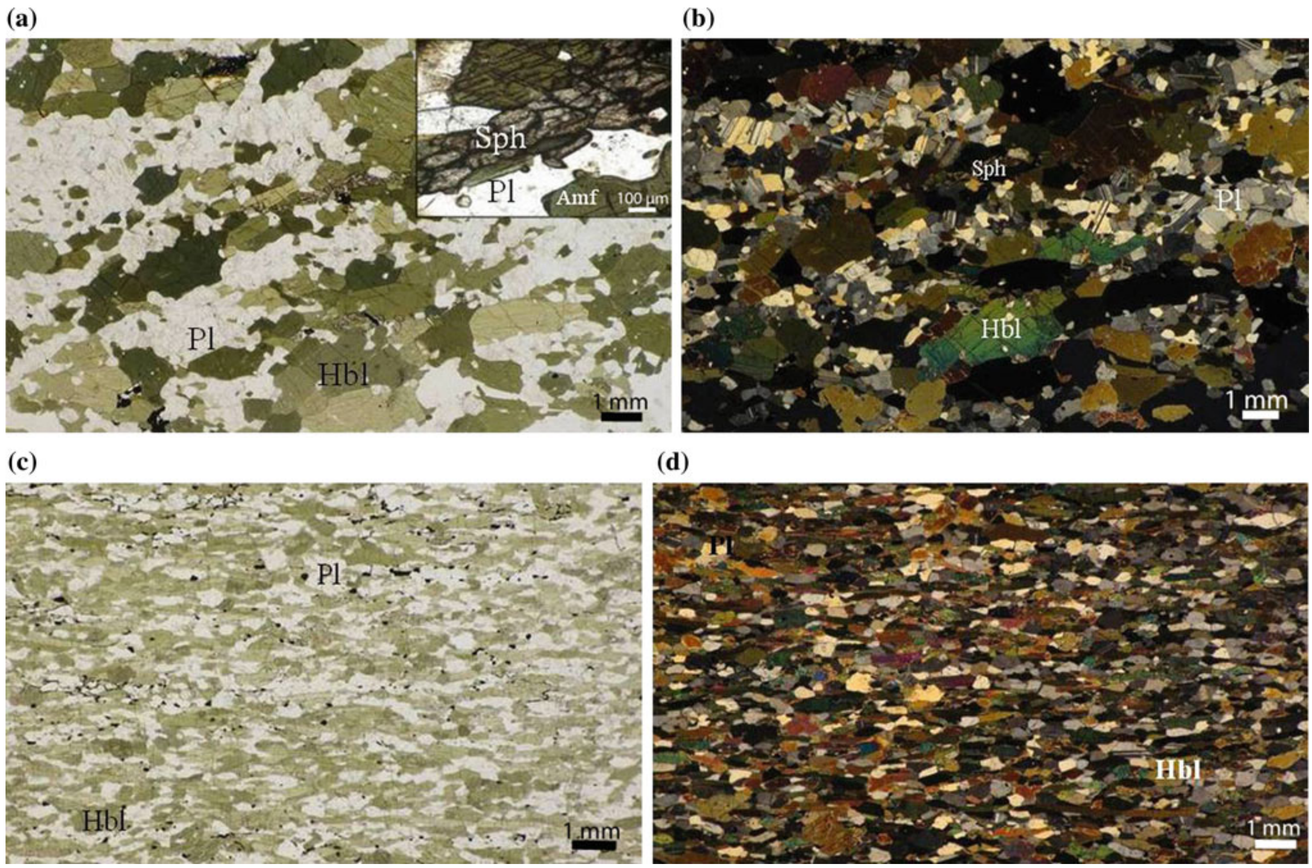

Fig. 2.51 Light microscope images of the thin sections of amphibolite from the monument to N.I. Utkin in the Necropolis of Masters of Art (**a**, **b**) and from the island of Syskyjansaari (**c**, **d**): **a**, **c** PPL; **b**, **d** XPL. Legend: amphibole (hornblende-Hbl), plagioclase-Pl, sphene-Sph

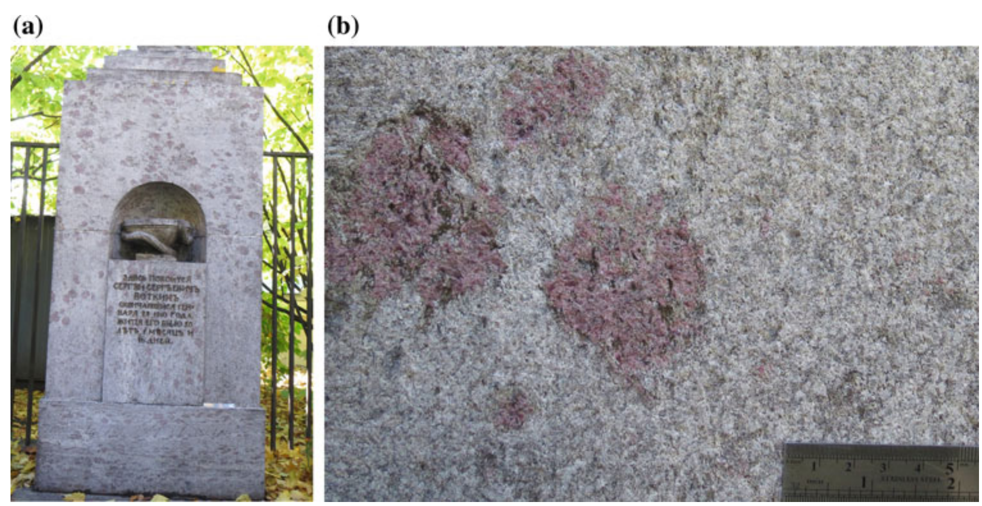

Fig. 2.52 Monument to S.S. Botkin from garnetiferous gneiss: **a** general view of the monument, **b** fragment of the rock

According to the results of the mineralogical and petrographic study, the rock consists almost entirely of basic plagioclase (Fig. 2.56). Pyroxene (probably diopside), biotite and quartz are present in small amounts. Plagioclase is represented by large (up to 12 mm) lathlike and tabular crystals, pyroxene—by small (up to 0.3 mm) tabular and isometric crystals, and biotite—by lamellar crystals (up to 0.8 mm). There are also grains of an ore mineral, possibly magnetite. Between the grains there are segregations of acid plagioclase. The obtained results proved that the examined

Fig. 2.53 Fragment of garnetiferous gneiss rock (monument to P.I. Shubin)

rock was anorthosite—the rock of the gabbro group, almost entirely composed of plagioclase.

Another rock among the most beautiful ones in the Necropoleis, labradorite, is practically a monomineral rock of the gabbro group composed of basic plagioclase, Labrador spar. From this rock the stele of V.F. Komissarzhevskaya's tomb in the Necropolis of Masters of Art (Fig. 2.57) was made. Thanks to the iridescence of feldspar (the sheen on the dark surface), labradorite is a valuable decorative stone. There is no information on the source of labradorite in the Necropolis in the archives of the Museum of Urban Sculpture.

The hardest rock in the Necropoleis is quartzite, *a homogeneous dense rock of red, crimson-red colour* (Fig. 2.58). Quartzite was used in the manufacture of decor elements, pedestals and sarcophagi. In the Necropolis of the

(a) (b)

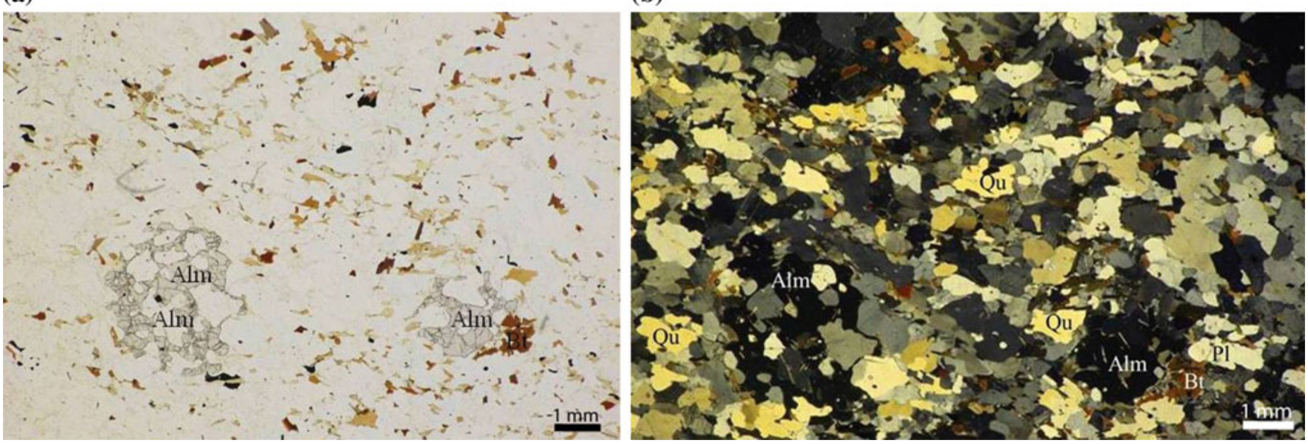

Fig. 2.54 Light microscope image of the thin section of garnetiferous gneiss (the monument to S.S. Botkin): **a** PPL; **b** XPL. In the biotite-quartz-feldspar mass phenocrysts of almandine garnet can be seen

(a) (b)

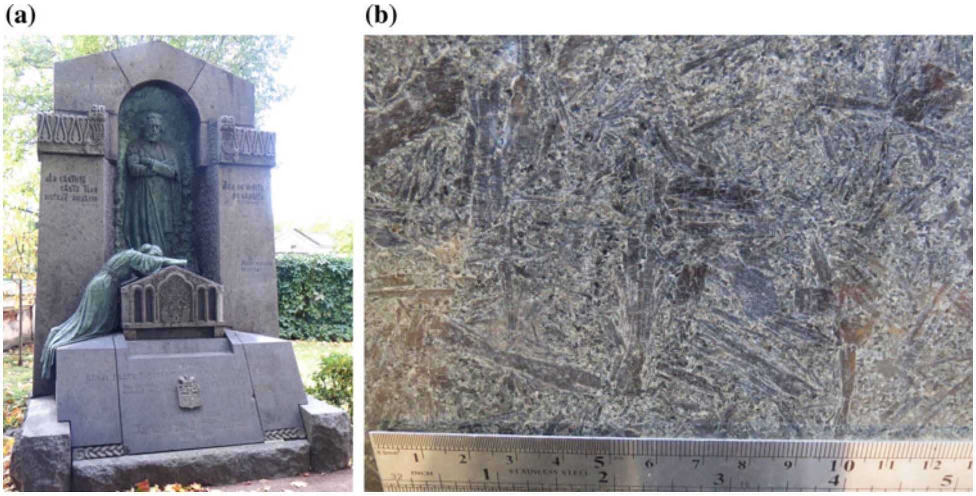

Fig. 2.55 Monument to I.R. Tarkhanov from anorthosite: **a** general view of the monument, **b** fragment of the rock

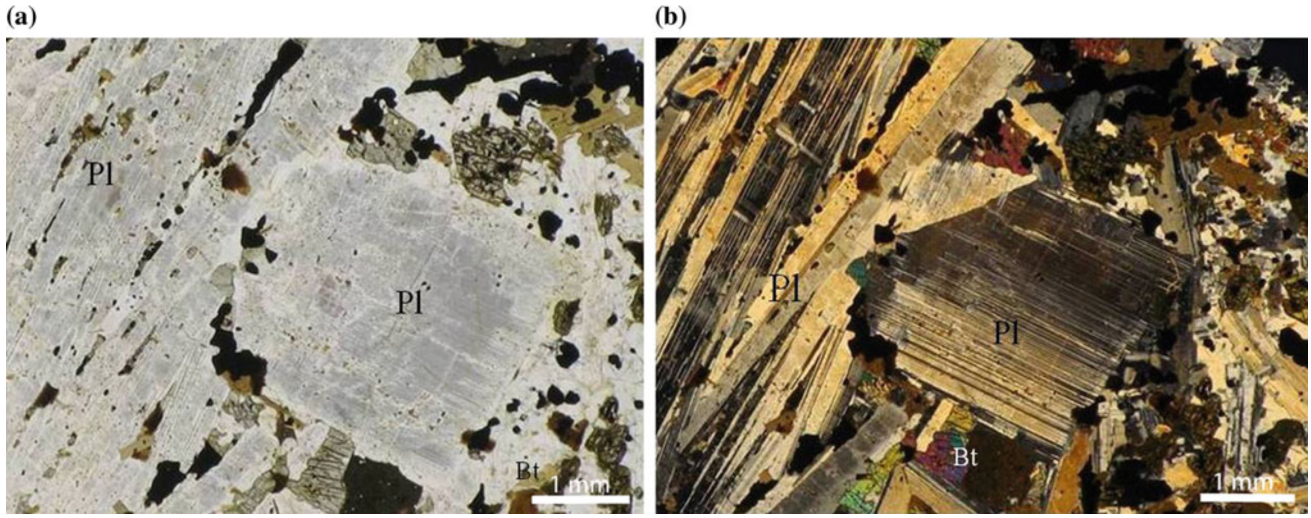

Fig. 2.56 Light microscope images of the thin section of anorthosite (the monument to I.R. Tarkhanov and E.P. Tarkhanova-Antokolskaya): **a** PPL; **b** XPL. The rock is almost entirely composed of large tabular and lathlike crystals of plagioclase (Pl). Small grains of biotite (Bt) can be seen

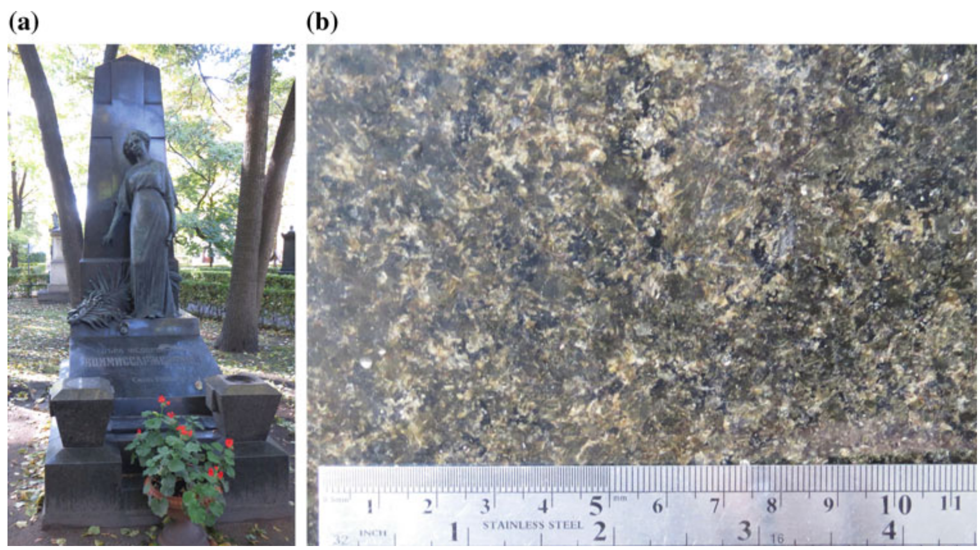

Fig. 2.57 Monument to V.F. Komissarzhevskaya with a stele from labradorite: **a** general view of the monument, **b** fragment of the rock

18th century. Details of the monuments to A.V. Skrypitsyn, A.F. Turchaninov, P.M. Arsenyev, N.S. Nertovskaya and others are made of this stone. The laboratory studies of the stone of A.F. Turchaninov's and the Unknown's tombs (N-18 No. 959) showed that it is a monomineral aggregate, composed of different-sized isometric quartz grains (0.05–1.50 mm) (Fig. 2.59). The crimson-red colour of the rock is due to the presence of iron oxides and hydroxides in the intergranular space.

The unique existing Shokshinskoye field of brightly colored crimson quartzites is located to the south of Petrozavodsk on the shore of Onega Lake (Ziskind 1989). Mining of Shokshinsky quartzites began at this deposit as far back as the 18th century. Outwardly, this stone resembles the famous porphyry from Egypt, and that is why in the old days it was often called "shohan porphyry" (Bulakh 2006). The pedestal of the monument to Nicholas I on St. Isaac's Square is made of it.

Fig. 2.58 Urn from red quartzite (the monument to A.V. Skrypitsyn in the Necropolis of the 18th century)

Thus, the diverse stone material in the museum Necropoleis is represented by marbles, limestones, granites and other hard rocks (gneisses, gabbroids, amphibolites, quartzites). To complete the picture, it is necessary to mention that in the Necropoleis there are also tombstones, separate parts of which are made of slate, and in the Necropolis of the Masters of Arts there is a monument to I.V. Tartakov, made of quartz sandstone. The results of observations, mineralogical and petrographic characteristics, archival data and published materials made it possible to ascertain the sources of stone supply to the Necropoleis, with varying degrees of reliability and detail. Basically, the stone came from Italy and the areas close to St. Petersburg (from the territory of the present Leningrad region, Karelia and Finland).

The museum Necropoleis are not inferior to the historical center of St. Petersburg in the variety of stone. Among the monuments there are unique ones (to N.A. Rimsky-Korsakov, I.R. Tarkhanov, etc.) made of stone, which has not yet been found anywhere else and whose origin is unknown.

The obtained characteristics of stone materials of the memorials are entered in the «Database on the state of the sculptural monuments in St. Petersburg» (www.opticalcomponents.ru). The data on the sources of stone supply for the tombstones serve and will continue to serve as indispensable information for restoration work.

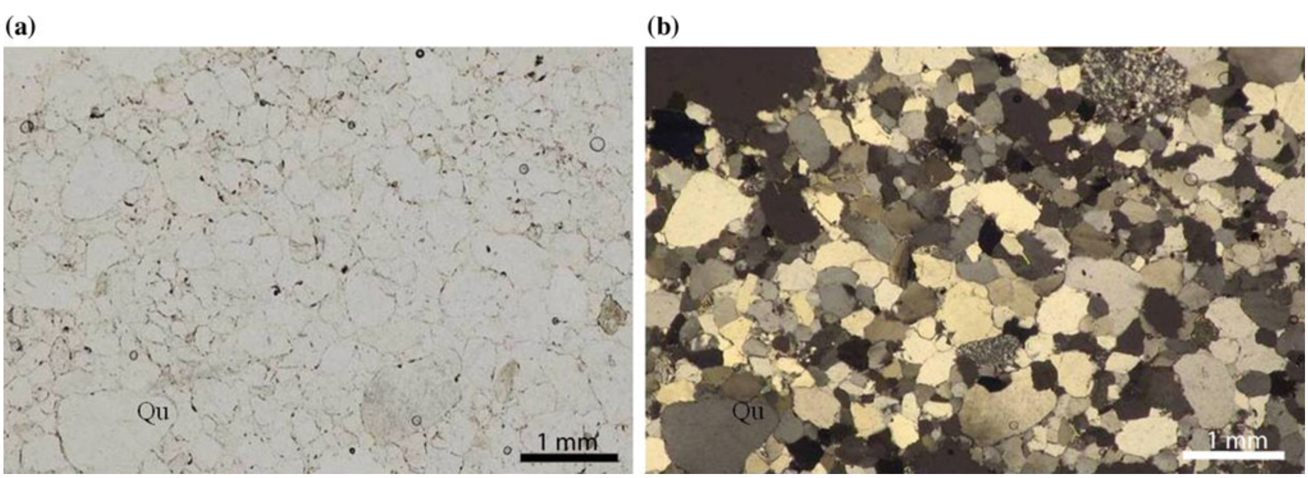

Fig. 2.59 Light microscope image of the thin section of Shokshinsky quartzite of the monument to the Unknown (N-18 No. 959): **a** PPL; **b** XPL

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3 Outdoor Environment of the Monuments in the Necropoleis

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Abstract

A study of the ambient air, soil, vegetation, and biogenic layers on the surface of the monuments was carried out in order to identify environmental factors that have an adverse effect on the condition of the monuments in the Museum necropoleis. It was found out that the corrosivity of the air at the Necropoleis corresponds to the medium category C3 and gradually decreases (primarily due to a reduction in the sulfur dioxide content). The soil near the monuments is another source of contamination of their surface, occurring with the participation of various microorganisms. Selective accumulation of miscellaneous elements on the surface of monuments from the environment and low-molecular organic substances depends, above all, on the species composition of the lithobiont community. The presence of woody plants produces microclimate effects in different parts of the Necropoleis, which has a significant impact on the condition of the monuments.

Keywords

Environmental factors • Ambient air • Soil
Vegetation • Biogenic buildups • Primary soil
Atmospheric corrosivity • Gaseous pollutants
Sulfur dioxide • Corrosive activity • Gypsum
Low molecular weight organic compounds
Algae • Lichens • Mosses • Woody plants

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Monuments of the Necropolises, being in the open air, are exposed to aggressive environmental factors. The interrelated processes of chemical, biological and physical weathering gradually destroy the materials of the monuments. Intensity of these processes depends significantly on the corrosivity of atmosphere, soil characteristics and biological environment (vegetation cover, microorganisms).

3.1 Ambient Air

Monitoring of ambient air in the museum Necropolises has been performed since June 2006. Its methods are described in a number of papers (Chelibanov et al. 2008, 2010, 2012; Gruzdev et al. 2010; Kozlovsky et al. 2013; Kozlovsky 2015). The main purpose is to assess the corrosive activity of the air environment and to track its seasonal changes for planning the measures of anticorrosion protection.

Corrosivity is associated with climatic conditions and atmospheric air pollution (Mihailov et al. 2004; Watt et al. 2009; ISO 9223: 2012). Mean annual values of the main corrosive parameters of the air in the Necropolis of the 18th century and, for comparison, on one of the transport thoroughfares of St. Petersburg—at 58 Maly Prospekt of Vasilyevsky Island, (hereinafter Maly Pr) for 2012–2013 are presented in Table 3.1.

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Table 3.1 Average annual values of the corrosive parameters of atmospheric air for 2012–2013 (Kozlovsky 2015)

Parameter	Designation, dimension	Parameter value in the Necropolis of the 18th century	Parameter value on Maly Pr
Rate of SO_2 deposition	K_{SO2}, mg m^{-2} day^{-1}	4.8 (2012); 4.64 (2013)	8.8 (2012) 8.4 (2013)
Rate of chloride ions deposition	K^{-}_{Cl}, mg m^{-2} day^{-1}	0.3 (2012) 0.4 (2013)	8 (2012) 10 (2013)
SO_2 concentration	C_{SO2}, μg/m^3	6 (2012) 5.8 (2013)	11 (2012) 10.5 (2013)
NO_2 concentration	C_{NO2}, μg/m^3	58.92 (2012) 41.59 (2013)	72.09 (2012); 72.79 (2013)
HNO_3 concentration	C_{HNO3}, μg/m^3	0.76 (2012) 0.68 (2013	1.04 (2012) 1.09 (2013)
O_3 concentration	C_{O3}, μg/m^3	16.22 (2012) 17.15 (2013)	23.93 (2012) 26.08 (2013)
Dust concentration	C_{PM10}, μg/m^3	16 (2013)	40 (2013)
Concentration of chloride ions in the fallout	C^{-}_{CL}, μg/l	0.8	0.8
Concentration of hydrogen ions in the fallout	C_{H+}, μg/l	0.003	0.003
Hydrogen index of the fallout	pH	5.5	5.5
Amount of the fallout	T_R, mm	610	610
Relative humidity	RH, %	78.74 (2012) 78.87 (2013)	77.97 (2012) 77.25 (2013)
Temperature	T °C	7.19 (2012) 7.98 (2013)	7.29 (2012) 7.87 (2013)

Among air pollutants sulfur dioxide and chlorine compounds, as well as nitrogen oxide and dioxide plus ozone, have the greatest corrosive effect (Watt et al 2009). Interaction of sulfur dioxide with carbonate materials leads to gypsum formation, which adversely affects the state of the monuments of marble and limestone (see Sect. 4.3). Synergetic effect of the chlorine compounds and sulfur dioxide results in activation of corrosion processes on the surface of bronze monuments, their deep ingress into the copper alloy (see Sect. 4.4). Ozone and nitrogen oxides act as strong oxidants and catalysts for reactions between pollutants in the air and materials of the monuments and in many ways determine the rates of these reactions.

Parameters of microclimate and air pollution vary near the surface of the monuments because of their complex shape. The effect of pollutants on a monument, as distinct from that on humans, depends not so much on their concentrations as on the rate of deposition on the surface. This rate may change because of turbulence of air currents, the surface relief, available moisture. As a result, the local corrosive activity of the air is not the same for different parts of the monument.

This is why the relationship between the corrosive parameters of the air and the material losses due to corrosion is determined not on the monument itself, but with special tools—corrosion coupons, whose shape, roughness and surface dimensions ensure uniform corrosion (Mihailov et al. 2004). These relationships, obtained by regression analysis of large data arrays on corrosion of coupons made from different materials and exposed to different environmental and climatic conditions, are called dose—response functions (Table 3.2).

The category of atmospheric corrosivity in the Necropoleis was determined by the corrosion rate of copper (Table 3.3) using two methods: the computational method—with dose-response functions and the experimental one—using specially manufactured copper corrosion coupons.

Copper was chosen as a material for corrosion coupons because it has a durable corrosion layer of cuprous oxides (patina), which does not flake off when the coupons are packed, shipped and weighed. Other advantages are the ease of stripping this patina without losing the copper from the coupons, comparative convenience of storing etchants, and the independence of corrosion rate from the thickness of the patina formed during the first year of exhibiting coupons.

Coupons of various shapes were tested (Figs. 3.1 and 3.2). A shortcoming of flat (strip) coupons was established, which demonstrated a considerable difference in corrosion losses (up to 20%), associated with different pathways of the pollutants' fallout, running parallel or perpendicular to the surface of the strip.

Table 3.2 Dose-response functions for calculation of corrosion losses of materials exposed to different environmental conditions (Vapirov et al. 2010; Mikhailov 2000; ISO 9223:2012; Kucera 2005; Lan et al. 2005)

Material	Dose—response functions
Carbon steel	$V_K = 1.77K_{SO2}^{0.52}\exp[0.020RH + 0.150(T - 10)] + 0.102K_{Cl-}^{0.62}\exp(0.033RH + 0.040T)$
Copper	$V_K = 0.0053K_{SO2}^{0.26}\exp[0.059RH + 0.126(T - 10)] + 0.01025K_{Cl-}^{0.27}\exp(0.036RH + 0.049T)$
Copper	$ML = 0.0027C_{SO2}^{0.32}C_{O3}^{0.79}RH\exp[0.083(T-10)]t^{0.78} + 0.05\,T_R\,C_{H+}t^{0.89}$
Cast bronze	$ML = 0.026C_{SO2}^{0.44}RH\exp[0.060(T - 11)]t^{0.86} + 0.029\,T_R\,C_{H+} + 0.00043\,T_R\,C_{Cl-}t^{0.76}$
Cast bronze	$ML = 1.33 + \{0.00876C_{SO2}RH_{60}\cdot\exp[0.060(T-11)] + 0.0409\,T_R\,C_{H+} + 0.0380PM10\}t$
Limestone from Portland	$TL = t^{0.96}[2,7\,C_{SO2}^{0.48}\exp(-0,018T) + 0,019\,T_R\,C_{H+}]$
Limestone from Portland	$TL = 3.1 + (0.85 + 0.0059C_{SO2}RH_{60} + 0.054\,T_R\,C_{H+} + 0.078C_{HNO3}Rh60 + 0.0258PM10)\,t$
Sandstone from Mansfield	$TL = t^{0.91}(2.0\,C_{SO2}^{0.52} + 0.028\,T_R\,C_{H+})$
Marble from Italy	$TL = (0.00233RHC_{SO2})t + 0.00309\,T_R$

Note Parameters: V_K—corrosion rate, g/(m^{2}year); ML—specific corrosive weight loss, g/m^2; TL—the thickness of the corrosion layer, μm; t—duration of exposure, yrs, $V_K = ML/t = TL\cdot\rho/t$; $C_{HNO3} = 516\exp[-3400/(T + 273)]\,(C_{NO2}C_{O3}\,RH)^{0.5}$; other parameters see in Table 3.1

Table 3.3 Intervals of the corrosion rate (V_K) values corresponding to different categories of corrosion activity (CA) of the air, for the first year of exposure of standard copper samples (Mikhailov 2000; ISO 9223: 2012)

CA	CA category	$V_{K,}$ gm^{-2} yr^{-1}
Very low	C1	≤ 0.9
Low	C2	$0.9 < V_K \leq 5$
Average	C3	$5 < V_K \leq 12$
High	C4	$12 < V_K \leq 25$
Very high	C5	$25 < V_K \leq 50$
Extreme	CX	$50 < V_K \leq 900$

The cone-shaped coupons showed stable work, with them the corrosion losses did not depend on the direction of the pollutants' flow.

A system of two corrosion coupons can also be used to assess non-stationary microclimatic conditions caused by sharp temperature changes due to weather events. For this assessment, the coupons (Fig. 3.2) have to be made with the same surfaces of heat exchange with the environment, but with different thermal inertia (Marugin et al. 2013). The difference is provided by using in one of the coupons a built-in heat-retaining element with reflective thermal insulation. The relative difference in the corrosion losses of the two coupons is used to determine the degree of the non-stationary character of the microclimate on which the life span of the fractured materials depends. At present, with these systems of coupons, statistic data are collected for their standardization and certification.

The computational method was used to predict the rates of material corrosion in the Necropolis of the 18th century and, for comparison, near the motorway (Maly Pr), taking into account the corrosivity parameters given in Table 3.1. The experimental method was used to determine the category of the atmospheric corrosive activity in the most famous heritage sites, as well as on Maly Prospect in 2012–2014. Corrosion losses of the coupons were determined by the change in their weight after stripping of the corrosion film in accordance with the ISO 9226:2012 standard. To identify the seasons of higher corrosion activity, the weight loss of a separate group of coupons was measured monthly between July 2012 and June 2014. In addition to the Necropolis of the 18th century, to compare the conditions of the existence of monuments, corrosion coupons were also installed in the museum complexes of Pavlovsk and Petrodvorets. The uncertainty of corrosion rate estimation by the computational method may exceed 30%, in the case of the experimental method this uncertainty may be ±2% (ISO 9223:2012).

To monitor the air environment in the Necropolises, a certified *Skat* measuring system was used, supplied by OPTEC JSC, St. Petersburg (www.optec.ru). The complex automatically transmits archival and current measurement data via the Internet to a remote computer. A similar

Fig. 3.1 Devices used to determine the corrosivity of atmospheric air: at the top—corrosion coupons of various shapes, at the bottom—the "wet candle"

Fig. 3.2 A system of two corrosion coupons to determine the corrosivity of the ambient air and the nonstationary microclimate near the monuments. Dimensions of the truncated copper cone: base diameter—70 mm, height—24 mm, wall thickness—1 mm, cone angle —90°

complex is installed on Maly Prospekt. A "wet candle" was used to determine the average annual fallout of chloride ions in accordance with ISO 9225:2012 (Fig. 3.1). This standard does not recommend the "wet candle" for a short exposure time, therefore, monthly fallouts of chloride ions were not measured.

The results of seven-year monitoring of the air environment given below allow us to evaluate the circumstances wherein the Necropoleis monuments exist, and make predictions on the change in their condition in the future.

Gaseous pollutants

Sulfur dioxide. Analysis of the results of sulfur dioxide monitoring in the atmospheric air at the Necropolises of the Museum of Urban Sculpture over a seven-year period demonstrated a significant decrease in the content of this pollutant, which is well traced both in the mean annual (Fig. 3.3a) and monthly concentrations (Fig. 3.4). Improvement of the environmental situation in regard to sulfur dioxide is associated with the commissioning of new waste treatment facilities and transition to new fuel standards (Golubev et al. 2009, 2010).

The first period of observations, from June 2006 to May 2007, was characterized by the maximum average content of sulfur dioxide (0.01 mg/m^3) and a broad range of variations in mean monthly concentrations reaching 0.022 mg/m^3 (Fig. 3.4a). A surge in the mean monthly concentration of sulfur dioxide associated with the anthropogenic factor was observed three times: in September 2006—to 0.011 mg/m^3, in January 2007—to 0.027 mg/m^3, in February 2007—to 0.023 mg/m^3. Concentrations higher than the maximum allowable one-time concentration (MAC_{OT}) were recorded only twice (Table 3.4).

In the second year of observations, from June 2007 to May 2008, the mean annual concentration of sulfur dioxide decreased to a level of 0.006 mg/m^3 by approximately 2 times compared to the previous year due to commissioning of treatment facilities at the nearest cogeneration plants. The maximum value of its mean monthly content (0.01 mg/m^3) was observed in April 2008 (Fig. 3.4b). At the same time, the variation range of mean monthly concentrations also went down, not exceeding 0.01 mg/m^3. Maximum permissible concentrations were not exceeded.

In the subsequent observation period, from 06.2008 to 05.2012, the mean annual concentration of SO_2 was approximately at the same level (0.004–0.003 mg/m^3), which is 4 and 2 times lower than in the first and the second years of monitoring, respectively. The mean monthly

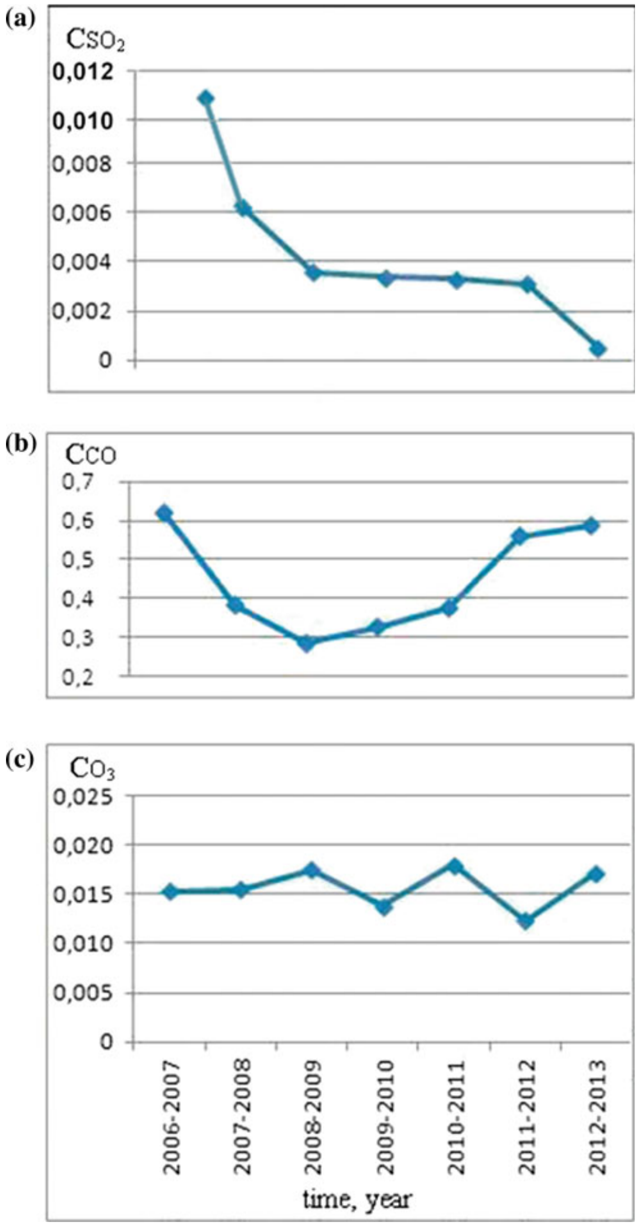

Fig. 3.3 Change in mean annual gas concentrations, in mg/m^3, in the atmospheric air at the Necropolis of the 18th century over seven years: **a** SO_2; **b** CO; **c** O_3

concentrations for this period varied from 0.004 to 0.012 mg/m^3 (Fig. 3.4c–e). Values over the MAC_{OT} were registered only once during the third year of observations.

In the last to be analyzed, the seventh year of monitoring (06.2012–05.2013) the mean monthly concentrations of SO_2 not exceeding 0.003 mg/m^3, the lowest in seven years of observations, were registered (Fig. 3.4g).

Over the seven-year period, only 3 episodes when the measured concentrations of SO_2 exceeding the MAC_{OT} were recorded (Table 3.4). The lowest mean monthly concentrations of sulfur dioxide were observed from October to January, which is probably due to an increase in the amount of precipitation cleaning the atmospheric air.

Carbon monoxide. Observations of the CO content over a seven-year period have shown that the mean annual concentrations of this gas had been decreasing until 2009, most likely due to a lower input from vehicles on the motorways (affected by the economic crisis), and then began to grow (Fig. 3.3b) as the motor traffic grew. In seven years the MAC_{OT} were exceeded twice (Table 3.4).

Ozone. Over the entire observation period, the mean annual ozone concentration changed insignificantly, from 0.012 to 0.018 mg/m^3 (Fig. 3.3c).

For the first five years the trend of mean monthly concentrations was approximately the same (Fig. 3.5). The lowest value (0.002 mg/m^3) was registered in the first year of observations, in February 2007. In the same year, the variations in concentration were in the widest range ~0.025 mg/m^3. In the next, sixth year of observations, the mean monthly concentration of this pollutant did not exceed 0.012 mg/m^3, but in the spring it increased sharply. The lowest value of the mean monthly ozone concentration was in September 2011 (0.006 mg/m^3), the range of variations in its content was 0.03 mg/m^3.

In the seventh year in August, the ozone content showed a sharp decline, which is explained by a higher humidity that month. The lowest concentrations of this gas were observed in the period from October to February; the minimum was in December and amounted to 0.007 mg/m^3. The variations in concentration were in the range of 0.02 mg/m^3. For the whole period of observations the MAC_{OT} were not exceeded (Table 3.4).

Nitrogen oxides. Observations of the content of nitrogen oxide and dioxide were conducted for four years (from October 2009 to May 2013). During the observation period, the mean annual concentrations of these gases did not significantly change (Fig. 3.6). The concentration of nitrogen oxide was gradually decreasing, and that of nitrogen dioxide fluctuated around the mean value. This trend can also be traced by average monthly concentrations (Fig. 3.7).

Unlike other gases, the values of the maximum allowable one-time concentration (MAC_{OT}) and the maximum allowable daily average concentration (MAC_{DA}) of nitrogen oxide for the three-year observation period were exceeded many times: MAC_{OT}—387 times (in total—for about four months); MAC_{DA}—384 times. The value of MAC_{OT} of nitrogen dioxide was exceeded 117 times, while the values of MAC_{DA} for this gas were exceeded almost all the time—

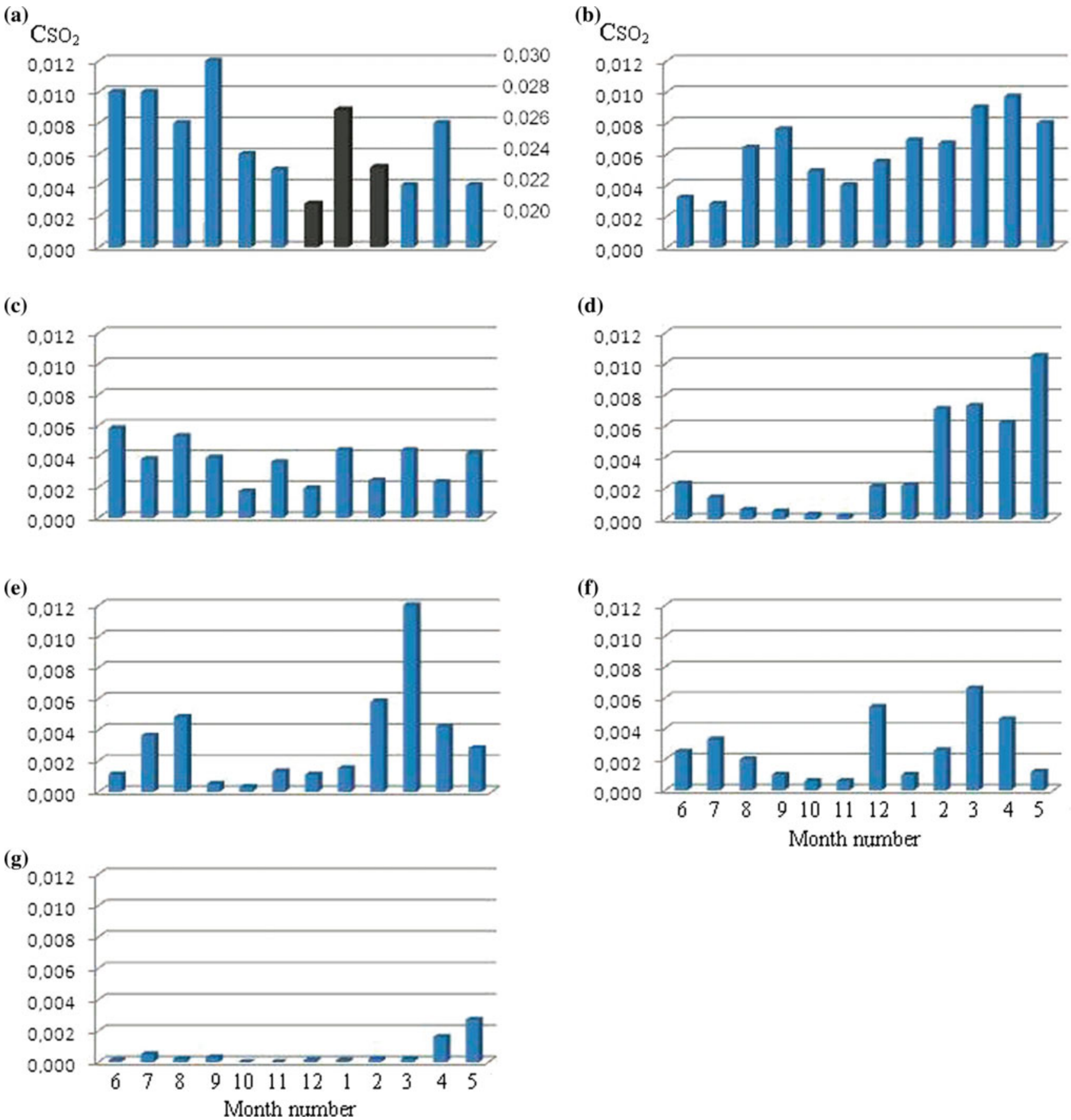

Fig. 3.4 Mean monthly concentrations of SO_2 (mg/m^3) in the atmospheric air at the Necropolis of the 18th century over seven years: **a** 2006–2007 (months with abnormally high sulfur dioxide content are in black, see the scale on the right); **b** 2007–2008; **c** 2008–2009; **d** 2009–2010; **e** 2010–2011; **f** 2011–2012; **g** 2012–2013

Table 3.4 Date and the scale of the SO_2, CO and O_3 concentrations excess over the MAC_{OT} in the atmospheric air of the Necropolis of the 18th century

Pollutant	Date (month, year)	Excess of MAC_{OT}
SO_2	09.2006 02.2007 10.2008	6 7 6.1
CO	10.2006 10.2008	1.6 4.9
O_3	07.2006	1.0

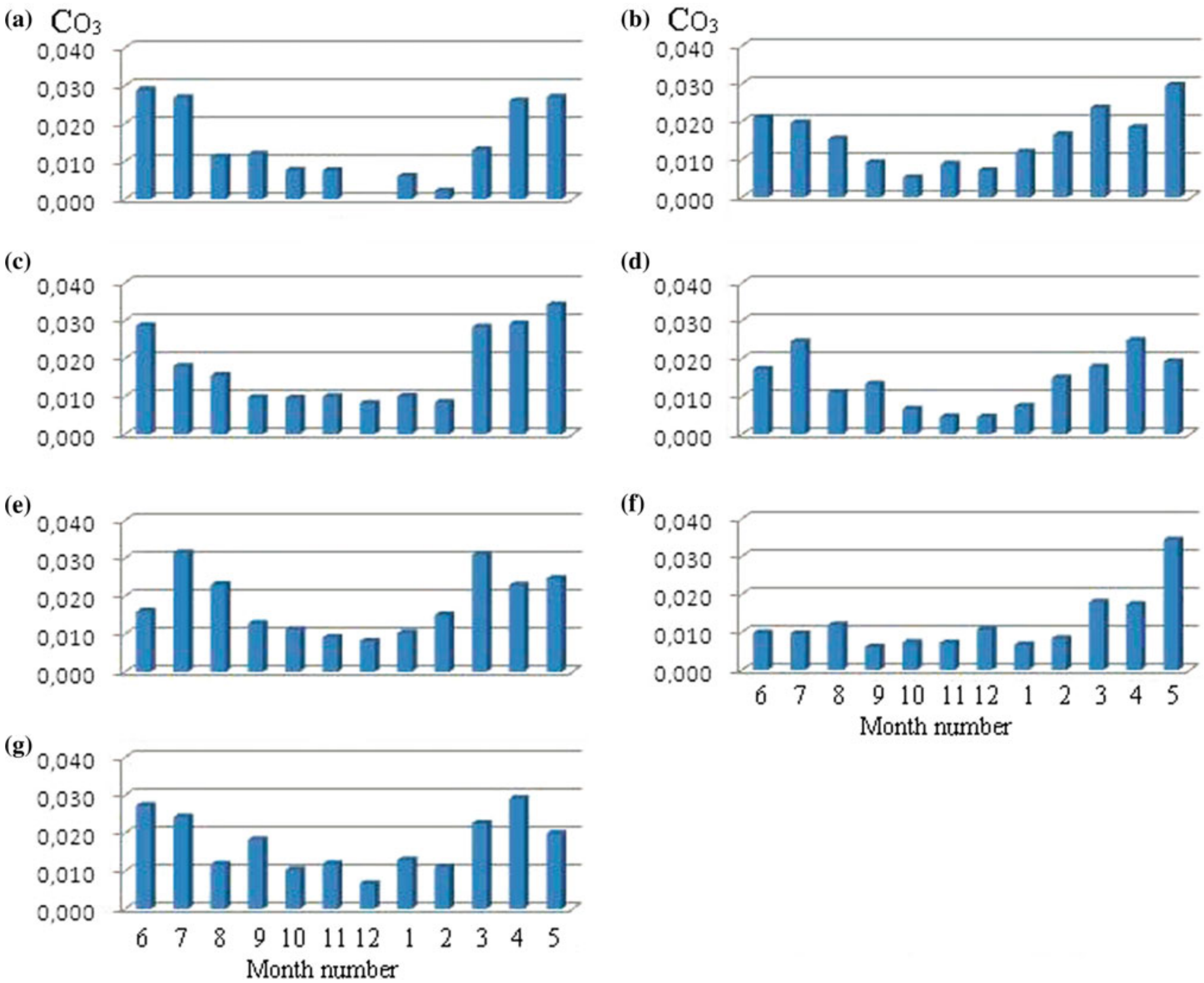

Fig. 3.5 Mean monthly concentrations of ozone (mg/m^3) in the atmospheric air of the Necropolis of the 18th century over seven years: **a** 2006–2007; **b** 2007–2008; **c** 2008–2009; **d** 2009–2010; **e** 2010–2011; **f** 2011–2012; **g** 2012–2013

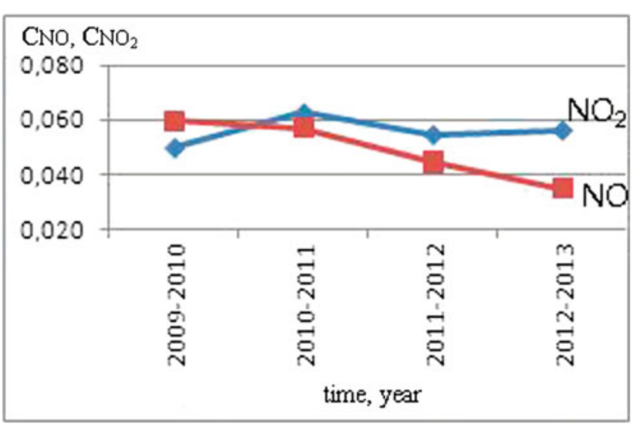

Fig. 3.6 Change in average annual concentrations (mg/m^3) of nitrogen oxides in the atmospheric air in the Necropolis of the 18th century in 4 years

1113 times. Pollution of the atmospheric air in the Necropolis of the 18th century with nitrogen oxides is most likely due to their location near busy public highways with heavy traffic round the clock.

Chloride ions. Because there are a high wall (2.5–2.7 m) and shrubs, which prevent deicing agents from getting inside from public highways, the average annual rate of precipitation of chloride ions in the Necropolis of the 18th century did not exceed 0.4 mg/m^2 day. For comparison, the average annual rate of chloride ion fallout, measured by a "wet candle" near the public road (Maly Pr) in 2013, was 10 mg m^{-2} day^{-1}.

Corrosive activity of the atmospheric air

The results of calculating the corrosion rate of various materials (Table 3.5) using empirical dose-response

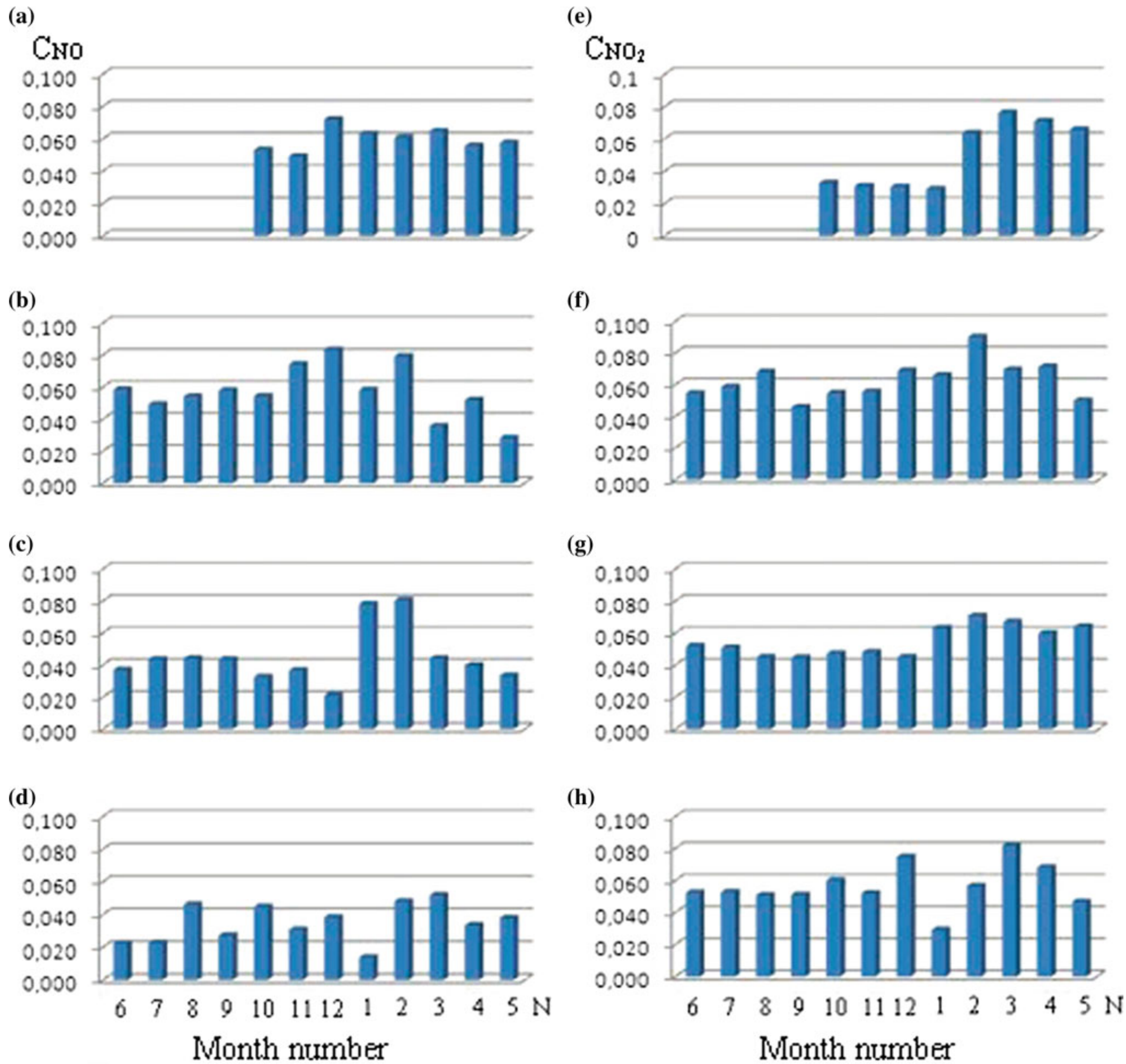

Fig. 3.7 Mean monthly concentrations of nitrogen oxides (mg/m^3) in the atmospheric air of the Necropolis of the 18th century over seven years NO: **a** 10.2009—2010, **b** 2010–2011, **c** 2011–2012, **d** 2012–2013. NO_2: **e** 10.2009–2010; **f** 2010–2011, **g** 2011–2012; **h** 2012–2013

Table 3.5 Estimated corrosion rate, g/(m^{2}yr), of various materials in the atmospheric conditions of the Necropolis of the 18th century and Maly Pr, in 2012–2013

Material	Necropolis of the 18th century	Maly Pr	Necropolis of the 18th century	Maly Pr
	2012		2013	
Carbon steel	107	202	109	143
Copper	8	12	7	11
Cast bronze	4	5	4	5
Limestone	15	20	14	19
Sandstone	13	18	13	18
Marble	8	10	8	10

functions (Table 3.2) and the values of corrosive parameters (Table 3.1) showed that the corrosion rates of various materials in the Necropolis of the 18th century are substantially lower than in Maly Pr and in 2012–2013 changed little. The exception was the rate of corrosion of carbon steel, which in 2013 decreased drastically—by 59 g m^{-2} yr^{-1}.

According to the international standard ISO 9223-2012, the corrosivity of the air in those places in St. Petersburg for which calculations were made, corresponds to C3category. On Maly Pr, the corrosivity is close to the boundary between categories C3 and C4.

The highest corrosion rate, measured experimentally (Table 3.6), was observed near the public highway (Maly Pr). At the other observation points, V_K was significantly lower ($\sim$3.5 times). In the first year of observation in the Necropolis of the 18th century, Pavlovsk and Peterhof, the corrosion rates were close (from 6 to 8 gm^{-2} yr^{-1}). The lower level of air corrosivity in the Necropolis of the 18th century, despite a motor road nearby with traffic as heavy as that in Maly Pr, can be explained by the high wall and shrubbery. They were helpful in reducing the concentration of sulfur dioxide (0.003 and 0.025 mg/m^3 in the Necropolis of the 18th century and Maly Pr, respectively) and the fallout rate of chloride ions (0.4 and 10 mg/m^2 day in the Necropolis and Maly Pr, respectively). In the second year of observations, the corrosion rate in the Necropolis decreased (from 7 to 5 gm^{-2} yr^{-1}), which is probably due to lower humidity in this period (84% in the first year and 80% in the second year). This fact cannot be linked with sulfur dioxide, since its content in comparison with the first year increased slightly (from 0.001 to 0.002 mg/m^3). At the same time, the corrosion rate of copper in Peterhof near the Cottage palace remained practically unchanged, and at the Pavlovsk Palace increased.

It should be noted that the values of the copper corrosion rate in the Necropolis of the 18th century and in Maly Prospekt, obtained by different methods, with allowance for the errors, are practically equal (Table 3.7), which proves that the obtained results are reliable and it is possible to apply the computational and experimental methods for assessing the corrosive activity of the atmospheric air.

Thus, the obtained values of the copper corrosion rate (Tables 3.6 and 3.7) according to the international standard ISO 9223-2012 (Table 3.3) correspond to the C3 category of air corrosivity. In Maly Prospect this category is close to C4. These categories should be taken into account when selecting materials and carrying out conservation and restoration work.

The analysis of monthly measurements of the corrosion loss of mass by the copper coupons at all locations where they were placed (Fig. 3.8) showed that the maximum corrosivity of the air in the both years of monitoring was observed from December till February. In Maly Prospekt a higher corrosion activity was also registered between September and October 2012.

In the Necropolis of the 18th century, simultaneous measurements of corrosion losses by copper coupons and the concentrations of gaseous pollutants were taken (Fig. 3.9). According to the obtained data, the higher corrosivity of the atmospheric air corresponded to the period when the average monthly relative humidity exceeded 80%, and the average monthly temperature was low, in the negative, close to 0 °C. Analyzing the curves, it can be concluded that the changes in the corrosivity of atmospheric air correlate more with the changes in climatic parameters than with those in pollutant concentrations. This is probably due to the fact that the corrosion rate is less related to the volume concentration of pollutants than to the rate of their deposition, depending on the air humidity and the presence of water particles in the form of mist and fog. When nitrogen dioxide reacts with ozone and water, nitric acid aerosol is produced (its concentration can be determined from the relationship in the

Table 3.6 Copper corrosion rate (V_K), measured with exposed copper corrosion coupons

Place of measuring V_K	Exposure period 07.2012–06.2013 (V_K, g m^{-2} yr^{-1})	Exposure period 07.2013–06.2014 (V_K, g m^{-2} yr^{-1})
Necropolis of the 18th century	7.431	5.308
Maly Pr	10.970	11.677
Peterhof, Cottage Palace	8.139	7.785
Peterhof, Farmer's Palace	6.016	n/a
Pavlovsk Palace, near the roadside wing	8.493	10.262

Table 3.7 Results of measuring the copper corrosion rate (V_K) by the computational and experimental methods for the same period (from 07.2012 to 06.2013)

Method	V_K, g/(m^2 yr)	
	Necropolis of the 18th century	Maly Pr
Computational	7	11
Experimental	7.43	10.97

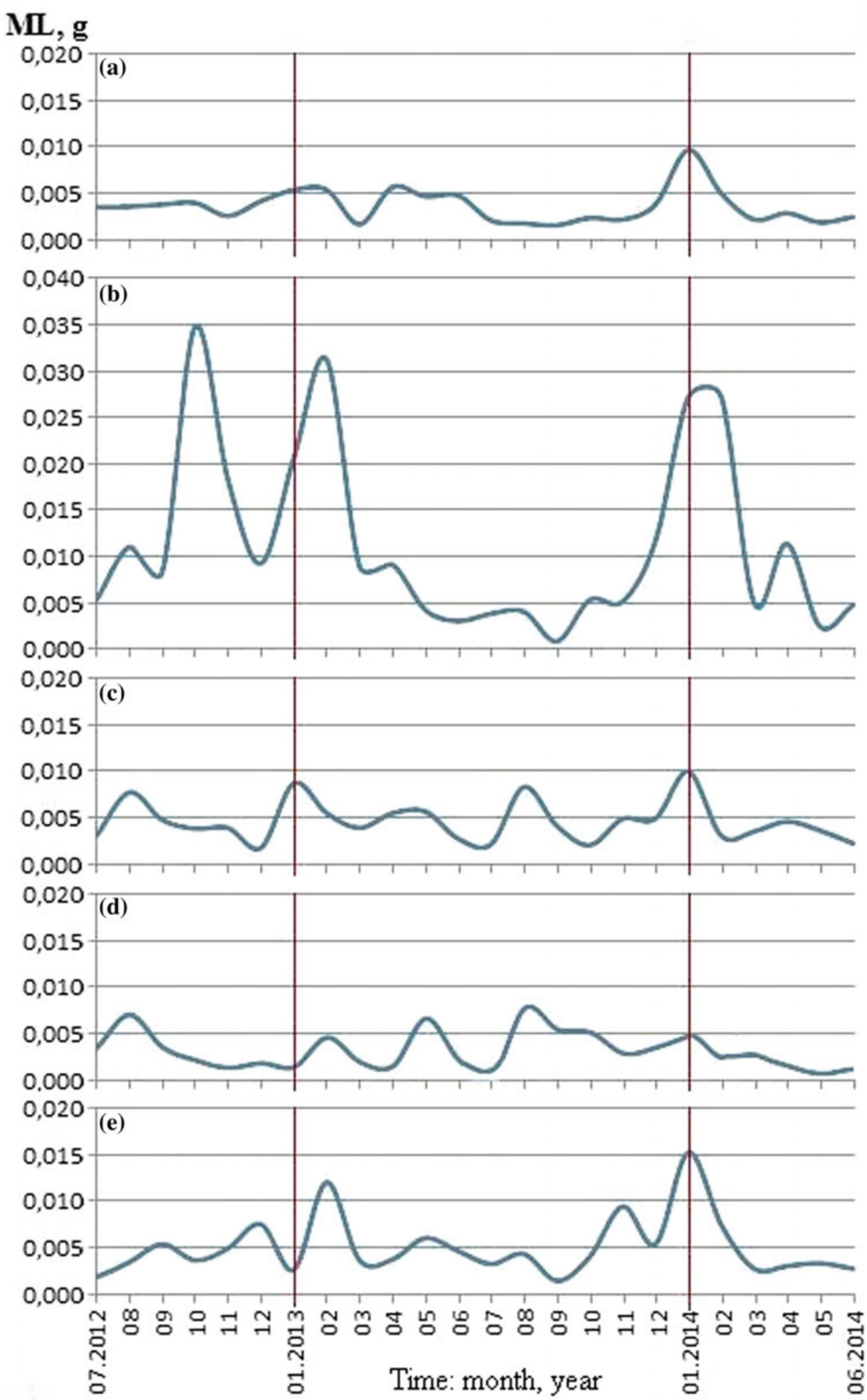

Fig. 3.8 Average monthly mass losses of copper coupons due to corrosion. The location of coupons: **a** Necropolis of the 18th century (3 m from St. Lazarus vault, 2 m from the ground surface); **b** Maly Pr (at a height of 3.5, 20 m from the avenue); **c** Peterhof, Cottage palace (at an elevation of 3.5 m, balcony); **d** Peterhof, Farmer's Palace (at an elevation of 3.5 m, balcony); **e** Pavlovsk Palace (the roadside wing, at an elevation of 2 m). For visual clarity, zigzag curves are smoothed

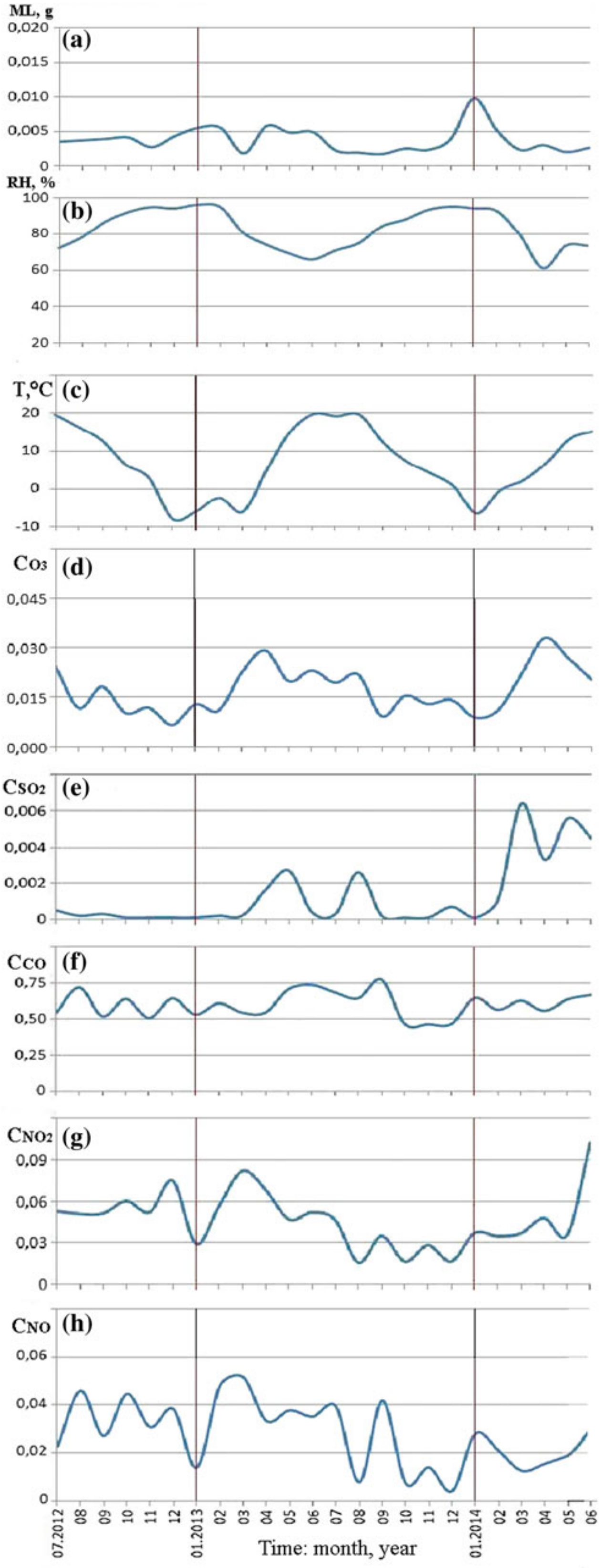

Fig. 3.9 Average monthly values of corrosion loss of mass by the copper corrosion coupons (**a**) and monthly averages of corrosive parameters of atmospheric air: relative humidity (**b**), temperature (**c**) and concentration, in mg/m^3, of ozone (**d**), sulfur dioxide (**e**), carbon monoxide (**f**), nitrogen dioxide (**g**), nitrogen oxide (**h**) in the Necropolis of the 18th century for the period from July 2012 to June 2014

Note to Table 3.2), deposited on the underlying surface. At that the concentration of nitrogen dioxide can drop. In the air and in water aerosols, the following processes can also take place: $SO_2 + NO_2 + H_2O \rightarrow H_2SO_4 + NO$; $NO + O_2 \rightarrow 2NO_2$, resulting in the deposition of sulfuric acid, destruction of copper patina and acceleration of copper corrosion. Taking into account the aerosols containing chlorine compounds (NaCl), this process can be described by the following reactions:

$Cu_2O + H_2SO_4 \rightarrow CuSO_4 + Cu + H_2O$; $Cu + CuSO_4 + 2NaCl \rightarrow 2CuCl + Na_2SO_4$. Following such interactions, the changes in the volumetric concentrations of gaseous pollutants and the corrosion losses of copper coupons may be in opposite phases.

The trend in the corrosive activity of atmospheric air over seven years is easily traced by the calculated copper corrosion rates (Fig. 3.10). In the Necropolis of the 18th century from 2006 to 2013, the corrosion activity corresponded to C3 category. At the same time, V_K values were steadily dropping till 2009 and then stayed at approximately the same level until 2013. The decrease in V_K values between 2006 and 2009 can be explained by a dramatic drop in SO_2 concentration. For the entire observation period, the copper corrosion rate in Maly Prospect was higher than in the Necropolis of the 18th century. In 2006–2007, V_K values for copper in Maly Prospect corresponded to the air of C4 category. In 2008 and 2012—to the borderline level between C4 and C3 categories, and in 2009–2011 and 2013—to C3 category. In general, the corrosivity of the air on Maly Prospect tends to decrease, albeit it is higher than in the Necropolis of the 18th century.

The results of the seven-year monitoring of the atmospheric air at the historical Necropolises showed that the corrosivity of the air in St. Petersburg is gradually decreasing. Now in the Necropolis of the 18th century it falls in the

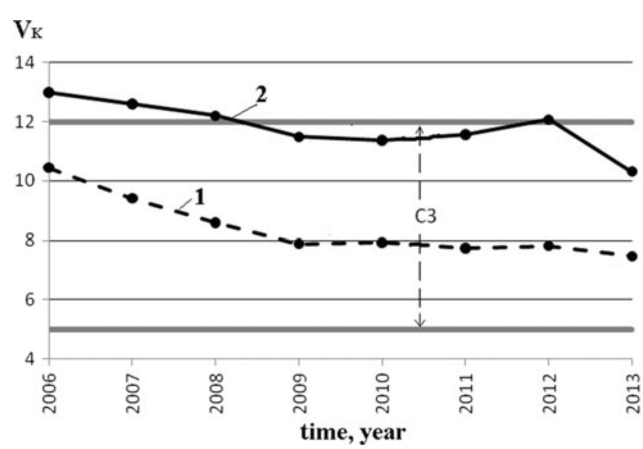

Fig. 3.10 Changes in the rate of atmospheric corrosion (V_K, g m^{-1} yr^{-1}) of copper: 1—in the Necropolis of the 18th century, 2—at 58 Maly Pr, VO, for 7 years. Direct lines delimit the zone of copper corrosion rates corresponding to the third category of atmospheric corrosivity-C3

middle category—C3, which requires annual cleaning of the monument surface with detergents. More serious anti-corrosion treatment is required for monuments located near public roads and not protected by walls. For such monuments, continuous monitoring of the corrosive activity of the air is needed, and here, as practice has shown, it is best to use the cone-shaped copper corrosion coupons.

Monitoring of the state of the sculptural monuments in the Necropolises conducted at the same time as the monitoring of the ambient air showed that despite the gradual decrease in the corrosive activity of the atmospheric air, due primarily to the fall in the content of sulfur dioxide therein, the intensity of corrosion processes of the monuments' materials does not decline (see parts 3, 4). This situation is most likely due to the climate change (Lan et al. 2005), memory effect in regard to previously higher levels of environmental pollution (Watt et al. 2009) , as well as the heavier road traffic (Golubev et al. 2009, 2010, 2011, 2012, 2013) and the prevalent influence of biological and microbiological damage of the monuments' materials.

Fig. 3.11 Places of soil sampling in the Necropolis of the 18th century. Sample numbers are shown

3.2 Soil Conditions

Soils or soil-like bodies are an essential part of terrestrial ecosystems in the areas where the monuments are located. Urban soils surround monuments, while newly-formed primary soils can be formed on the monuments themselves (more often on horizontal surfaces) (see Sect. 5.5.2). Soil sampling was conducted in the field season of 2006. Samples were taken by Yu. A. Gruzdev in various parts of the Necropolis of the 18th century, at different distances from the busy transport routes, the Neva and Monastyrka rivers (Fig. 3.11; Table 3.8).

In the course of the research, morphological descriptions of each process were made, and soil samples were analyzed for a set of parameters, the method being described in the literature (Arinushkina 1970; Ponomaryova and Plotnikova 1980; Kimble et al. 2001).

The soils of the Necropolis within the framework of the classification and diagnostics of soils in Russia (Shishov et al. 2004) should be attributed to the section of imperfectly developed soils and to the type of humus petrozems and grey-humus lithozems. Some macromorphological features of the Necropolis soils are reflected in Table 3.8.

This assignment of soils to the respective taxa is rather formal, in fact they are soil-like bodies. The examined soils contain different amounts of fine earth (particles smaller than 1 mm) and skeletal structures. Fine earth represents the most physically and chemically active part of the soil, where the main biogenic elements and nutrients are contained. The examined soils vary greatly in the ratio of the skeleton to fine earth (Table 3.9). The minimum content of fine earth was

Table 3.8 Macromorphological features of the soils in the Necropolis of the 18th century

No.	Sample	Place of sampling	Macromorphological features
1	4004	South-eastern part (at the wall next to the Monastyrka River and the wall next to the traffic lanes of the Neva River embankment), near St. Lazarus burial vault	Gray, lumpy, light loam, small fragments of bricks
2	4006	South-western part (at the wall next to the Monastyrka River, near the entrance to the Necropolis)	Gray, sandy loam, loose lumps, fragments of stones up to 0.5 cm, very loose and friable
3	4007	Central part, near the intersection of Masters of Arts path and Petrovskaya path	Light gray, pulverescent sandy loam
4	4008	Central part, near the intersection of Masters of Arts path and Zakharovskaya path	Gray, light loam, nuciform, solid structure, fragments of bricks up to 1 cm in diameter
5	4010	Central northern part (near the wall next to the traffic lanes on Alexander Nevsky Square)	Gray, sandy loam, weak granular lumpy, incidental brick fragments, incidental roots

Note Here and in Tables 3.3, 3.4, 3.5, 3.6, 3.7 and 3.8 sample numbers correspond to Fig. 3.7

Table 3.9 The content of skeletal structures and fine earth in the soils of the Necropolis of the 18th century

Sample	Skeleton (wt%)	Fine earth (wt%)	Ratio of the skeleton to fine earth
4004	5	95	0.05
4007	10	90	0.11
4010	15	85	0.18
4008	10	90	0.11
4012	20	80	0.25
4006	30	70	0.42

found in Sample 4006, the maximum one in Sample 4004. The ratio of fine earth and skeleton in natural soils and eluvia is used to judge the intensity of weathering. But with urban soils, dust and other substances can be imported due to the aeolian factor. For this reason, we can only conclude that the studied soils of the Necropolis are very heterogeneous, if judged by the ratio of fine earth and skeletal structures.

No less heterogeneous are the examined soils also in the content of organic carbon (carbon of the humus—C_{to}) (Table 3.10), which ranges from 1.63 to 5.39% of the mass of the soil.

This is a significant difference, but in general, samples 4004, 4007, 4012, and 4006 by the content of organic carbon are at the zonal level (i.e., they contain the same amount of humus as the sod-podzolic soils of the southern taiga). Samples 4010 and 4008 are more humous, which may be due to local accumulation of organic matter in places that are less trampled by people, or where fallen leaves are not removed from the surface.

The nitrogen content (N_{to}) in the examined samples (Table 3.10) can be estimated as average, except for samples 4007, 4008 and 4006. In these samples, the index of nitrogen content in the organic matter (C/N ratio) is higher. Here, probably, fresh organic matter is accumulated, or, conversely, dehumidification occurs due to trampling or other factors. The system of organic matter in the remaining samples is more stable, there the ratio of carbon to nitrogen does not exceed 13.0.

According to the pH of the soil-water suspension (Table 3.10), the samples studied are in a mildly alkaline range, which indicates that the alkalinity of the soil depends on calcium carbonate. Probably, there are no readily soluble salts in the studied soils, or their content is minimal. In any case, they do not affect pH very much.

As to the content of calcium carbonate (Table 3.10), the examined soils differ a lot (it varies from 2.21 to 11.55%). In general, the accumulation of calcite is typical for urban soils, especially in the downtown areas.

Humic acids (HA) of three groups were found in the Necropolis soils (Table 3.11): HA-1 (free and bound with amorphous iron), HA-2 (bound with calcium), HA-3 (bound to clay minerals and immobile oxides of iron and aluminum). All fractions of the fulvic acids (FA) were also found: FA-1a (aggressive to the mineral part of the soil), FA-1 (free and bound with iron, also relatively aggressive to the mineral part of the soil), FA-2 (bound with calcium), FA-3 (bound to clay minerals and immobile sesquioxides). In addition, the samples contained a non-hydrolyzed residue (NR) of organic matter, which was very strongly bound to the mineral part of the soil. In general, the organic matter in the examined soils was very dissimilar in composition.

The studied samples can be divided into two groups: soils with humate-fulvate organic matter (C_{HA}/C_{FA} = 0.50–0.90) and soil with fulvate-humate humus (C_{HA}/C_{FA} = 1.03–1.62), where $C_{HA,}$ C_{FA} are carbon of humic and fulvic acids, respectively. From the fact that in samples 4008 and 4012 HA dominate over FA in the composition of organic matter, it follows that the humus of these samples is less aggressive to the mineral phase than the humus of samples 4004, 4007, 4010 and 4006, where FA dominate over HA. It should be noted that, despite the general high content of fulvic acids, which are generally considered to be aggressive, in these soils they do not fully realize their geochemical potential for weathering, because they are mostly bound with the mineral phase (FA-2 and FA-3). The stable ratio of HA-1, HA-2 and HA-3 fractions confirms that weathering of the mineral part of soils is of low intensity.

Table 3.10 General analytical characterization of the soils in the Necropolis of the 18th century

Sample	C_{to} (wt%)	N_{to} (wt%)	C/N	pH of the soil-water suspension	$CaCO_3$ (wt%)
4004	2.45 ± 0.50	0.40	7.2	7.43	5.50
4007	1.63 ± 0.22	0.10	19.0	7.33	6.05
4010	5.39 ± 0.70	0.76	8.3	7.38	11.55
4008	3.04 ± 0.41	0.30	11.9	7.56	9.91
4012	2.59 ± 0.17	0.33	9.2	7.36	4.40
4006	1.78 ± 0.17	0.17	12.3	7.50	2.21

Table 3.11 Fractional and group composition of the organic matter of technozems in the Necropolis of the 18th century

Sample	C_{TOC} (wt%)	HA-1a	HA-2[a]	HA-3[a]	Total HA[a]	FA-1a[a]	FA-1[a]	FA-2[a]	FA-3[a]	Total FA[a]	NR[a]	C_{HA}/C_{FA}	E4/E6
4004	2.45	$\frac{0.05}{2.00}$	$\frac{0.16}{6.50}$	$\frac{0.18}{7.30}$	$\frac{0.39}{15.90}$	$\frac{0.08}{3.30}$	$\frac{0.37}{15.10}$	$\frac{0.17}{6.90}$	$\frac{0.14}{5.70}$	$\frac{0.76}{31.00}$	$\frac{1.30}{53.10}$	0.51	4.26
4007	1.63	$\frac{0.19}{11.70}$	$\frac{0.14}{8.60}$	$\frac{0.17}{10.40}$	$\frac{0.50}{30.70}$	$\frac{0.07}{4.30}$	$\frac{0.04}{2.40}$	$\frac{0.73}{44.80}$	$\frac{0.17}{10.40}$	$\frac{1.01}{62.00}$	$\frac{0.12}{7.40}$	0.50	3.30
4010	5.39	$\frac{0.27}{5.00}$	$\frac{0.32}{5.90}$	$\frac{0.20}{3.70}$	$\frac{0.79}{14.70}$	$\frac{0.13}{2.40}$	$\frac{0.05}{0.90}$	$\frac{0.31}{5.80}$	$\frac{0.57}{10.60}$	$\frac{1.06}{19.70}$	$\frac{3.54}{65.70}$	0.74	4.85
4008	3.04	$\frac{0.27}{8.90}$	$\frac{0.33}{10.90}$	$\frac{0.13}{4.30}$	$\frac{0.73}{24.00}$	$\frac{0.10}{3.30}$	$\frac{0.02}{0.70}$	$\frac{0.17}{5.60}$	$\frac{0.16}{5.30}$	$\frac{0.45}{14.80}$	$\frac{1.86}{61.20}$	1.62	4.33
4012	2.59	$\frac{0.36}{13.90}$	$\frac{0.21}{8.10}$	$\frac{0.13}{5.00}$	$\frac{0.70}{26.90}$	$\frac{0.23}{8.80}$	$\frac{0.03}{1.20}$	$\frac{0.16}{6.20}$	$\frac{0.26}{10.00}$	$\frac{0.68}{26.30}$	$\frac{1.21}{46.50}$	1.03	3.90
4006	1.78	$\frac{0.23}{12.90}$	$\frac{0.17}{9.60}$	$\frac{0.08}{4.50}$	$\frac{0.48}{27.00}$	$\frac{0.09}{5.10}$	$\frac{0.01}{0.60}$	$\frac{0.17}{9.60}$	$\frac{0.26}{14.60}$	$\frac{0.53}{29.80}$	$\frac{0.77}{43.30}$	0.90	4.64

Note [a]In the numerator—the content of humus acids as percentage of fine earth, in the denominator—the content of humic acids as percentage of the carbon content

Table 3.12 Basal and substrate-induced soil respiration (CO_2 emission) in the Necropolis of the 18th century (mg of CO_2 per 100 g of soil per day)

Sample	Basal 1st week	Basal 2nd week	Substrate induced 1st week	Substrate induced 2nd week
4004	72	158	135	122
4007	90	63	99	62
4010	81	158	90	79
4008	18	40	117	79
4012	45	118	108	119
4006	54	87	117	126

The chromaticity coefficient of humus acids of the studied soils (E4/E6, Table 3.11) indicates the average degree of organic matter humification, i.e., the soil humus is well transformed and organic matter is not fresh, being introduced accidentally. It had probably accumulated there before transformation.

Among the parameters characterizing soils in the Necropolis there is basal respiration - CO_2 emission associated with the normal respiration of soil microorganisms under natural conditions, reproduced in the laboratory. Substrate-induced breathing is the same emission of CO_2, but after the addition of nutrients to stimulate the biological activity of microbiocenoses (glucose and ammonium ion). The results of two weeks of observations (Table 3.12) showed that the level of basal breathing of the examined soils can be estimated as average for all samples except Sample 4008.

During the second week there was a sharp increase in the respiration intensity in all the samples except for Sample 4007. In the latter case, apparently, the microflora was suppressed and capable of metabolism during the first week only, when it was decomposing the labile humus of the soil. In the remaining samples, the maximum activity of microorganisms manifested itself in the second week, which is indicative of active mineralization of organic matter. Samples 4004, 4010 and 4012 were the most biologically active in this respect. The level of substrate-induced respiration during the first week was higher than the level of basal respiration in all samples, that is, addition of nutrients led to the stimulation of respiration and development of microbiocenosis. But during the second week in a number of samples the level of carbon dioxide emission was lower in comparison with the level of basal and substrate-induced respiration of the first week. This trend can be attributed to the fact that in samples 4004, 4008, 4010 and 4007 the microorganisms were more active and able to mineralize glucose and part of the humus as soon as more favorable humidity and temperature were provided. High biochemical activity of microorganisms living in the soil indicates their ability to find a new habitat on the Necropolis monuments under certain conditions, especially in contaminated areas where there are traces of soil and biofouling.

As gypsum-rich patina has been found on the surface of various monuments in the Necropolis, a special attention was paid to the content of sulfur in the soils there (Table 3.13). In the samples studied by us, the sulfur content did not exceed the maximum concentrations standard for natural soils.

Table 3.13 SO_4^{2-} content in the soils of the Necropolis of the 18th century

Sample	SO_4^{2-} water soluble (%)	SO_4^{2-} acid soluble (%)	Water-soluble sulfur as a percentage of acid soluble	$CaSO_4 \cdot 2H_2O$ wt in mg—eq/g of sulfur
4004	0.08	0.10	80.0	0.07
4006	0.11	0.15	73.3	0.11
4007	0.32	0.37	86.5	0.27
4008	0.12	0.18	66.7	0.13
4010	0.10	0.14	71.4	0.10

Note Calculation of gypsum content is made as per the equation: $CaSO_4 \cdot 2H_2O = SO_4^{2-} \cdot 0.737$ (weight in mg—eq/g of sulfur)

It is noteworthy that the maximum amount of sulfur is in a water soluble form. This implies that there is no connection between the processes of sulfur and organic matter accumulation in the soils (the correlation coefficient of sulfur and organic carbon = −0.44). Thus, from the obtained data it follows that the accumulation of sulfur in the soils occurred, most likely, due to the arrival of sulfate anion from the outside. It can be expected that part of sulfur entering the soils of the Necropoleis will get on the surface of the monuments and bind with calcium ions, producing gypsum.

Given the location of the museum Necropoleis and the data on the environmental situation in the Central District of St. Petersburg, it is easy to assume that the examined soils will be seriously contaminated with heavy metals. The obtained results confirm this assumption (Table 3.14). In the soils of the Necropolis of the 18th century the following elements were found: Pb, Zn, Cu, Ni, Co, Cr, V, Sr, Fe, Mn, Ti and As. Their average content corresponds to the series: Fe ≫ Ti > Mn ≈ Zn > Pb > Sr > Cr > As > V > Ni > Cu > Co, and the maximum content—to the series: Fe ≫ Ti ≈ Zn > Pb > Mn > Sr > As > Cr > V > Ni > Cu > Co.

The content of zinc in the Necropolis soils exceeds the background values for the North-West region of the Russian Federation 1.3 to 15.9 times, that of lead—3.6 to 49.3 times. The values of MPC established by the hygienic norms HN 2.1.7.2041-06 for the soils of settlements, agricultural lands, sanitary protection zones of water supply sources, resort zones and individual institutions, are exceeded in the Necropolis soils 3 to 27 times in lead content and 16–88 times in that of arsenic. Sample 4010 taken in close proximity to Alexander Nevsky Square (Fig. 3.11) was the most contaminated. It had seven metals, Pb, Zn, Ni, Co, Fe, Mn, As, at the maximum level. The greatest amount of lead was found in samples 4010, 4004, 4001, 4011, which were taken at the borders of the Necropolis (or not far from Alexander Nevsky Square, or Prospect of Obukhov Defense), that is, not far from the busy transport routes. In the samples picked on the periphery (4011, 4010, 4002), there is also a large amount of zinc. Thus, the obtained results clearly indicate that the main source of soil pollution in the Necropolis is road traffic. Another possible source of zinc contamination of the examined soils may be the walls enclosing the Necropolis, which are flashed with galvanized iron.

Table 3.14 Heavy metals content (ppm) in the Necropolis of the 18th century according to the XRF analysis

Sample	Fe	Ti	Mn	Zn	Pb	Sr	Cr	As	V	Ni	Cu	Co
4001	18612.10	584.51	431.67	377.10	344.90	176.40	77.16	73.82	43.41	38.47	30.00	3.05
4002	27767.80	1268.54	614.82	855.50	272.40	198.70	91.90	58.46	71.58	47.53	20.30	<LLOQ[a]
4003	16422.90	977.19	423.77	183.60	143.20	179.80	53.98	32.92	33.94	28.05	26.48	7.75
4004	23962.80	1135.45	561.38	508.00	431.20	191.60	73.25	89.78	44.08	38.68	2.61	<LLOQ
4005	18689.00	500.58	366.77	117.30	153.70	210.90	52.29	34.85	38.74	29.07	29.50	<LLOQ
4006	18458.20	787.74	465.05	270.40	248.60	178.60	63.91	54.41	42.71	29.59	25.38	<LLOQ
4007	16520.80	883.66	326.81	113.40	102.50	192.00	52.68	24.84	32.04	29.17	30.41	2.81
4008	27285.20	1657.02	600.49	292.70	201.90	209.20	69.44	44.10	58.53	44.56	27.63	1.46
4009	16919.50	856.09	384.81	96.71	158.40	182.00	55.88	36.10	40.45	21.77	22.69	<LLOQ
4010	39140.70	895.05	785.27	1215.00	888.20	170.30	74.11	176.40	37.21	48.06	<LLOQ	19.57
4011	20836.30	98.32	408.12	782.60	325.80	183.30	53.75	68.59	20.04	32.73	23.16	<LLOQ
4012	19885.10	1296.12	467.45	417.70	298.70	176.40	61.70	63.26	49.93	33.31	20.22	2.49
Average	22041.70	911.69	486.37	435.83	297.46	187.43	65.00	63.13	42.72	35.08	23.49	6.19

Note [a]LLOQ means the lower limit of quantification

The assumption that since there are bronze and brass elements in the monumental structures, the content of copper in the soil should exceed the background values, was not confirmed. *The results of the studies showed that the soils can have a noticeable effect on the monuments of the museum Necropoleis*. First of all, they are a source of contamination of the stone material by various microorganisms accumulating in the soil, and, as will be shown below, play an active part in the deterioration of monuments. Accumulation of sulfur compounds in the soil, associated with the microorganism activity, promotes the formation of gypsum-rich patina. Aggressive chemicals in the soil contribute to chemical corrosion of the stone material.

3.3 Biogenic Deposits and Primary Soil on the Monuments

The main forms of deposits on the stone surfaces at the Museum Necropoleis are fouling with dominant algae or microscopic fungi, lichens and mosses (see Sect. 3.4). Algae and fungi often develop together forming a homogeneous black-green biofilm. As a result of the interaction of microorganisms with the stone, a surface layer is formed that contains, in addition to the organisms themselves, organic substances (metabolites), products of rock weathering, as well as various elements getting on the surface from the air and soil. In the places where moss develops, formation of a layer of primary soil is usually observed on the stone surface, where the activity of microscopic fungi and bacteria increases. A specific type of biomineral deposits is gypsum-rich patina (gypsum crust) formed on the surface of carbonate rocks as a result of the transformation of calcite into gypsum (see Sect. 4.3), which also contains numerous microorganisms.

In order to assess the biochemical potential of rock-inhabited communities and their role in the deterioration of the stone material of monuments (see Sects. 4.1, 4.2 and 4.3), it is necessary to know the elemental composition of biofouling on the surface of the monuments and the mechanisms of its formation.

The results of the study of chemical composition of various deposits on the surface of the Necropoleis monuments made of various rocks are considered (Table 3.15). The following types of biofouling formed by different biodeterioration agents were examined: I—with domination of microscopic algae; II—with domination of lichens; III—with domination of mosses. Alongside with that, the primary soil under the moss cover (IV type of deposits), as well as gypsum-rich patina (primary and secondary) were studied. In all types of buildups numerous microscopic fungi were found, typical for lithobiont communities (see Sect. 4.2).

The content of low molecular weight organic compounds in biofouling was determined by gas chromatography—mass

Table 3.15 Characteristics of the types of the examined deposits

Deposits types	Sample number	Monuments	Underlying material	Type of analysis performed	Species composition of dominant group
I—with domination of microscopic algae	AF 1	E. A. Rummel N-18[a]	Ruskeala marble	GC-MS	*Chlorophyta*, mainly genera *Trentepohlia* and *Trebuxia*.
	AF 2	Monument to Unknown N-18, № 901	Pudost travertine	GC-MS	
	AF 3	A. A. Lobanova N-18	Carrara marble	GC-MS	
	A 1	A. E. Martynov NMA[b]	"Serdobolsky" granite	ICP	
	A 2	M. P. Zotova N-18	"Serdobolsky" granite	ICP	
II—with domination of lichens	L 1	B. M. Kustodiev NMA	Wood	ICP	*Physcia hispida, Physcia pulverulenta, Hypogymnia physodes, Xanthoria parietina.*
	L 2	E. H. Minich N-18	Pudost travertine	ICP, GC-MS	
	L 3	S. M. Yakovlev N-18	Rapakivi granite	GC-MS	
	L 4	L. N. Shubina N-18	Ruskeala marble	GC-MS	

(continued)

Table 3.15 (continued)

Deposits types	Sample number	Monuments	Underlying material	Type of analysis performed	Species composition of dominant group
III, IV—primary soil with moss cover	M 1a[c], b[d]	M. S. Zotova N-18	Carrara marble	ICP	*Ceratodon purpureus, Schistidium apocarpum, Bryoerythrophyllum recurvirostrum, Brachythecium salebrosum, Bryum pseudotriquetrum, Marchantia polymorpha, Schistidium apocarpum, Sanionia uncinata.*
	M 2 a,b	A.O. Miklashevich N-18	Putilovsky limestone	ICP	
	M 3 a,b	Lions NMA	Pudost travertine	ICP	
	M 4 a,b	A. N. Avdulin N-18	Granite	ICP	
	M 5 a,b	T. D. Von-Fewson N-18	Putilovsky limestone	ICP	
	M 6 a, b	E. D. Chaplina N-18	Rapakivi granite	ICP	
	M 7 a,b	G. I. Ogarevu N-18	Putilovsky limestone	ICP	
	M 8 a,b	I. A. Myasnikov N-18	Putilovsky limestone	ICP	
	M 9 a,b	T. A. Vetoshnikova N-18	Putilovsky limestone	ICP	
	M 10 a,b	V. S. Bespalov N-18	Putilovsky limestone	ICP	
	M 11 a,b	I. M. Lavrov N-18	Putilovsky limestone	ICP	
	M 12 a,b	E. A. Rummel N-18	Ruskeala marble	ICP, GC-MS	
	M 13 a,b	P. V. Skvortsov N-18	Rapakivi granite	ICP	
	M 14 a,b	V. I. Potemkin N-18	Pudost travertine	GC-MS	
	M 15 a,b	E. H. Minich N-18	Carrara marble	GC-MS	
	M 16 a,b	Monument to Unknown N-18	Granite	GC-MS	
	M 17 a,b	P. E. Osokina NMA	Rapakivi granite	GC-MS	
Primary gypsum crust with fungi	G 1	E. H. Minich N-18	Carrara marble	GC-MS	*Aureobasidium pullulans, Cladosporium sphaerospermum.*
Secondary gypsum crust with fungi	G2	E. H. Minich N-18	Carrara marble	GC-MS	*Alternaria altarnata, Aureobasidium pullulans, Candida* sp., *Cladosporium cladosporioides, Cladosporium sphaerospermum.*

Notes [a]N-18—Necropolis of the XVIII century
[b] NMA—Necropolis of Master of Arts
[c]a—vegetation plants
[d]b—primary soil

spectrometry (GC-MS), and the content of chemical elements—by inductively coupled plasma mass spectrometry (ICP) and X-ray fluorescence analysis. The content of the main elements in the gypsum crust and dust on marble surfaces was measured by EDX analysis.

In the samples of various biofouling were identified different low-molecular organic compounds (Table 3.16): mono-, di- and trisaccharides, carboxylic acids of the aliphatic series (succinic acid, glyceric acid, gluconic acid, fatty acids (palmitic, myristic, linoleic, stearic, arachidonic, behenic acid), sugar alcohols (glycerol, erythritol, arabitol, mannitol, chiro-inositol, myo-inositol, xylitol, glucitol), sterols (cholesterol, campesterol, sigmasterol, sitosterol), glycerol-3-phosphate, tocopherol, abietic acid, phenolic compounds.

Statistical analysis, performed by the principal component method (PCA), showed that the biological depositions differing in the dominant microorganisms and the primary soil form separate groups (clusters) with different organic components (Fig. 3.12). In the biofouling with algae

Table 3.16 Relative content[a] of main low molecular compounds in various deposits on the surface of the monuments in the Museum Necropoleis

Compounds	Type of deposits															
	I—Algae			II—Lichens			III—Mosses					IV—Primary soil				
	AF1	AF2	AF3	L2	L3	L4	M12a	M14a	M15a	M16a	M17a	M12b	M14b	M15b	M16b	M17b
Amino acids																
Alanine	0.86	1.00	0.03	0.03	0	0	0.03	0.66	0.08	0	0.32	0	0	0	0	0
Valine	1.00	0.45	0.24	0	0.42	0.03	0.32	0.03	0.05	0.32	0.02	0	0	0	0	0
Serine	1.00	0.93	0.03	0.05	0.04	0.07	0.07	0.16	0.73	0.32	0.32	0	0	0	0	0
Carboxylic acid																
Succinic acid	1.00	0.18	0.23	0	0	0.02	0.03	0	0	0	0.08	0	0	0	0	0
Glyceric acid	0.16	1.00	0.14	0	0.72	0	0	0	0	0	0	0	0	0	0	0
Gluconic acid	0	0	0	0	0	0	0	1.00	0.01	0	0	0	0	0	0	0
Fatty acids																
Palmitic acid	1.00	0.27	0.32	0.38	1.22	0.28	0.54	0	0	0.19	0.40	0.02	0.93	0.67	0.04	0.05
Myristic acid	0	0	0	0	0	0	0	0.99	0.01	0	0	0.42	1.00	0.53	0.02	0.43
Linoleic acid	0.93	0.53	1.00	0.29	0	0.10	0.32	0.10	0	0.04	0	0.05	0.03	0.04	0.82	0.13
Stearic acid	0	0	0	0	0	0.53	1.00	0	0	0	0.05	0.03	0.05	0	0.01	0.09
Arachidonic acid	0	0	0	0	1.00	0.44	0.92	0	0	0	0	0.02	0.01	0.01	0	0
Behenic acid	0	0	0	0	0	0.61	1.00	0	0	0	0.05	0	0	0	0	0
Sterines																
Camposterol	0	0	0	0	0	0.03	0.08	1.00	0.01	0.09	0.04	0	0	0	0	0
Stigmasterol	0	0	0	0.48	0	0.04	0.05	1.00	0.01	0.08	0.07	0	0	0	0	0
Sitosterol	0.77	0.05	0	0	0	0.06	0.10	1.00	0.01	0.06	0	0	0	0	0	0
Cholesterol	0	0	0	0	0	0	0	1.00	0.01	0	0	0	0	0	0	0
Polyols																
Erythritol	0.01	0.02	0.01	0.24	0.44	1.00	0.02	0	0	0	0	0	0.06	0.06	0	0.07
Glycerol	0.46	0.24	1.00	0.15	0.38	0.06	0.06	0.21	0.34	0.07	0.43	0	0	0	0	0
Arabitol	0.06	0.08	0.67	1.00	0.42	0.03	0	0	0	0	0	0.04	0.03	0.02	0	0
Mannitol	1.00	0.61	0.14	0.94	1.00	0.83	0.02	0.02	0.03	0.00	0.03	0.02	0.03	0.05	0.04	0.03
Chiro-inositol	1.00	0	0.06	0	0.09	0	0	0	0	0	0	0	0	0	0	0
Myo-inositol	0.84	0.72	0.35	0.07	0.99	0.03	0.07	0.09	0	0.06	0.04	0.03	0.01	0.01	0.02	0.01
Xylitol	0	0	0	1.00	0	0	0.96	0	0	0	0.06	0	0	0	0	0
Glucitol	0	0.72	1.00	0	0	0	0	0	0	0	0	0	0	0	0	0
Sugars																
Glucose	0.21	0.11	1.00	0.22	0.31	0.02	0.03	0.08	0.19	0.17	0.43	0.04	0.05	0.03	0.53	0.04
Fructose	0.38	0.19	1.00	0.36	0.28	0.04	0.17	0.04	0.02	0.19	0.64	0.02	0.03	0.05	0.03	0.02
Galactose	0	0	1.00	0.20	0	0	0.03	0	0	0.07	0.07	0.06	0.05	0.05	0	0
P[b] Rt[d] 18.3	0.24	1.00	0.06	0	0.30	0	0	0	0	0	0	0	0	0	0	0
F[c] Rt 18.4	0.21	1.00	0	0	0.19	0	0	0	0	0	0	0	0.06	0	0	0

(continued)

Table 3.16 (continued)

Compounds	Type of deposits															
	I—Algae			II—Lichens			III—Mosses					IV—Primary soil				
	AF1	AF2	AF3	L2	L3	L4	M12a	M14a	M15a	M16a	M17a	M12b	M14b	M15b	M16b	M17b
F Rt 19.0	0.15	1.00	0.02	0	0.15	0	0	0	0	0	0	0	0	0.04	0	0
F Rt 20.6	1.00	0	0	0.36	0	0	0	0	0	0	0	0	0	0	0.05	0
F Rt 21.4	0.05	1.00	0.20	0.09	0	0	0.01	0.02	0	0	0	0	0	0	0	0
F Rt 23.0	0.11	0.39	1.00	0.04	0	0	0	0	0	0	0	0	0	0	0	0
P Rt 23.5	0.02	0.06	1.00	0	0	0	0	0	0	0	0	0	0	0	0	0
P Rt 23.6	0	0.03	1.00	0.64	0	0	0	0	0	0.02	0.03	0	0	0	0	0
F Rt 27.3	0.05	0.04	1.00	0.02	0.19	0.05	0.05	0	0	0	0.01	0	0	0	0	0
P Rt 27.6	0	0	0	1.00	0	0	0.68	0	0	0	0	0	0	0	0	0
P Rt 28.5	0.06	1.00	0.02	0.04	1.62	0	0.03	0	0	0	0,06	0	0	0	0	0
P Rt 28.8	0	0	0.32	1.00	0	0	0	0	0	0	0	0	0	0	0	0
P Rt 29.0	0.04	0.99	0.07	0	0	0	0	0	0	0	0	0	0	0	0	0
P Rt 29.2	0.05	1.00	0	0.08	0	0	0	0	0	0	0	0	0	0	0	0
P Rt 30.0	0.06	0.38	1.00	0.26	0	0	0.04	0.25	0	0	0.04	0	0	0	0	0
Disaccharides (summarized)	0.18	0.16	1.00	0.03	0.06	0.01	0.02	0.03	0.03	0.03	0.02	0.03	0.01	0.01	0.05	0.06
Trisaccharides (summarized)	0.76	0.67	1.00	0.13	0	0.32	0	0	0	0.74	0	0.01	0.02	0.04	0.02	0.01
Others compounds																
N.i.[e] Rt 21.6	1.00	0	0	0	0.02	0	0	0	0	0	0	0	0	0	0	0
N.i. Rt 305	1.00	0	0.84	0	0	0	0	0	0	0.09	0	0	0	0	0	0
N.i. Rt 24.6	0	0	0	0	0.42	0	1.00	0	0	0	0	0	0	0	0	0
N.i. Rt 24.7	0	0	0	0	0	0.21	0	1.00	0.01	0.16	0	0	0	0	0	0
N.i. Rt 24.8	0	0	0	0	0	0	0	1.00	0.01	0	0	0	0	0	0	0
N.i. Rt 27.6	0	0	0	0	0	1.00	0	0	0	0.72	0	0	0	0	0	0
N.i. Rt 28.6	1.00	0.27	0.92	0	0	0.01	0	0	0	0.04	0	0	0	0	0	0
N.i. Rt 40.0	0.25	0.19	1.00	0	0	0	0	0	0	0	0	0	0	0	0	0
1-Hydroxy-3-methoxy-6-methylquinone	0	0	0	1.00	0.77	0.54	0	0	0	0	0	0	0	0	0	0
Abietic acid	1.00	0.12	0.13	0	0	0	0	0	0	0	0	0	0	0	0	0
Eudesmol	0	0	0	0.66	1.00	0.03	0	0	0	0	0	0	0	0	0	0
a-tocopherol	0	0	0	0	0	0.44	1.00	0	0	0.02	0	0	0	0	0	0

Notes [a]Maximum concentration of every compound (mg/g of substrate) is taken as 1
[b]P—pyranose
[c]F—furanose
[d]Rt—retention time
[e]N.i.—not identified compound

domination (type I), the amount of mono- and disaccharides, amino acids and organic acids in free form is significantly higher in comparison with other types of biofouling and the primary soil. In biofouling with lichens domination (type II), sugar alcohols and phenolic compounds predominate. The composition of the organic component of the mosses' vegetative part (III type) is close to that of the organic component of type I biofilms, but is characterized by a smaller variety of metabolites in general (particularly products of secondary metabolism), a relatively low content of sugar alcohols, and a large quantity of fatty acids. The organic component of the primary soil layer (type IV) without the vegetative part of plants consists mainly of sugars and polyols, fatty acids and sterols. Generally, the diversity of metabolites and their quantitative content is much lower than in other samples of biofouling. A comparison of the composition of low-molecular compounds of the primary soil layer from the stone surface, with the data for an ordinary soil sample collected in the Necropolis of the 18th century, showed a similarity in the metabolite composition of these two samples. Spatial divergence of the main components of clusters that characterize the composition of small organic

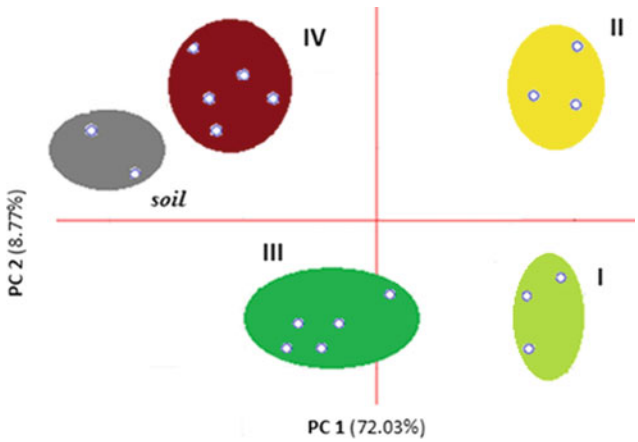

Fig. 3.12 PCA results for small organic molecules in surface buildups and soil on the monuments of the Museum Necropoleis: I—biofouling with algae domination; II—biofouling with lichens domination; III—mosses; IV—primary soil under the moss cover

molecules in the ordinary and primary soils is not great (Fig. 3.12).

The main contribution to the statistical model for PC 1 is made by gliceric acid, F Rt 19.0, F Rt 18.4, P Rt 18.3, F 27.3, 1-Hydroxy-3-methoxy-6-methylanthraquinone, eudesmol and by glucose, fructose, abietic acid, P Rt 29.2, P Rt 25.5, sucrose, linoleic acid for PC 2.

In the spatial model obtained with the help of PCA, the features of community types grouping relative to one another can also be traced. Type I and type II are grouped most closely along the first principal component (PC 1). The second principal component (PC 2), most closely groups types III and I. This distribution is probably due to the general specifics of the metabolism of lichens and free-living fungi and algae, as well as the common biochemical features of autotrophic organisms: free-living algae and mosses.

The results of analysis of the composition of low molecular substances in the gypsum crust enabled us to establish the biochemical differences in the stages of its formation (Table 3.17). At the first stage of crust formation, only trace amounts of organic substances are present. During the second stage, sugars (galactose, xylose, glucose, disaccharides) and polyols (glycerol, sorbitol, myo-inositol, arabitol) and gluconic acid accumulate on the crust surface. In some samples, oxalic and citric acids were present in amounts up to 10 μg/g. The total content of sugars and polyols was 0.1–0.2 mg/g of the examined substrate. Accumulation of these compounds as the gypsum-rich patina is formed indicates a greater role of the biogenic factor, mainly associated with the development of microscopic fungi colonies.

In the samples of the examined deposits, 45 elements were identified, which can be conditionally split into 2 groups—the basic ones, whose content is not less than 1 wt% (Table 3.18) and impurities (Figs. 3.13 and 3.14). Of the elements belonging to the 1st and 2nd hazard classes (toxic and highly toxic) there were Cd, Hg, Pb, Zn, Ti, Co, Ni, Mo, Cu, Sb, Cr. These elements are mainly of anthropogenic origin, and serious pollutants of the environment. Comparison of the concentrations of elements with the maximum allowable limits for soils shows a 4 to 10 times excess of the (maximum allowable concentration) MAC for zinc, copper, antimony and lead in the biofilm samples, and in some cases more than 20-fold.

Comparison of the elemental composition of primary soils and biofouling on the monuments of the Necropoleis with the content of the elements in ordinary soils (Sect. 4.2) showed that the primary soils and biogenic deposits on the surface of the monuments are characterized by a much higher content of Cu (10–20 times), V (3–5 times), Co (6–10 times), Ni (2–4 times) and Fe (3–5 times).

Table 3.17 Concentration of low molecular compounds in the gypsum crusts, mg/g of substrate

Compounds	Primary gypsum crust (G 1)	Secondary gypsum crust (G 2)
Oxalic acid	0.011	0.019
Phosphate	0.109	0.202
Succinic acid	0.010	0.060
Malic acid	0.009	0.016
Citric acid	0.005	0.018
Glucose	0.008	0.107
Galactose	0	0.086
Xylose	0.003	0.004
Disaccharides	0.002	0.240
Glycerol	0	0.002
Arabitol	0	0.003
Sorbitol	0.006	0.009
Mio-inositol	0	0.870

Table 3.18 Content of the main elements in the deposits (wt%)

Type of deposits	Data	TiO_2^a	$Al_2O_3^a$	MgO^a	Na_2O^a	K_2O^a	MnO^a	FeO^b	SiO_2^b	CaO^b
I—Algae	Range	0.6–1.3	8.1–13.8	2.9–17.5	1.2–2.9	2.8–12.3	0.1–0.2	1.9–2.7	11.1–13.5	1.0–1.3
	Medium	0.9	10.9	10.2	2.0	7.6	0.1	2.3	12.3	1.1
II—Lichens	Range	1.7–2.1	16.1–17.1	4.0–4.1	2.6–3.4	4.9–11.1	0.2–0.2	0.8–2.2	5.1–17.1	2.9–3.1
	Medium	1.8	16.6	4.0	3.0	8.0	0.2	1.5	11.1	3.0
III—Mosses	Range	0.7–1.1	8.3–13.0	3.2–5.1	1.3–1.9	2.5–5.6	0.1–0.2	6.9–12.8	1.2–55.3	2.5–6.1
	Medium	0.9	11.2	3.8	1.7	3.9	0.1	10.7	31.9	4.6
IV—Primary soil	Range	0.2–1.0	5.7–10.6	0.7–2.9	1.2–2.0	1.8–2.3	0.03–0.1	1.8–6.2	44.3–73.8	1.4–6.8
	Medium	0.6	8.5	1.9	1.5	2.1	0.09	4.3	50.3	4.8

[a]ICP analysis
[b]X-ray fluorescence analysis

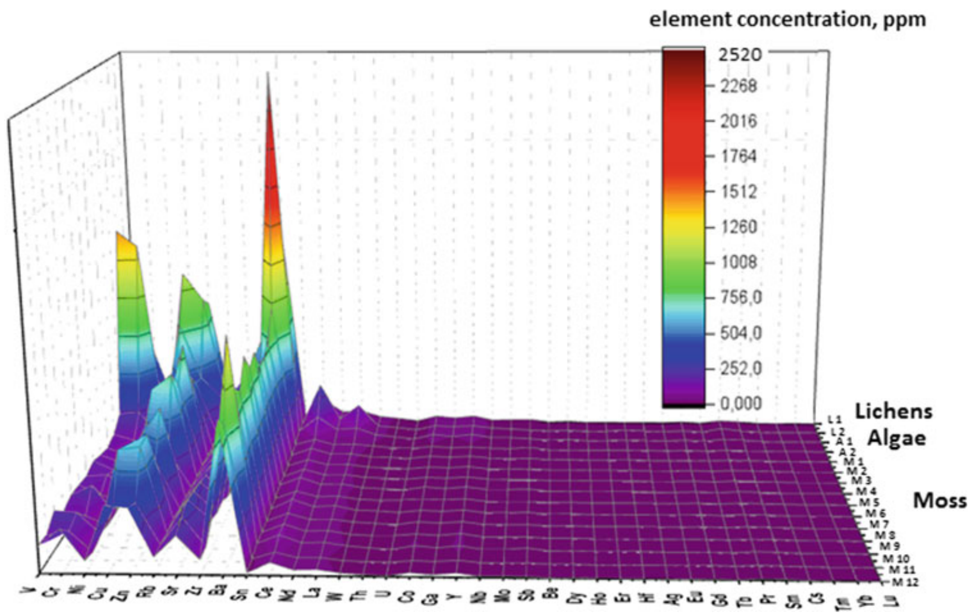

Fig. 3.13 Content (ppm) of impurity elements in different types of deposits

The statistical analysis performed by the principal component method showed that the biological fouling, different in the composition of the dominant microorganisms, and the primary soil form clusters that also differ in the content of the main and impurity elements (Figs. 3.15 and 3.16). Differences in the elemental composition of the upper vegetative part of mosses and the lower layer of the primary soil were found with both the impurity and the basic elements, but these differences were more significant for impurity elements. Clumping of algae and lichens into separate clusters by the impurity elements did not occur.

In general, for biofouling with the predominance of algae and lichens (type I and type II), accumulation of all elements in higher concentrations than in the vegetative part of mosses and the primary soil with a moss cover (type III and type IV biofouling) is characteristic. For biofouling with dominant lichens (type II), accumulation of the basic elements, with the exception of magnesium, is also more pronounced than in biofouling with dominant algae (type I). However, it should be borne in mind that the data on accumulation of the basic elements in biofouling with dominant algae significantly vary in different samples (Table 3.18). Some impurity elements (Zn, Cu, V, Se) also accumulated mostly in lichens. For most basic and impurity elements (with the exception of Zr, Nb, Hf), predominant localization in the vegetative part of mosses (type III of biofouling) is characteristic, and not in the primary soil (type III of biofouling), which indicates that they get there from the environment, and not from the substrate (Table 3.19).

A comparative analysis of the content of chemical elements in the gypsum crust and the bedrock (Italian marble) (Table 3.19) showed that they (with the exception of calcium and manganese) accumulate mostly in the gypsum crust. Analysis of the dust collected from the surface of the monuments showed (Table 3.19) that the content of all chemical elements (but for calcium) in it is greater than in the gypsum

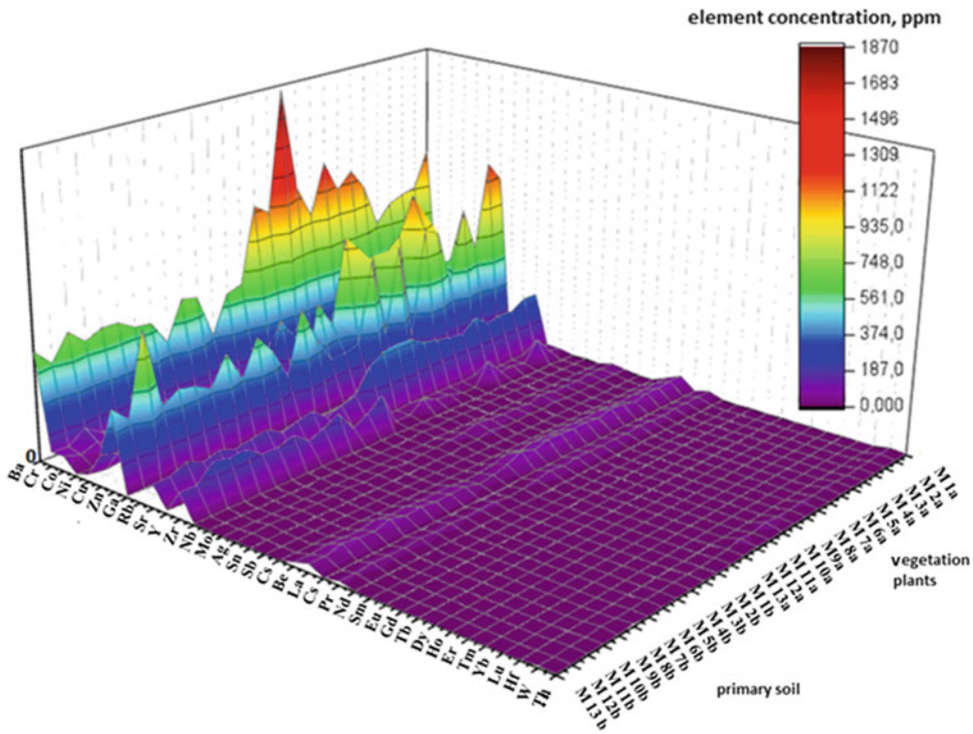

Fig. 3.14 Content (ppm) of impurity elements in the vegetative part of mosses (**a**) and in the primary soil (**b**)

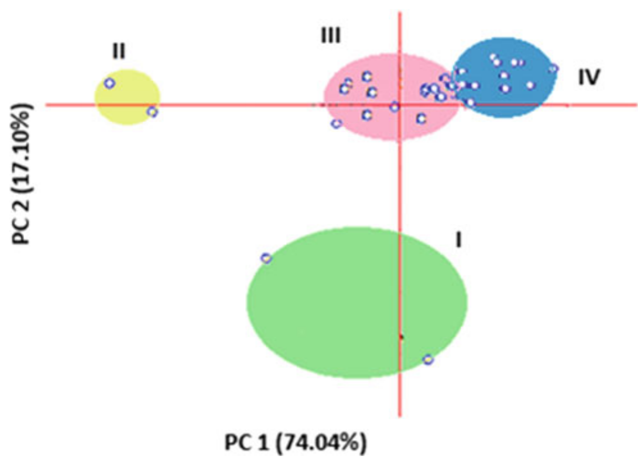

Fig. 3.15 Results of the PC analysis of the basic elements in deposits on the surface of monuments of the Museum Necropoleis: I—with algae domination; II—with lichens domination; III—vegetative part of mosses; IV—primary soil under the moss cover. The main contribution to the statistical model for PC 1 is made by TiO_2, Na_2O, Al_2O_3 and by MgO, K_2O, MnO for PC 2

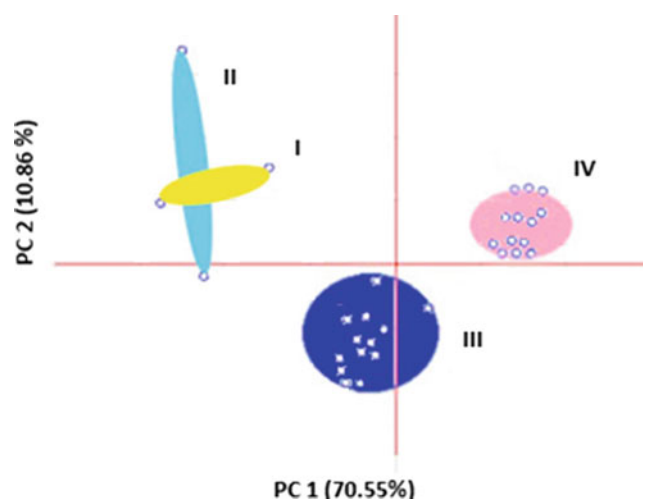

Fig. 3.16 Results of the PC analysis of the impurity elements in deposits on the surface of monuments of the Museum Necropoleis: I—with algae domination; II—with lichens domination; III—vegetative part of mosses; IV—primary soil under the moss cover. The main contribution to the statistical model for PC 1 is made by Eu, Sm, Pr, Nd, Ce, Gd, Zn, Rb, Dy, Sn and by Lu, Sr, Y, Pb, Ge, Ag, Cs, Ba, Zr, Ni for PC 2

crust, which also indicates that the impurity elements get into the gypsum-rich patina from the environment.

Comparison of the concentrations of chemical elements in biofouling and dust on the surface of the monuments (Tables 3.18 and 3.19) shows that the content of phosphorus, aluminum, magnesium, potassium, sulfur, manganese and titanium in biogenic deposits, especially those formed by lichens and algae, is much higher. At the same time, the concentration of calcium, silicon and iron is higher in the dust. Thus, although the environment is the source of many elements in biofouling, the organisms themselves play an important selective part in their accumulation.

Table 3.19 Element composition (wt%) in the dust, gypsum crust and underlying marble

Object of study	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
Dust	1.93	2.09	8.59	46.30	0.45	1.84	7.90	0.65	0.07	10.0
Gypsum crust	0.54	0.43	1.74	8.02	0.21	0.61	19.20	0.08	0.01	1.99
Underlying Carrara marble	0.01	0.17	0.09	0.01	0.02	0.009	99.0	0.07	0.01	0.02

The results of the study of chemical composition of various types of biofouling and primary soil on the surface of the monuments of the Museum Necropoleis made of various rocks demonstrated the differences in the composition and quantity of low molecular organic substances and chemical elements. It is shown that the primary soil formed under the moss cover is a specific type of deposits on the surface of the stone being in contrast with biofouling both in the composition and amount of low-molecular-weight organic substances and in the composition of chemical elements. The environment contributes to the accumulation of elements in the layers of biofouling much more than the underlying bedrock substrate (the rock from which the monument is made). In this case, the clumping of biological deposits by their composition and content of low-molecular-weight compounds and chemical elements is due, above all, to the taxonomic composition of organisms. This indicates the leading role of the respective active physiological processes in the selective accumulation of elements from the environment (probably, mainly from the air in the form of aerosols) in the biofouling on the surface of the monuments.

3.4 Vegetation

A plant community (phytocenosis) developed in the Necropoleis for many years, represented mainly by tree species. The trees create an intrinsic microclimate that affects the distribution of light and moisture in the Necropoleis (Fig. 3.17).

The first storey of the stand is dominated by such hardwood species as *Acer platanoides* and *Tilia cordata*. In addition, there are *Populus tremula, Quercus robur, Castanea sp., Ulmus glabra, Betula pubescens and Larix sibirica*. In the second storey, *Crataegus laevigata* predominates, with *Caragana arborescens, Syringa vulgaris, Sorbus aucuparia, Frangula alnus*.

Among herbaceous plants, the following species prevail: *Taraxacum officinale, Plantago major, Poa* spp. (the projective cover of these species is about 50%). *Chamerion angustifolium, Aegopodium podagraria, Urtica dioica, Epilobium parviflorum, Senecio vulgaris, Spergula vernalis* and *Matricaria chamomilla* occur incidentally. There is no grass on much of the soil. It is important to note that herbaceous plants also occur on the monuments themselves, especially at the base. So, for example, *Poa annua* grass often grows in tiny cracks or in joints between blocks of stone. And this species was found on monuments of various types of stone - granite, limestone (Putilovo and Pudost), marble. The roots of the plants penetrate deeply into the material of the monument, which tells on its condition. The roots produce a mechanical impact, facilitate penetration of moisture into the rock mass, and provide favorable environment for accumulation of organic matter and development of an aggressive microbial community. When trying to extract a plant from the crack, the roots often remain inside the rock.

Excretory products of plants and pollutants from the air, getting on the stone substrate with rainwater (Fig. 3.18), are the main source of nutrition for fungi and bacteria. On the tree leaves one can often see a black coating («sooty mold») formed by fungal colonies, plant excreta, and settling airborne dust. This picture is most typical for the leaves of lime trees growing on the territory of Necropolis (Figs. 3.19 and 3.20). It is important to note that fungi occurring in black deposits on tree leaves easily get on the surface of monuments, where they continue to develop. These include black yeast-like fungi from the genera *Aureobasidium* and *Hormonema*. In the Necropoleis, they are found everywhere in dark-colored biofilms on the surface of marble, limestone and granite. The same fungi were discovered in gypsum crusts, mud deposits and places where the stone surface disintegrated. In general, the most intensive development of biological stains is observed on the surface of monuments under the trees.

The condition of the woody plants themselves is an important indicator of the ecological situation in the Necropoleis. Using biological objects for assessment of the environmental health (bioindication) allows, first of all, to comprehend the true level of atmospheric pollution. High content of toxic gases in the atmosphere leads to a noticeable inhibition of plant growth. This is manifested in changes in the leaf color, development of necroses, and twig blight. Weakening of trees under the influence of atmospheric pollution makes them prone to various infectious diseases. The main etiologic factors of such diseases are phytopathogenic fungi. Some of them develop on the leaves during the growing season, causing spots, stains, pustules and other characteristic signs of damage that are clearly visible in a visual examination.

Aerial algae (aerophyton), that is, algae capable of surviving in the air environment (Fig. 3.21), also actively develop on tree trunks in the Necropoleis. These organisms form continuous green deposits (fouling) on the lower part

(a)
(b)


Fig. 3.17 Trees and shrubs: **a** in the Necropolis of Masters of Arts, **b** in the Necropolis of the 18th century

of the trunks, which consist, mainly, of green algae (Chlorophyta). It is important to note that the conditions of the Necropoleis with their soft microclimate and shadows promote rapid development of aerophilic algae on various substrates, including woody plants, stone and metal materials, also painted surfaces. The proximity of the Neva River and Monastyrka River also has a significant influence on the formation of extensive green stains. Especially noticeable is their development in wet periods, when the fresh growth of algae acquires a bright green color. The surface of old tree trunks is the most favorable substrate for aerophyton in the Necropoleis. At the base of the trunks, one can find clusters of diatomic algae, the cells of which are clearly visible under the electron microscope. Cells of these algae are often found on the surface of monuments (Fig. 3.22).

Over the periods of environmental surveys in the Necropoleis, formation of fruit bodies of wood-attacking fungi was repeatedly registered (Fig. 3.23). They developed both on living trees and on stumps remaining after felling. High incidence of wood destroyers is characteristic of the suppressed tree growth.

It is obvious that the impact of anthropogenic factor contributes to the weakening of tree plantations, which, in turn, increases their infestation with fungi. Rapid

Fig. 3.18 Black streaks on the marble surface (gravestone of Z.A. Khitrovo, Necropolis of the 18th century), appearing in the places where rain water flowed

Fig. 3.19 Black stains on lime tree leaves

Fig. 3.20 Micromycetes isolated from the black coating on the surface of lime tree leaves

development of disease indicates the need for monitoring the stand, which could make it possible to assess the ratio of healthy, weakened and severely affected trees, and to determine the root causes contributing to the inhibition of plant development.

One of the important elements of the vegetation cover in the museum Necropoleis is moss. Mosses are found on the soil, at the bases of tree trunks, as well as on monuments of various materials (Figs. 3.24 and 3.25). Especially intensive development of mosses is observed in borderline biotopes, for example, on the boundary between the soil and the pedestal of the monument. The largest variety of mosses was registered on the monuments of the museum Necropolis of

Fig. 3.21 Aerial algae colonies (Chlorophyta division) on the bark of trees: **a** in the Necropolis of Masters of Arts, **b** in the Necropolis of the 18th century. The same algae develop on the trunk of a tree and on a neighboring monument of gray granite

the 18th century, 10 species of 9 genera. Clumps of moss develop most abundantly on highly eroded monuments, preferring wet places. Heterogeneous weathered surface of the stone offers the most favorable conditions for mosses to get fixed and begin growing. Mosses can grow both on vertical and horizontal surfaces of monuments. The most extensive growth of mosses is on horizontal surfaces. Often they cover most of the monument surface, which is characteristic of horizontal slabs of Putilovo limestone (Fig. 3.25). In the places where mosses develop, a considerable weakening of the surface stone layer can be observed, formation of depressions and accumulation of moisture around moss clusters. The degree of moss attachment to the surface of the substrate turned out to be different. Under some of the mosses, the stone was badly damaged. In the colonized areas, formation of primary soil can be observed. Among the species identified on the carbonate substrata, mosses of genera *Didymodon* and *Hypnum* dominate. It is known that the mosses of these genera are confined to stony substrates and are calciphilic. Besides, species

Fig. 3.22 Cluster of diatom algae cells on the surface of quartzite. Tomb of the Unknown (N 18 No. 959), Necropolis of the 18th century

of the genus *Bryum* were constantly present in the collections. It should be noted that in mosses and herbaceous plants growing on monuments, there is an intensive accumulation of corrosive chemicals that settle down from the air (for example, heavy metals), which contribute to changes in the chemical composition of the surface layer of the stone.

As a result of the studies it was established that influence of vegetation on the state of monuments is not the same for different types of stone. Higher plants have the most significant effect on the monuments of carbonate rocks. This is especially true of limestones, which is explained by their structure. Thus, for example, the laminated structure of flaglike limestone, its natural cavities and cracks often serve as another factor promoting its colonization by mosses, grassy and even woody plants. In this case, distribution of algae and biofilms of complex composition on carbonate rocks depends not so much on the properties of the stone, as on microclimatic conditions at the site of the monument. In a number of cases, there is a certain confinement of aerial algae to the minerals that make up the rock. So, on granite monuments algae more often develop on mica.

On the whole, the studies have shown that the condition of monuments, manifestation of various forms of damage to their materials depend on their biological environment. The features of the vegetation cover, its spatial characteristics exert a local influence on the state of monuments, create microclimatic conditions that often determine the development of destructive processes, and also characterize the overall ecological situation that has taken shape in the museum Necropoleis.

Fig. 3.23 Development of the fruiting body of a wood-destroying basidiomycete. Necropolis of the Masters of Arts

Fig. 3.24 Development of mosses along the junction of stone elements of the monument, where the substrate is more humid. Necropolis of the 18th century

Fig. 3.25 Intensive fouling by mosses of a monument from the Putilovo slab. The patches of moss merge in places, forming a continuous cover on the horizontal surface of the monument. Necropolis of the 18th century

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4 Decay of the Monuments

Dmitry Yu. Vlasov, Olga V. Frank-Kamenetskaya, Vera V. Manurtdinova, and Marina S. Zelenskaya

Abstract

The processes of stone and bronze destruction of the monuments in the Necropoleis were studied as a result of the monitoring. All forms of stone weathering, (mechanical damages, deposits, stone loss) are examined, their classification is proposed, the frequency of occurrence on various rock types is assessed. Particular attention is paid to biodegradation of the stone under the influence of microorganisms (bacteria, fungi, lichens and algae), formation of gypsum-rich patina on the surface of carbonate rocks and patina on the surface of bronze monuments.

Keywords

Weathering • Mechanical damages • Deposits
Stone loss • Biological colonization • Detachment
Roughening of the surface • Crumbling • Microfissures
Biodegradation • Bacteria • Fungi • Algae
Lichens • Gypsum-rich patina • Atmospheric corrosion
Copper alloys • Bronze disease

In the previous chapter the conditions in the Necropoleis, which have a significant effect on the monuments, were discussed. In this section, we will focus on the main “diseases” of stone and bronze monuments, trying to understand the causes of their emergence and development.

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4.1 Main Types of Weathering of Stone Materials

We propose a classification of the stone weathering types in St. Petersburg (Fig. 4.1), developed from the well-known scale of Professor B. Fitzner (Technical University, Aachen) (Fitzner et al. 1995; Fitzner and Heinrichs 2002).

The system is based on many years of investigation into the decay of various rocks of the museum Necropoleis monuments (see Chap. 2). The classification includes three larger types (mechanical damages, deposits and stone loss), where specific forms of deterioration to the stone material are distinguished (Figs. 4.2, 4.3 and 4.4).

Along with traces of background weathering dirt depositions, biological colonization (discussed in Sects. 3.4 and 4.2), detachment (Fig. 4.2a), roughening of the surface due to crumbling (Fig. 4.2b), and microfissures are present in almost all types of stone. For heterogeneous Ruskeala marble, microkarst is characteristic (Fig. 4.2c), and for porous Pudost limestone—formation of a structure like bone tissue (Fig. 4.2d). Gypsum-rich patina (gypsum crust) (Fig. 4.3) is present on all types of marbles and limestones, besides the white, primarily coarse-grained marble Deep fissures (Fig. 4.4) often have an anthropogenic origin and are found on all types of rocks, regardless of their hardness.

According to the qualimetric estimate (see Sect. 6.3) of the state of 632 monuments, the degree of stone destruction (ΔQ) in the museum Necropoleis varies from 2 to 51% (Fig. 4.5). In most cases, the extent of carbonate rock deterioration does not exceed 25% (Fig. 4.5a, b), and that of granite and other hard silicate rocks—10% (Fig. 4.5c). This is due to the considerable contribution of chemical weathering (sulphation) in the deterioration of memorials of marble and limestone, which are more susceptible to processes of deterioration in comparison with silicate rocks

The incidence of the primary gypsum crust on the surface of limestones is more frequent than on the surface of marbles (Fig. 4.6).

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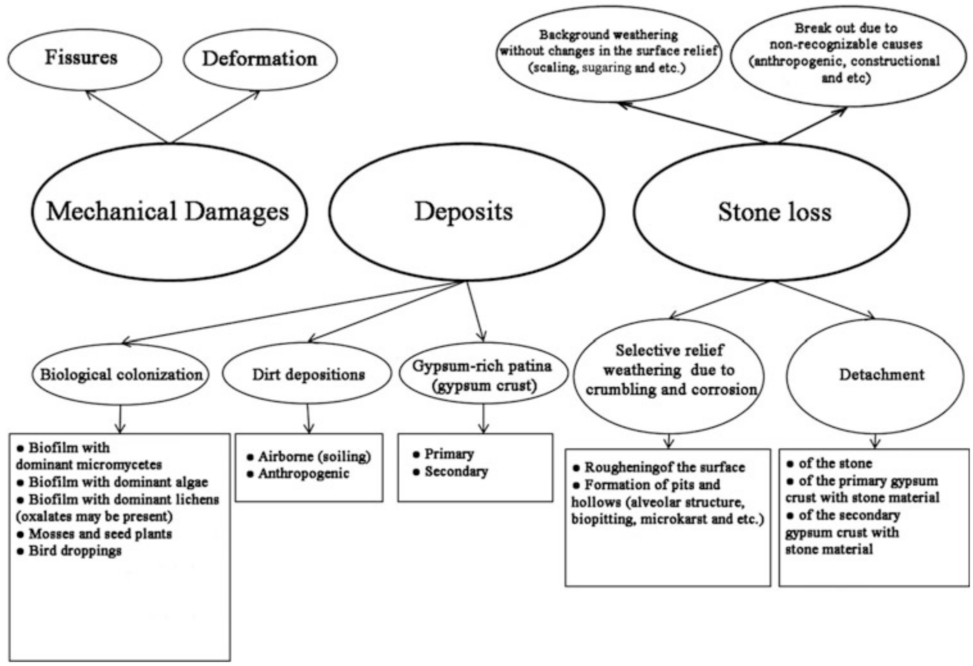

Fig. 4.1 Classification of the forms of weathering of the stone of St. Petersburg monuments

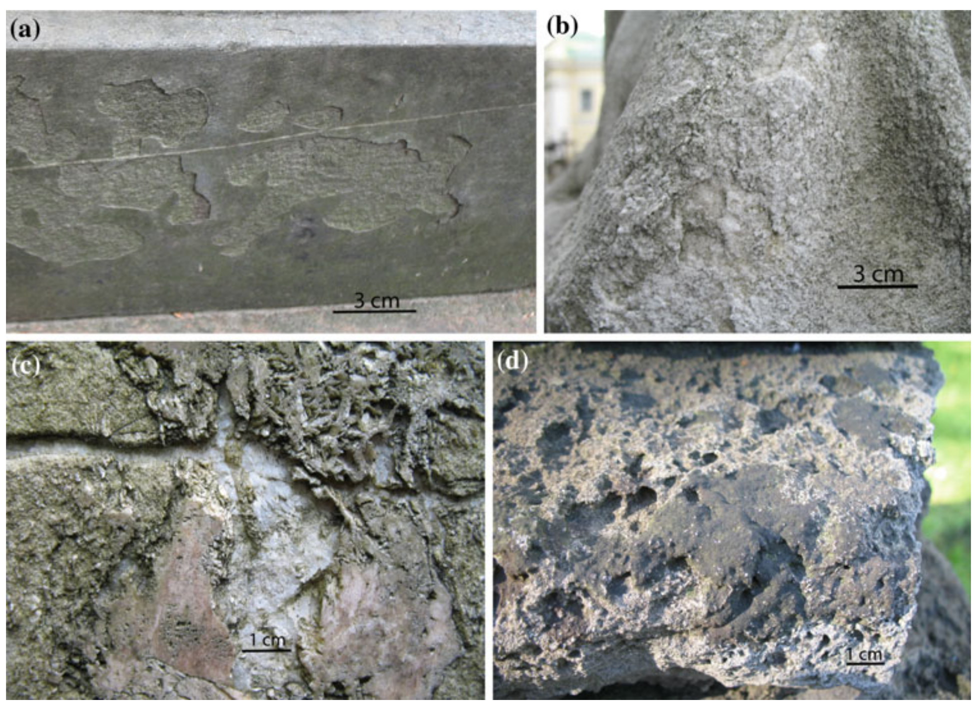

Fig. 4.2 Loss of stone on the monuments of the Necropolis of the 18th century: **a** flaking of the Serdobol granite on Monument to I.P. Bogdanovich; **b** roughening of the surface and flaking of statuary white marble due to crumbling. Monument to G.A. Demidov; **c** microkarst on the Ruskeala marble. Monument to P.P. Bakunin; **d** structure like bone tissue on the Pudost limestone. Tomb of the Unknown (N-18 No. 901)

Among limestones, the gypsum-rich patina is most often found on the surface of the porous Pudost travertine (on the surfaces of 50% of examined monuments). Among marbles, it is most often seen on the homogeneous Carrara marble (on the surfaces of 26% of the surveyed monuments). Its detachment together with marble and the formation of a secondary gypsum crust (Fig. 4.3b) are observed only on the monuments with a complex surface relief made of dense homogeneous marble: (white Carrara and light gray Bardiglio). The maximum harm from sulphation to the monuments of white Carrara marble reaches 35% (the monument to A.N. Shemyakin). The input of sulphation to the deterioration of monuments of Bardiglio marble does not exceed 19% (the monument to A.K. Imeretinsky).

In fouling, biofilms with dominant fungi are widespread on the surface of all rocks (Fig. 4.7). The input of

Fig. 4.3 Gypsum-rich patina and its detachment on carbonate rocks of the monuments in the Necropoleis: **a**, **b** on white statuary marble. Monuments to L. O. Premazzi, A.N. Shemyakin; **c** on the Pudost travertine. Monument to A. G. Demidov; **d** on the Putilovo limestone. Monument to A.Ya. Potemkina

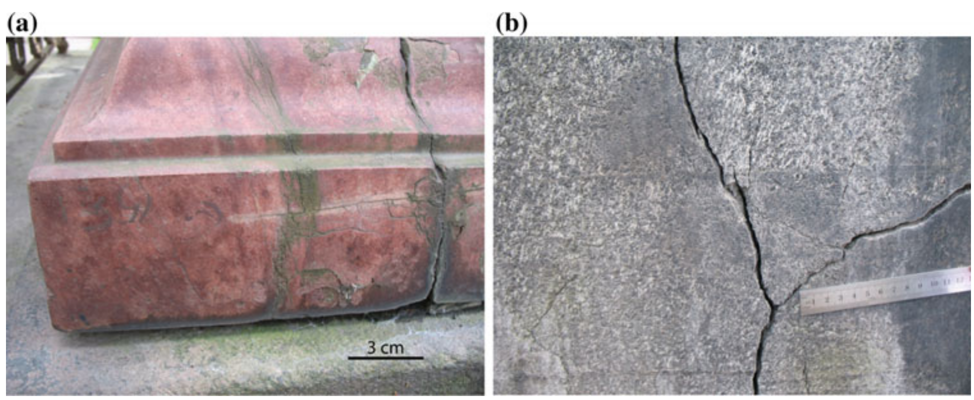

Fig. 4.4 Fissures on silicate rocks of the monuments in the Necropoleis: **a** on quartzite. Monument to A.F. Turchaninov. Necropolis of the 18th century; **b** on amphibolite. Monument to N.I. Utkin. Necropolis of Masters of Arts

microorganisms (fungi, algae, lichens) in rock deterioration varies from 2 to 10% and is most pronounced on the monument of A.I. Apaischikova.

Cracks occur on the surface of carbonate rocks that are heterogeneous in composition and structure (Ruskeala, Italian breccia and brecciated marbles, Pudost and Putilovo limestones) at least 10% more often than on other denser and more homogeneous marbles and limestones (Fig. 4.8a). But on more dense solid silicate rocks (granites, etc.), cracks occur no less frequently than on carbonate rocks (Fig. 4.8). At the same time, they are much more common (found on 80% of monuments) on such dense homogeneous rocks as Serdobol granite and Shokshinsky quartzite, which indicates a possibility of their anthropogenic or constructional origin. Fracturing does not play a great part in the deterioration of stone materials of the monuments. For carbonate rocks contribution of it in rock deterioration does not exceed 2% (the monument to N.T. Shemyakin of Carrara marble), on silicate rocks—4% (monument to the Unknown No. 959 of red quartzite).

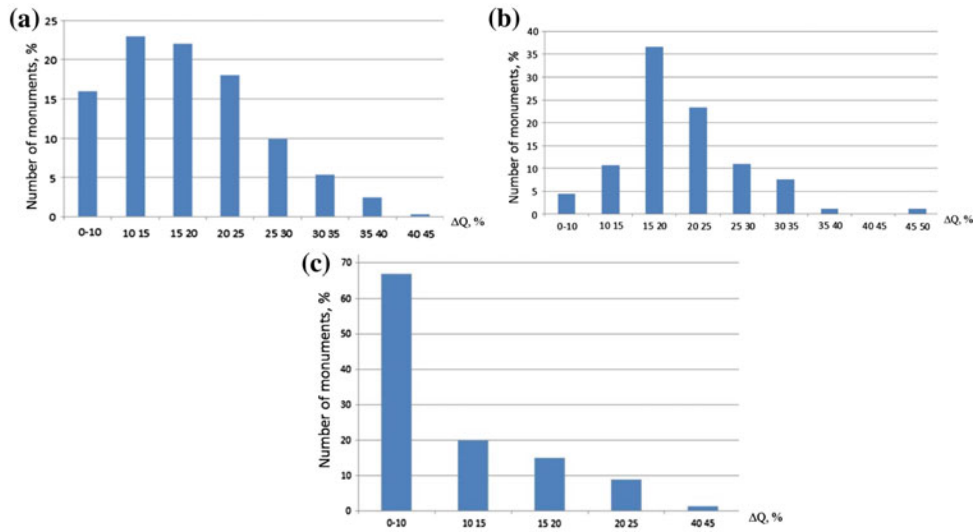

Fig. 4.5 The degree of the stone material deterioration (%) in the Necropolis of the 18th century of the surveyed monuments: **a** of marble, **b** of limestone, **c** of granite and other hard rocks

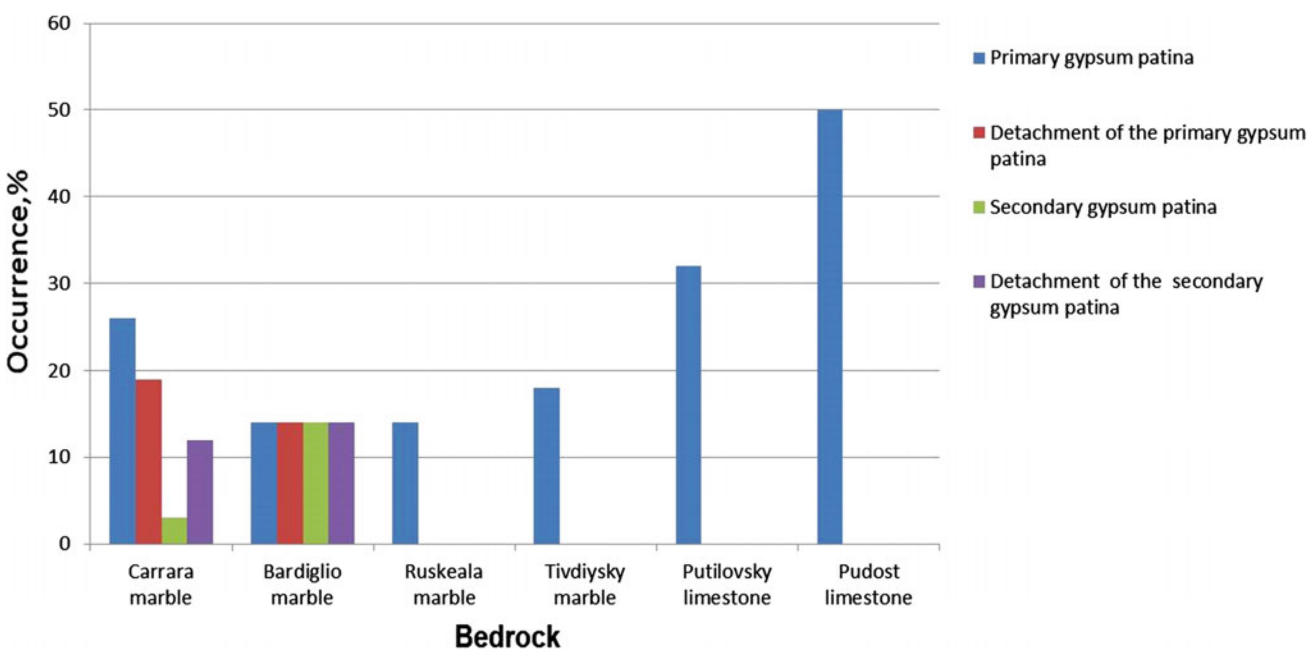

Fig. 4.6 The occurrence (%) of gypsum-rich patina on the surface of the examined monuments of carbonate rocks in the Necropolis of the 18th century

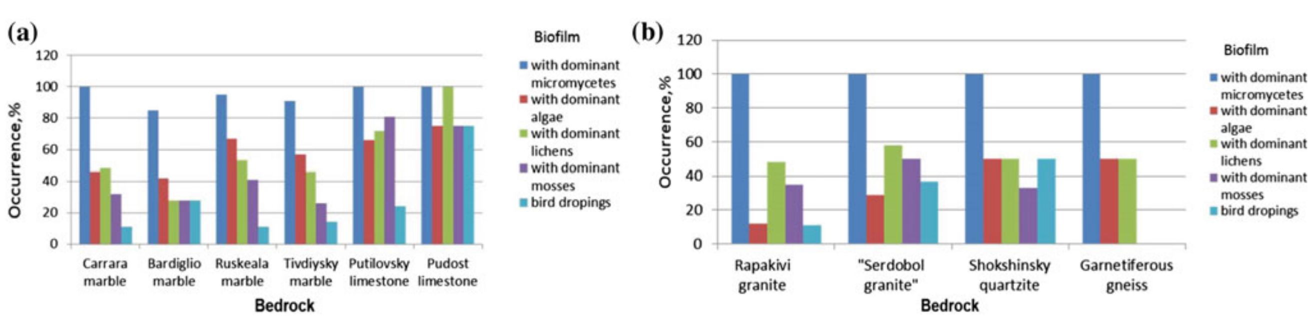

Fig. 4.7 The occurrence (%) of various forms of biofouling in the Necropolis of the 18th century on the surface of the surveyed monuments of: **a** marbles, **b** limestones, **c** granite and other hard rocks

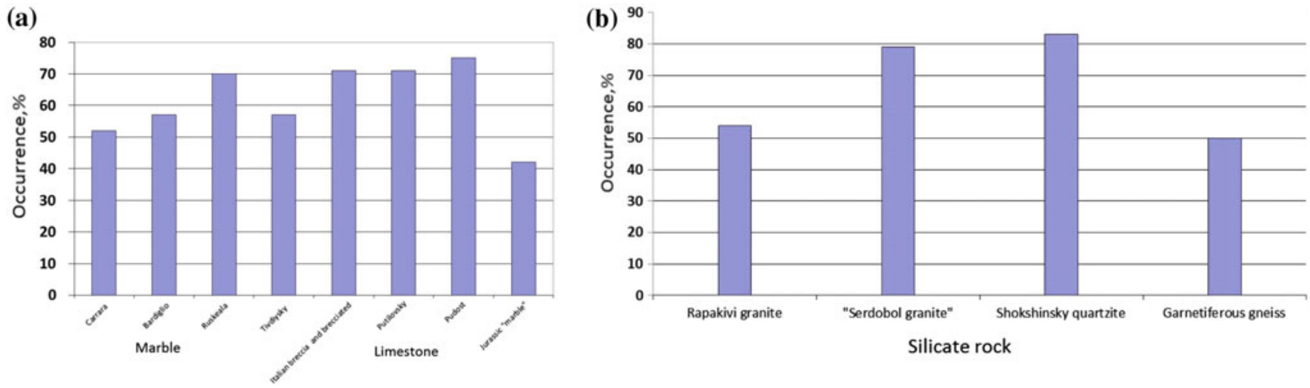

Fig. 4.8 The occurrence (%) of cracks on the surface of the surveyed monuments in the Necropolis of the 18th century: **a** of carbonate rocks, **b** of silicate rocks

4.2 Biological Damage to Stone Monuments

Biological fouling is very common on the monuments of the museum Necropoleis and is present on all types of stone (Vlasov et al. 2002; Vlasov and Frank-Kamenetskaya 2006). The rock may be destroyed by bacteria, algae, fungi, lichens, mosses, seed plants, invertebrate and vertebrate animals (Fig. 4.9).

The principal damage to the monuments of cultural heritage is caused by microorganisms (bacteria, fungi and algae). Microorganisms in most cases affect the monument together, forming complex and highly aggressive microbial communities (biofilms). The most common are extensive biofilms of green or gray-black color (Fig. 4.10). The green color is due to massive colonization by aerophilic algae, whereas mold-line fungi dominate in gray-black fouling.

Microbes can exist in huge amounts on damaged monuments, penetrating into the thickness of the stone to a considerable depth. In one gram of weathered limestone in a moist environment, hundreds of thousands or millions of bacterial cells and microscopic fungi can be found. Cells of microorganisms are usually immersed in an organic matrix, which is represented by polymeric substances: polysaccharides, proteins, glycoproteins, lipids, glycolipids, fatty acids and enzymes produced by microorganisms themselves. This matrix provides additional protection of the microbial community from the hostile environment. The main danger of the microbial community is its chemical and physical effects on the stone material. Microorganisms produce aggressive acids and other metabolites, which destroy the stone, changing its structure and chemical composition.

On the monuments of the museum Necropoleis the experts from the St. Petersburg State University identified more than 150 species of microorganisms capable of causing stone decay. Most biodestructors are microscopic fungi (micromycetes). On the monuments of the museum Necropoleis, 105 species of microscopic fungi were identified, the dominant being:

1. *Alternaria alternata*
2. *Aureobasidium pullulans*
3. *Cladosporium cladosporioides*
4. *Cladosporium herbarum*
5. *Cladosporium sphaerospermum*
6. *Coniosporium* sp.
7. *Epicoccum nigrum*
8. *Fusarium oxysporum*
9. *Hormonema dematioides*
10. *Monodyctis levis*
11. *Penicillium brevicompactum*
12. *Phaeococcomyces exophialae*
13. *Phaeosclera* sp.
14. *Scytalidium lignicola*
15. *Ulocladium chartarum*

Some species of micromycetes—*A. alternata*, *A. pullulans*, *C. cladosporioides*—can be considered unquestionable dominants on the stone monuments of the Necropoleis, as they have been registered in all periods of observation on all examined stone substrates showing the signs of biological decay. The largest number of species of micromycetes (82) was observed on various kinds of marble (fine- and medium-grained, coarse- and uneven-grained). On the surface of limestones (porous travertine and flaglike limestone), 68 species of microscopic fungi were found. Only 46 species were discovered on the surface of granites and other hard rocks, which is probably

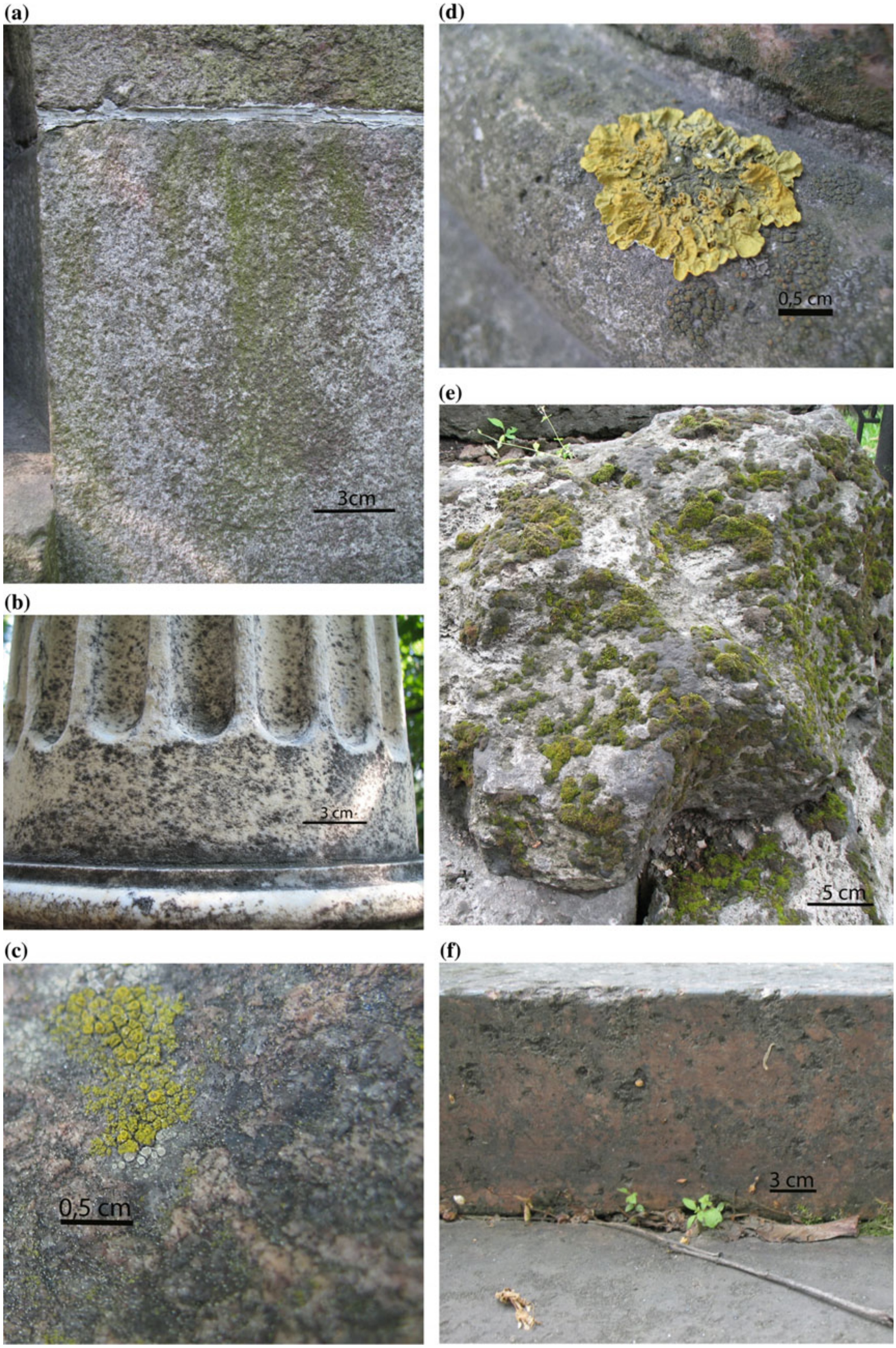

Fig. 4.9 Biofouling on the surface of stone monuments of the museum Necropoleis: **a** algae (Chlorophyta division). Monument to S.S. Botkin; **b** colonies of dark-colored micromycetes. Monument to E.I. Zagryazhskaya; **c** crustose lichens. Monument to I.I. Labensky; **d** foliose lichens. Monument to N.V. Shenshin; **e** mosses. The tomb of P.P. Saker; **f** seed plants. Monument to E.I. Olkhina

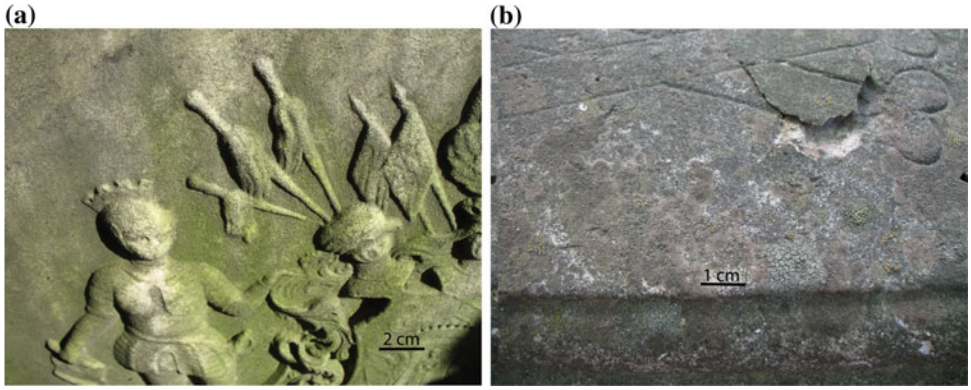

Fig. 4.10 Extensive biofilms on the surface of stone monuments: **a** continuous biofilm with the dominance of green algae. Development of biological damage leads to the erosion of the surface of white statuary marble. Monument to S. Kh. Münnich; **b** continuous biofilm with domination of crustose lichens and micromycetes on the limestone surface (Putilov slab). Monument to A. F. Nadarzhinsky

due to the poorer state of knowledge about the latter and the properties of the stone material itself, which is more resistant to biodeterioration and exposure to the environment than carbonate rocks.

Lichenized fungi (lichens) in the Necropoleis occur locally (Fig. 4.9d). However, often crustose lichens form continuous crusts on the surface of the stone (Fig. 4.10b). They are most active on limestones, making restoration of such monuments very difficult. In the course of surveys of the Necropoleis monuments, the following species of lichens were identified: *Phaeophyscia nigricans*, *Phaeophyscia orbicularis*, *Xanthoria parietina*, *Lecanora* spp., *Candelariella* sp., *Caloplaca* sp., *Verrucaria* spp., *Bacidina* sp. (The identification of lichens was made by D.E. Himmelbrandt).

Mosses and vascular plants also can develop on the surface of the stone monuments in the Necropoleis (mainly of high degree of deterioration) (Fig. 4.9d, e). When they appear, the structure of the whole community changes dramatically, becoming more aggressive.

The presence of relatively large natural hollows in the surface layer of the stone, for example, microcracks, micropits and caverns, is one of the main prerequisites for the biological colonization of the rock, as can be clearly seen in the SEM images of the weathered stone surface (Fig. 4.11). The images show the disintegrated rock, microcolonies and hyphae of microscopic fungi, as well as bioclusters (clusters of microorganism cells). Numerous tabular gypsum crystals surrounded by colonies of microorganisms are visible in the depression on the surface of Ruskeala marble (Fig. 4.11b). In general, the colonization of the surface of carbonate rocks by microorganisms proceeds more intensively (Fig. 4.11a–c) than that of granite (Fig. 4.11d). The study of the species of macro- and microorganisms involved in the processes of stone deterioration in the Necropoleis made it possible to give scientific credence to a number of conservation measures, described in detail in Sect. 7.1.

4.3 Gypsum-Rich Patina Formation on the Surface of Monuments of Marble and Limestone

The greatest danger for the monuments of marble and limestone in the museum Necropoleis is the process of sulphation, which results in transformation of calcite into gypsum and formation of firm black crust on the surface of carbonate rocks—gypsum-rich patina (Timasheva et al. 2007; Ekspertiza 2005; Camuffo et al. 1983; Frank-Kamenetskaya et al. 2009; Garcia-Vallès et al. 1998; Kramar and Mirtič 2008; Maravelaki-Kalaitzaki 2005; Siegesmund et al. 2007). The coefficients of thermal expansion of calcite and gypsum differ greatly (Filatov 1990), so the gypsum crust cracks and then exfoliates together with the parent rock, which requires costly restoration and often results in irreparable loss of unique cultural heritage sites. It is known that formation of gypsum on the surface of carbonate rocks is associated, first of all, with the presence of sulfur dioxide SO_2 in the atmosphere of industrial megacities (see Sect. 3.1). Monitoring carried out since 1998 (Pamyatniki 2008; Lepeshkina et al. 2005) made it possible to identify the monuments struck with this “disease” in the museum Necropoleis (Table 4.1), and answer the question why marble and limestone monuments exposed practically to the same atmospheric conditions, are characterized by varying degrees of sulphation.

The results of field observations showed that gypsum-rich patina as black crust (Fig. 4.12) is found in the museum Necropoleis on the surface of marble and limestone monuments, differing in mineral composition, structural and textural features (Table 4.1). According to X-ray phase analysis (XRD), the mineral composition of the patina is represented by gypsum and minerals of the bedrock. The amount of gypsum varies considerably (Table 4.2).

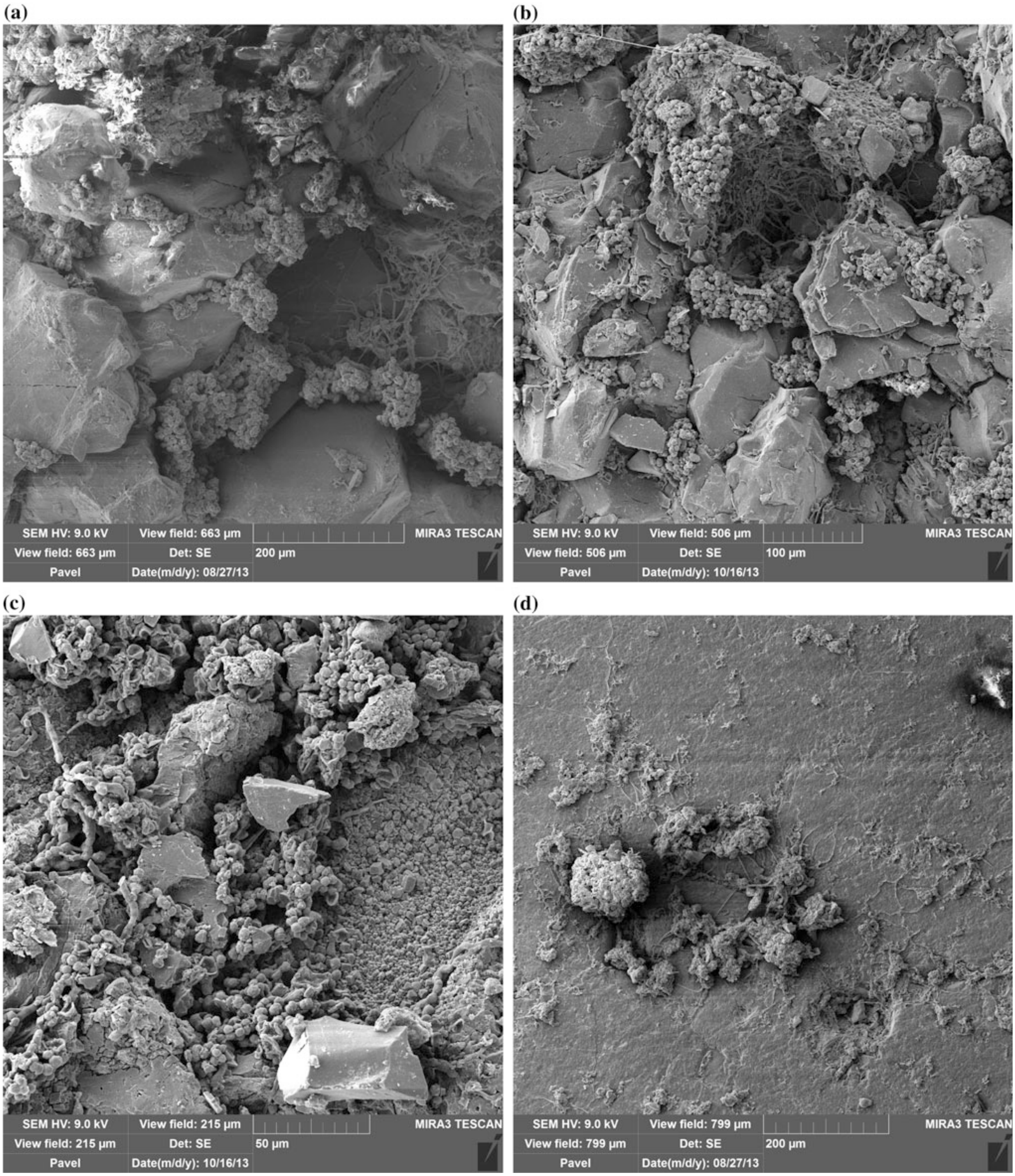

Fig. 4.11 SEM images of weathered stone surface, colonized by microorganisms: **a** homogeneous statuary marble; **b** heterogeneous Ruskeala marble; **c** flaglike Putilovo limestone; **d** Serdobol granite. Microcolonies and hyphae of fungi are visible, as well as bioclusters in microfissures and microcavities on the stone surface

Table 4.1 Tombstones on which gypsum-rich patina was discovered

Necropolis	Monument		Expert review (restoration)
	Name of the deceased	Shape	
White Homogeneous Carrara Marble			
NMA (Necropolis of Masters of Art)	A.I. Kosikovsky[a]	Sarcophagus inside a portico	2001 (2008)
N-18 (Necropolis of the 18th century)	V.B. Golitsyna	Ledger	2007
N-18	E.A. and V.N. Kochubey[a]	Sculpture (bas-relief)	2002 (2006)
N-18	A. Ya. Okhotnikov[a]	Sculpture	2009 (2010)
N-18	P. V. Kindyakov[a]	Sculpture	2007 (2009)
N-18	E.S. Shenshina	Stele	2002
NMA	A.P. Veliashev	Bas-relief	2011
N-18	A.B. Chelischev	Vase	2013
N-18	M.A. Kolzakova	Stele	2012
N-18	S.N. Borozdina	Stele	2013
N-18	A.A. Borozdin	Stele	2013
N-18	M. Kiseleva	Canopy	2013
N-18	O.F. Dmitrieva	Cross on a pedestal	2013
N-18	E.S. Olsufieva	Pedestal	2013
N-18	A.P. Zhadimerovsky	Sarcophagus	2013
N-18	N.M. Yakovlev	Pedestal	2013
N-18	A.I. Apaischikova	Sculpture	2008
N-18	A.N. Shemyakin	Sculpture	2008
N-18	N.T. Shemyakin	Column	2008
N-18	A. A. Lvov	Sarcophagus	2013
N-18	G.A. Demidov	Sculpture	2013
N-18	A. A. Bolotnikov	Sculpture	2009
N-18	N.I. Vanifatiev	Pillar	2009
N-18	A. Glinka	Sculpture	2012
N-18	D.G. and V.I. Kiselev	Pedestal	2013
N-18	A.Dubyansky	Obelisk	2009
N-18	M.I. Kozlovsky	Plinth under the draped urn	2013
N-18	S.M. Korolev	Urn	2013
N-18	V.V. Davydov	Vase	2013
N-18	S.S. Razumovskaya	Sculpture	2013
N-18	E.M. Kozhina	Sculpture	2013
Gray-White Heterogeneous Ruskeala Marble			
N-18	A.N. and A.P. Mordvinovs	Decorative elements	2013
N-18	D.S. Olsufiev	Vase	2009
N-18	V.N. and V.P. Shenshins	Vase	2013
N-18	A.S. Strugovshchikova	Vase	2013
N-18	E.A. Rummel	Aedicula	2002
N-18	Unknown (H-18 No. 203) (next to I. R. Chirkin's monument)	Vase atop a pillar	2009
N-18	P.G. Demidov	Canopy	2013
N-18	G. Imeretinsky	Vase	2013

(continued)

Table 4.1 (continued)

Necropolis	Monument		Expert review (restoration)
	Name of the deceased	Shape	
Light Gray Homogeneous Bardiglio Marble			
N-18	A.K. Imeretinsky	Plaque (on the Necropolis wall)	2012
N-18	S.B. Strugovschikov	Vase	2013
Pink Patterned Tivdiysky Marble			
NMA	F.I. Ivanov	Sides of the aedicula	2010
Flaglike Putilovo Limestone			
N-18	S.I. Lavrov	Pillar on a pedestal	2006
N-18	E.A. Demidova	Canopy	2013
N-18	E.A. Mansurova	Pedestal	2013
N-18	A.A. Okuneva	Pedestal	2013
N-18	A.D. Paskaya	Pedestal	2013
NMA	F.I. Ivanov	Aedicula	2010
NMA	V.A. Scherbatova	Pedestal	2011
N-18	I.M. Lavrov	Pedestal	2009
N-18	A.Ya. Potemkina	Canopy	2009
Porous Pudost Travertine			
N-18	P.A. Golitsyna	Grotto	2006
N-18	N.S. Bem	Canopy - Grotto	2006
N-18	P.P. Saker	Mound (pedestal)	2013
N-18	V. I. Potemkina	Canopy	2009
N-18	A.G. Demidov	Grotto	2012

Notes N-18 stands for the Necropolis of the 18th century, NMI—the Necropolis of Masters of Arts
[a]Patina removed during restoration

Four stages of gypsum-rich patina formation can be distinguished (Table 4.3), which, as shown in the example of A.I. Kosikovsky's tomb of homogeneous dense Italian marble, are often present on different parts of the surface of the same monument (Fig. 4.12). The secondary gypsum crust can be easily distinguished from the primary one. It is usually thinner and develops on a fresh surface that appears after the primary crust has peeled off.

According to biological studies, gypsum-enriched patina contains numerous microorganisms (bacteria, microscopic fungi, algae and lichens). Microorganisms are instrumental for the dissolution of carbonate rock because the products of their metabolism (primarily organic acids) are aggressive, they enhance moisture and air pollutants accumulation in the outer layer of the stone (Vlasov and Frank-Kamenetskaya 2006). As the disease develops (in transition from stage I to stage IV), the number of species of microscopic fungi grows (Table 4.3). Some of the dominant species of fungi (*A. pullulans*, *C. sphaerospermum*) can be identified at all stages of the gypsum crust formation. These types of dark-colored fungi are characterized by a high degree of resistance to unfavorable environment. Their cells contain a pigment, melanin, which protects the fungi from the adverse effects of environment. They form microcolonies and mycelium masses in microfissures and between gypsum crystals.

According to the SEM data, morphology and dimensions of gypsum crystals on the surface of monuments of carbonate rocks considerably vary. On the surface of the monument to A.I. Kosikovsky, with a complex surface and made of dense, homogenous Italian marble numerous tabular crystals (of average size of 15–20 μm) are clearly seen (Fig. 4.13a). They form a thick rug of rosette intergrowths, which is indicative of a multitude of nucleation centers.

There are individual elongated prismatic crystals of gypsum (up to 120 μm in size), with a strongly developed facet of the 2nd pinacoid (Fig. 4.13b). Near the crystals of gypsum, rounded cells of algae are clearly visible. On the surface of Golitsyna's ledger grave mark of the same marble a continuous biofilm formed by microorganism cells and the products of their vital activity is visible (Fig. 4.13c).

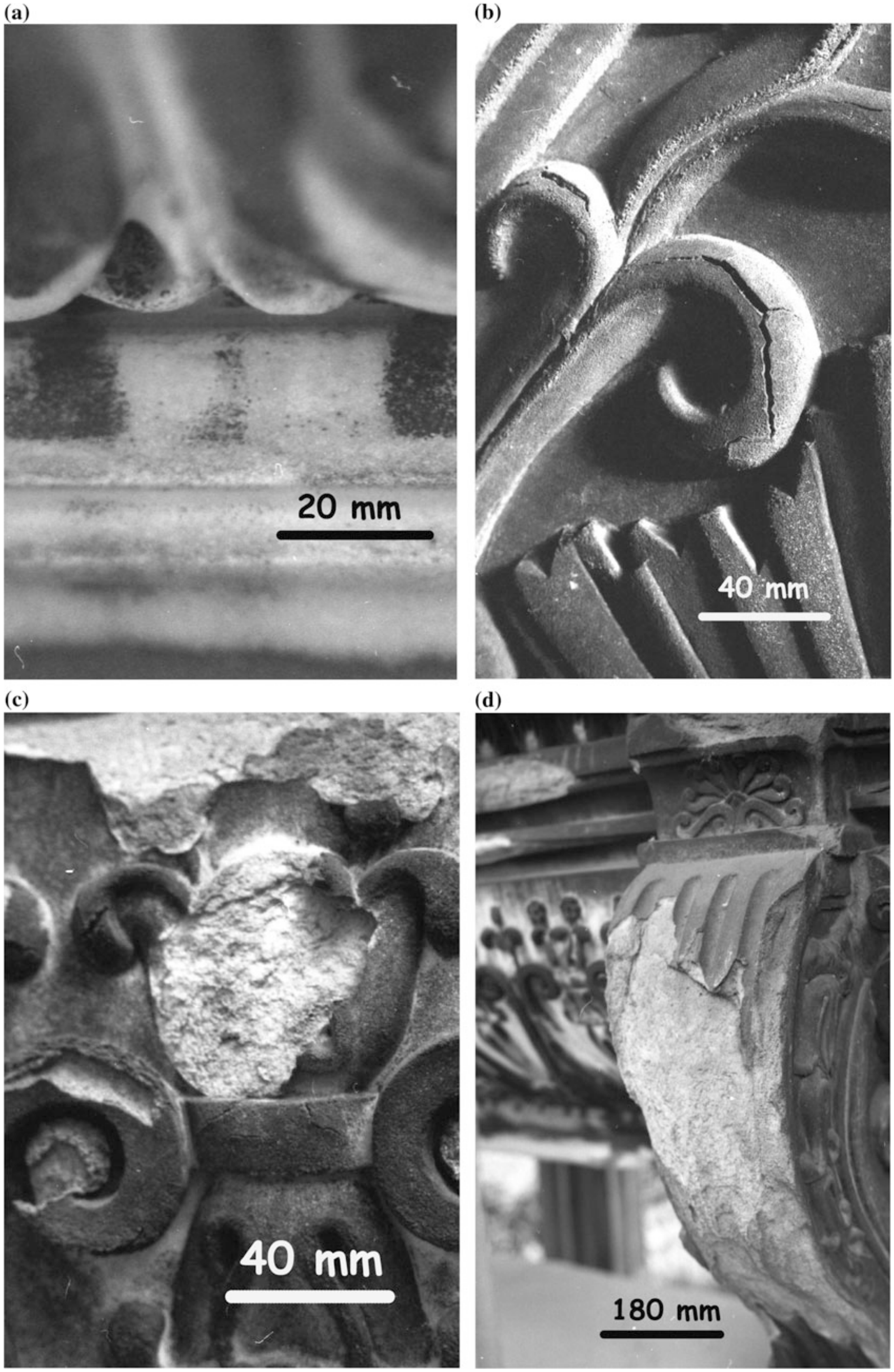

Fig. 4.12 Gypsum-rich patina on the surface of Carrara marble (monument to A.I. Kosikovsky, Necropolis of Masters of Arts): **a** primary thin patina; **b** primary formed thick patina with cracks; **c** sugaring marble surface after detachment of the primary patina; **d** young secondary patina

Table 4.2 Results of XRD analysis of Patina samples from monuments of various carbonate rocks

Monument	Place of sampling	Mineral composition	
		Bedrock	Patina
A.I. Kosikovsky	Sarcophagus, east side	Calcite, quartz	Gypsum (main phase); calcite, quartz (litle)
V.B. Golitsyna	Surface of the ledger	Calcite, quartz (traces)	Calcite (main phase); gypsum (traces), quartz (traces), feldspar (traces)
E.A. Rummel	Wall inside the arch (west side)	Calcite, dolomite, amphibole, talc, mica	Gypsum (a lot), calcite, dolomite, mica, talc, feldspar (traces), chlorite (traces)
Unknown (N-18 No. 203)	Vertical wall of the pillar (west side)	Calcite, dolomite	Calcite, dolomite (little), gypsum (traces)
S.I. Lavrov	Vertical face of the pedestal (east side)	Dolomite, calcite, quartz	Calcite, dolomite, quartz; gypsum not found
			Gypsum (a lot), calcite, quartz, feldspar (traces)
P.A. Golitsyna	Top of the grotto (south side)	Calcite, dolomite, quartz	Gypsum (main phase), dolomite, quartz

Table 4.3 The main stages of gypsum-enriched patina formation and the species of microscopic fungi typical for them (as in the case of the monument to A.I. Kosikovsky)

Stage of formation	Species of microscopic fungi (Vlasov et al. 2002)	
	Number	Dominant
I. Initial stage of primary gypsum crust formation (buildup thickness is negligible) (Fig. 4.12a)	4	*Aureobasidium pullulans* *Cladosporium sphaerospermum*
II. The final stage of primary gypsum crust formation (buildup thickness is significant) (Fig. 4.12b)	10	*Alternaria alternata* *Aureobasidium pullulans* *Candida* sp. *Cladosporium cladosporioides* *Cladosporium sphaerospermum*
III. Detachment of the primary gypsum crust together with marble (Fig. 4.12c)	11	*Alternaria alternata* *Aureobasidium pullulans* *Candida* sp. *Cladosporium cladosporioides* *Cladosporium sphaerospermum*
IV. Beginning of secondary gypsum crust formation (Fig. 4.12d)	9	*Alternaria alternata* *Aureobasidium pullulans* *Candida* sp. *Cladosporium cladosporioides* *Cladosporium sphaerospermum*

The gypsum crystals, found in a small amount by the X-ray phase analysis (Table 4.2), are under the biofilm. The fact that the amount of gypsum on the two monuments of the same marble is so different, means that sulphation depends on the relief of the monument surface. The complex relief of the surface of A.I. Kosikovsky's monument facilitates moisture accumulation, and sulphation becomes more intensive.

Gypsum content in the patina on the surface of heterogeneous, often fractured Ruskeala marble (monuments to E. A. Rummel, the Unknown N-18 No. 203) and of the flaglike Putilovo limestone (the monument to S.I. Lavrov) is also varied (Table 4.2). Numerous tabular gypsum crystals (30–40 µm in size) and hyphae of microscopic fungi are visible in the depressions and cracks typical for Ruskeala marble (Fig. 4.14a). Colonies of microorganisms, fungi and algae, often form specific bioclusters (Fig. 4.14b).

Under the electronic microscope small, unevenly distributed crystals of gypsum are seen in the patina on the vertical surface of the pedestal of S.I. Lavrov's monument of Putilovo flaglike limestone (Fig. 4.15). In some areas, individual rare crystals are observed under entangled hyphae of micromycetes (Fig. 4.15a). On others, a solid layer of gypsum crystals is visible, which covers the surface of the carbonate rock almost completely (Fig. 4.15b). There are rounded crystals with curved faces (the average size being

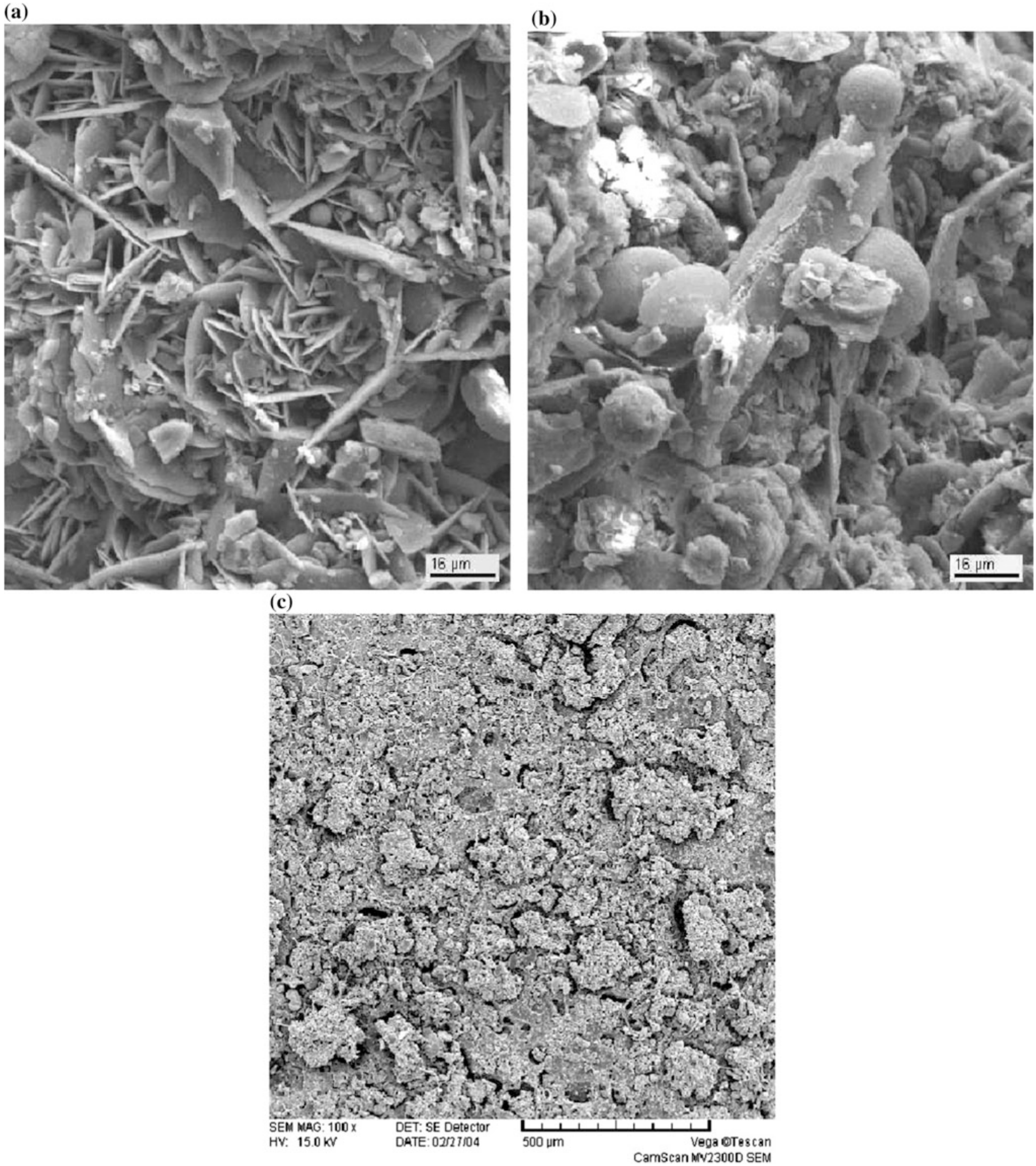

Fig. 4.13 SEM images of the surface of Carrara marble with different degrees of sulphation: **a** rosettes of tabular crystals, monument to A.I. Kosikovsky; **b** elongated crystal of prismatic habitus and algal cells, monument to A.I. Kosikovsky; **c** biofilm, monument to V.B. Golitsyna

10 µm). Thus, we can see that the processes of growth and dissolution alternate during the transformation of calcite into gypsum.

The largest gypsum crystals (up to 170 µm in size) were found on the surface of the grotto-shaped monument made of porous calcareous tufa (monument to P.A. Golitsyna) (Fig. 4.16). Elongated striated prismatic crystals (Fig. 4.16a) and acicular crystals are visible, with smaller (up to 30 µm) blade crystals in the indentations between them (Fig. 4.16b). Microorganisms, identified using the artificial Czapek-Dox

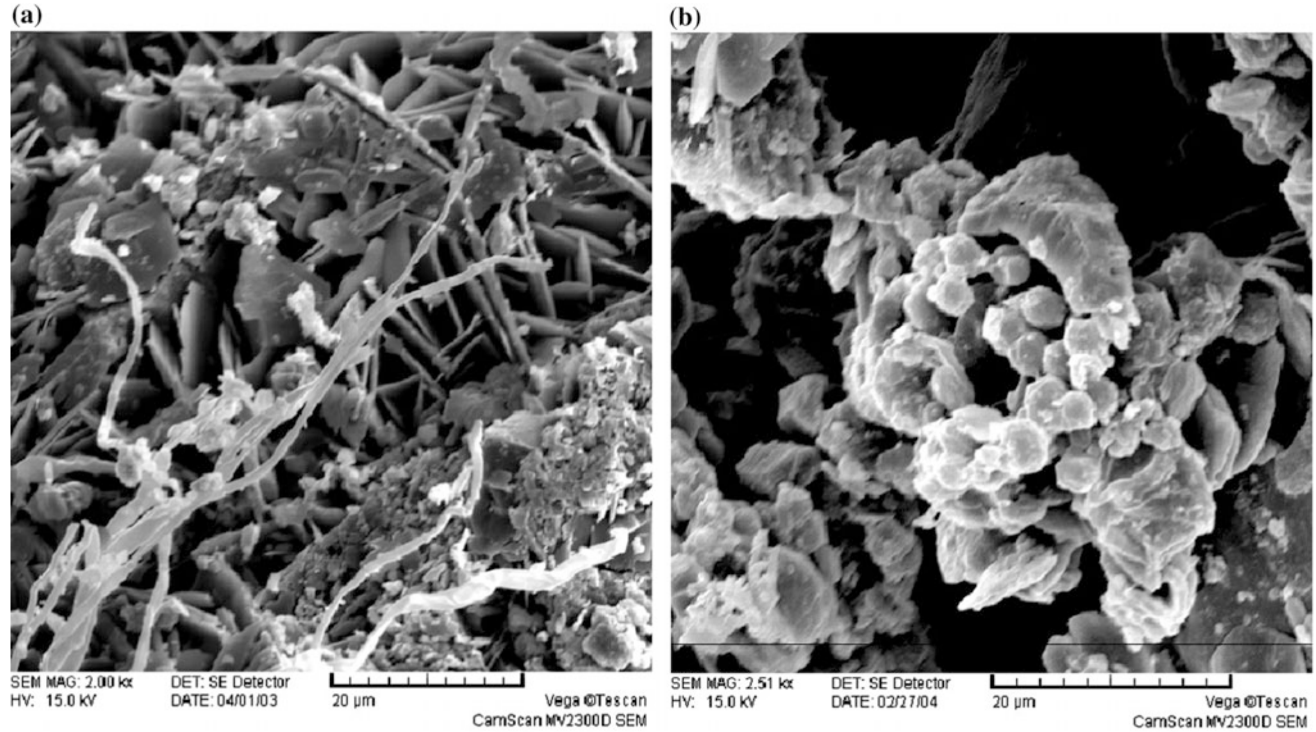

Fig. 4.14 SEM-images of the surface of Ruskeala marble, monument to E.A. Rummel: **a** lamellar gypsum crystals in the fissure, hyphae of fungi; **b** a biocluster

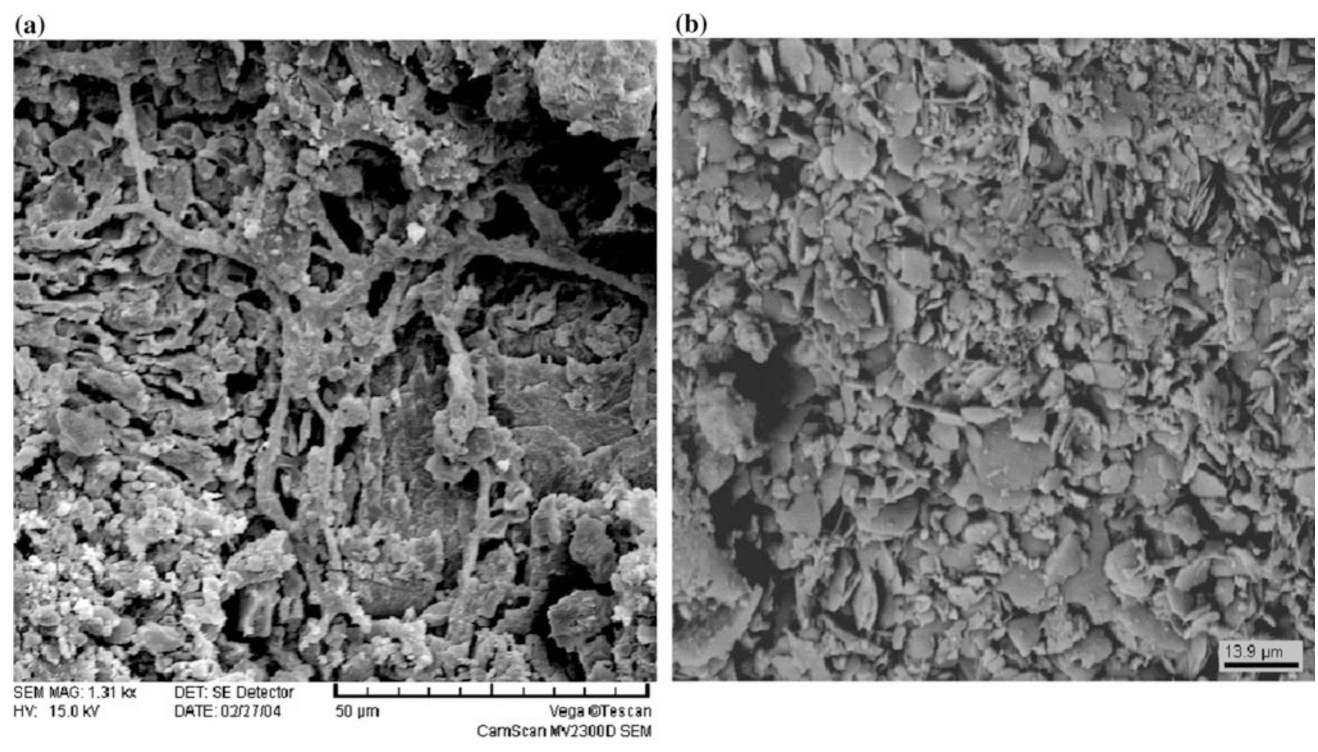

Fig. 4.15 SEM images of the surface of Putilovo limestone, monument to S.I. Lavrov: **a** rare small crystals of gypsum under the biofilm; **b** a layer of gypsum crystals

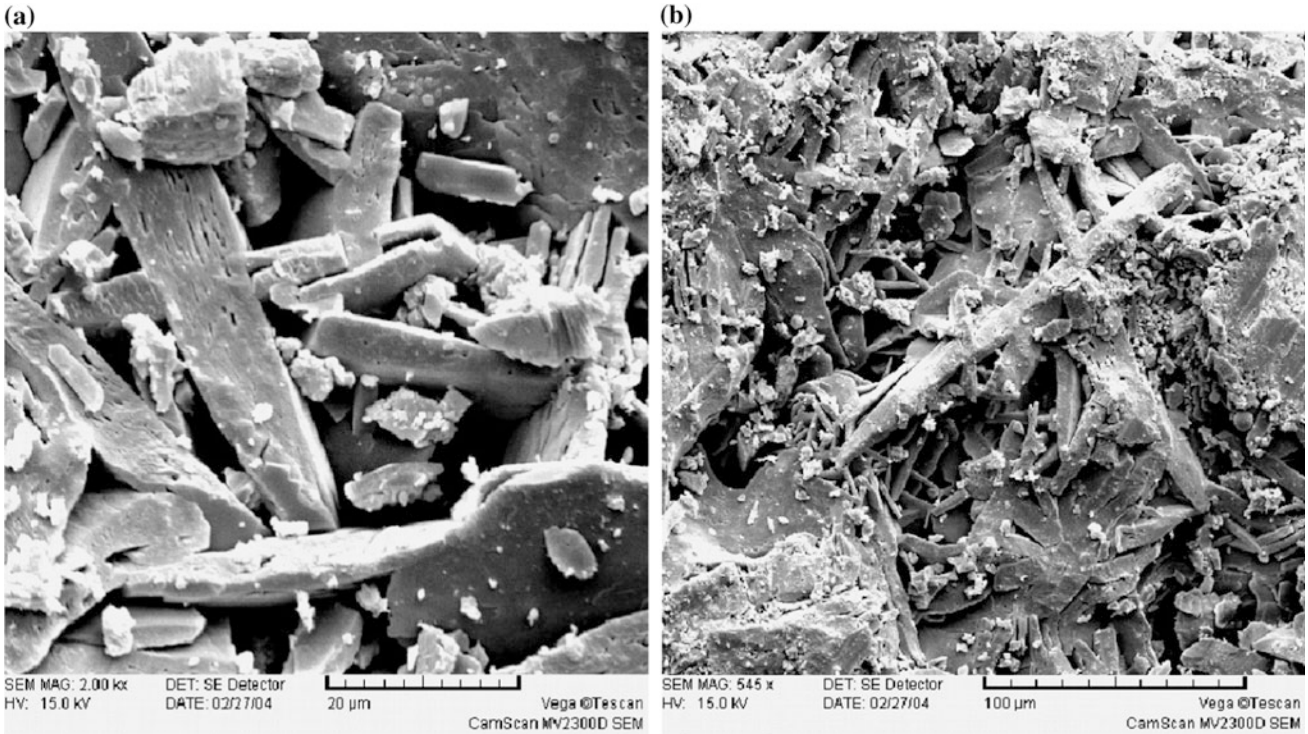

Fig. 4.16 SEM images of the surface of porous travertine: **a** layer of large prismatic gypsum crystals with hatching; **b** needle-like and lamellar gypsum crystals

medium, are under a layer of gypsum. Thus, gypsum crystals of a maximum variety of shapes and sizes are observed on the surface of porous travertine.

The results presented above make it possible to distinguish three main stages in the formation of primary gypsum-rich patina, which proceed with the active participation of microscopic fungi and other microorganisms.

Initial. A biofilm is formed on the surface of the monument, under which small crystals of gypsum begin to grow. It is found on the Carrara marble and Putilovo limestone (Fig. 4.13c and 4.15a).

Intermediate. Characterized by the presence of numerous crystals of gypsum, with microorganisms in between. It is found on Carrara and Ruskeala marbles (Fig. 4.13b and 4.14a).

Intensive. There is a layer of gypsum crystals on the surface of the monument, with microorganisms under it. The stage is observed on the Carrara marble, Putilovo imestone and Pudost porous travertine (Fig. 4.13a, 4.15b and 4.16a, b).

Monitoring showed that the extent of marble and limestone sulphation of the monuments in the museum Necropoleis, exposed to the same environment, varies by a wide margin. The rate of gypsum-rich patina formation is directly dependent on the local conditions on the surface of the monument that contribute to the retention of moisture. Such conditions can evolve due to the carbonate bedrock properties (primarily porosity and fracturing), connecting with its heterogeneous mineral composition, fabrics, and to the complex surface relief. That is why the most intensive gypsum-rich patina formation occurs on the surface of monuments of very porous Pudost travertine, and of those with complex surface relief, which are usually made of dense Carrara marble.

All stages of carbonate rock sulphation take place with the participation of microorganisms, primarily microscopic fungi, whose destructive activity grows as the gypsum-rich patina is formed.

4.4 Patina Formation on the Surface of Bronze Monuments

On the surface of copper and its alloys kept in the open air, patina are formed, which consist of corrosion products and other components from the environment (Fig. 4.17). A dense homogeneous patina, strongly adhered to the substrate, has protective properties—its appearance results in a gradual alleviation of atmospheric corrosion (Kalish 1971). In the humid industrial atmosphere typical for St. Petersburg, a non-uniform loose patina containing copper chlorides is often formed on the surface of the monuments (Fig. 4.18).

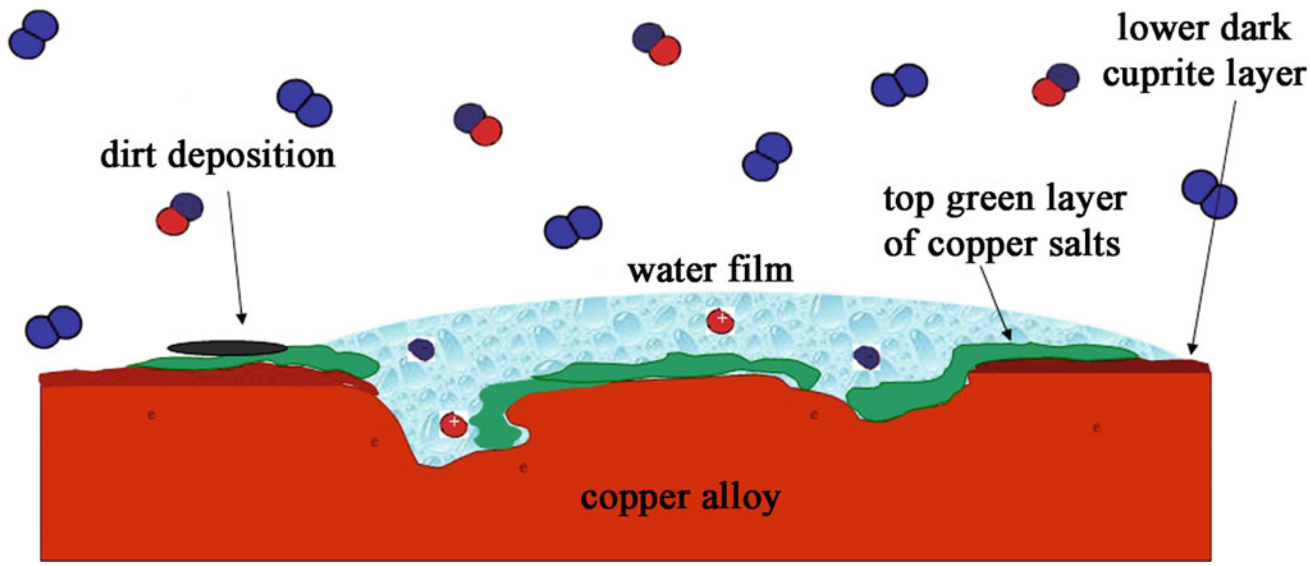

Fig. 4.17 Water film and different deposits on the surface of copper alloys in urban environment (http://www.icom-cc.org/54/document/meeting-at-dac-s1-p-letardi/?id=467#.W4fPlMJ9iUk)

On the surface of such monuments, foci of the "bronze disease" often appear when corrosion penetrates deep into the alloy (Scott 2002; Yagovkina and Sorin 2003; Pamyatniki 2008; Watt et al. 2009; Skul'ptura 2010) . In order to identify this disease at the initial stage and save bronze monuments, constant monitoring of the patina composition is necessary, which serves as an indicator of the state of both the monument itself and the ambient air (Pamyatniki 2008; Chelibanov et al. 2012). This control is exercised in the process of monitoring, which is carried out in the Necropoleis of the Museum of Urban Sculpture since 1998 (Nesterova 2000; Meshchanova 2004; Zolotareva 2008; Vasilieva 2011; Vasilieva et al. 2011).

Over the past years, all the monuments of copper and its alloys were surveyed (40 in the Necropolis of Masters of Arts and 5 in the Necropolis of the 18th Century), whose time in the open air was 3 to 180 years. Samples of patina were taken from 29 monuments in the surveying seasons of 1998–1999, 2003–2004, 2005–2007 and 2008–2010.

The results of visual inspection and light microscopy showed that the patina on the surface of bronze and copper monuments of the Necropoleis is usually a multi-layered formation: the upper dark layer, under which green and blue grains are distributed with varying degrees of density, and in the gaps between a lower solid black layer is seen (Fig. 4.19). The top layer is the mud component of the patina, the two lower ones are corrosion components.

The chemical composition of the patina is characterized by elements coming both from the copper alloy (Cu, Zn, Pb, Sn, Ti, Fe) and from the environment (Fe, Al, S, P, Cl, Si, Mn, K, Ca, Mg). The presence of silicon is mainly due to the presence of quartz in many samples, and that of calcium—of gypsum, i.e., of minerals getting on the patina surface from the environment. The other elements do not form independent compounds. It can be assumed that Zn, Pb, Sn cations coming into the patina from the copper alloy as impurities may also incorporate into copper sulfates and carbonates as isomorphic ones.

The mineral composition of the mud patina component is represented primarily by quartz, as well as by calcite and gypsum.

On the surface of the monument to V.F. Komissarzhevskaya 25 species of microscopic fungi were found in the mud component of patina: *Alternaria alternata, Aureobasidium pullulans, Cladosporium herbarum*, *Epicoccum nigrum*, *Paecilomyces javanicus*, *Penicillium diversum*, *Penicillium herqueri* and others.

The mineral composition of the corrosion component, according to X-ray diffraction analysis, is represented by copper oxides and salts (Table 4.4), whose ratio gradually changes with time (Table 4.5). The most common patina minerals are red oxide of copper, cuprite Cu_2O and copper sulfates: brochantite $Cu_4SO_4(OH)$ and antlerite $Cu_3(SO_4)(OH)_4$. The ratio of brochantite and antlerite varies. Copper oxide tenorite CuO was found in the Necropoleis on two monuments only: to D.D. Ponomarev and I.N. Pevtsov. Copper carbonate malachite $Cu_2(CO_3)(OH)_2$ is found, according to XRD data, approximately three times less frequently than sulfates. However, the results of additional studies of black and colored patina from the surface of nine monuments in the Necropolis of Masters of Art (to P.Z. Andreev, A. Bozio, E.P. Korchagina-Aleksandrovskaya, V.F. Komissarzhevskaya, A.I. Kuindzhi, V.V. Stasov, F.I. Stravinsky, I.R. Tarkhanov and Yu. M. Yuryev) using IR

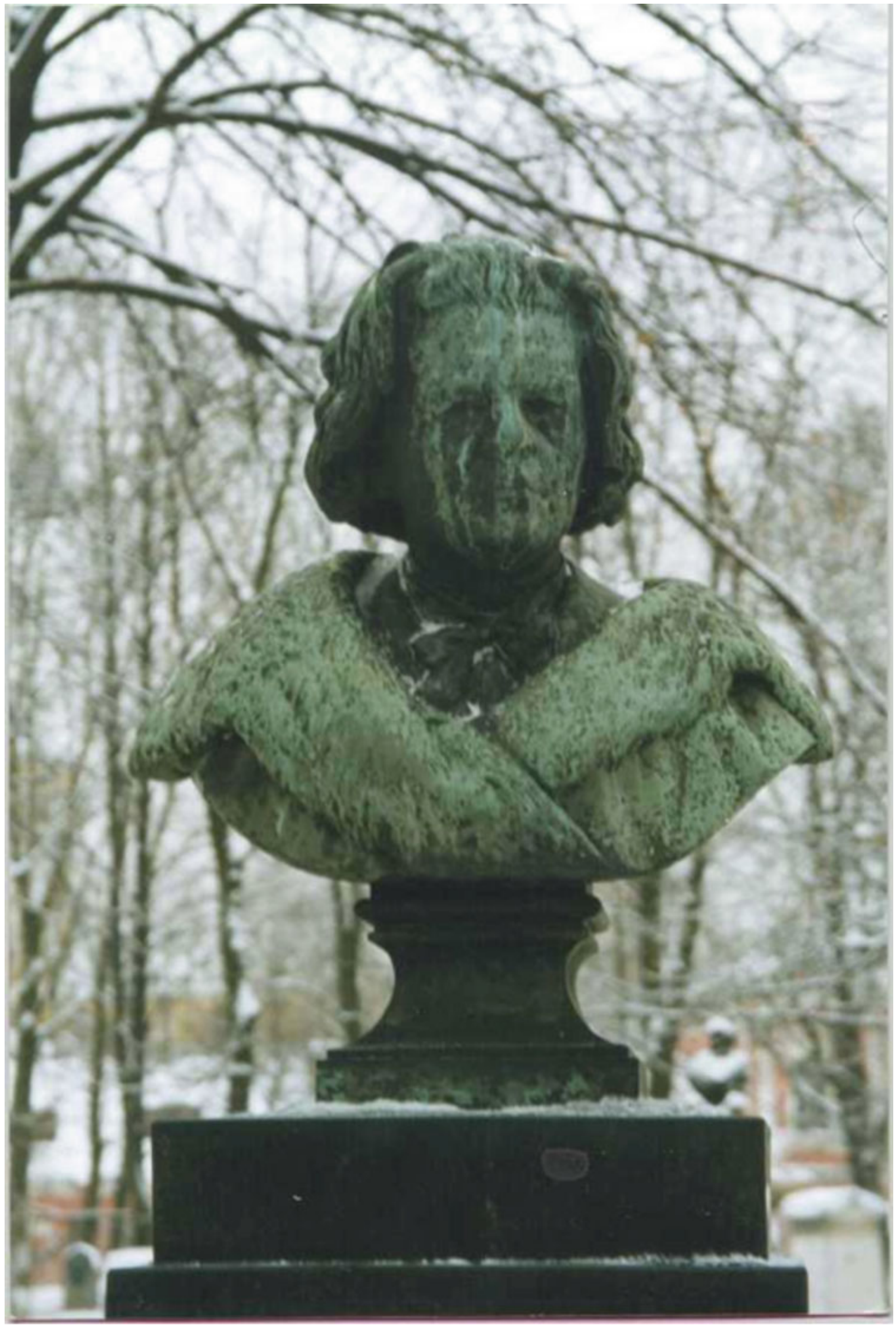

Fig. 4.18 Loose heterogeneous patina on the surface of the monument to A.G. Rubinshtein. Necropolis of Masters of Arts (1999)

spectroscopy detected the presence of carbonate ions. Thus, it was possible to find out that the X-ray amorphous component of patina on many bronze monuments of the Necropoleis contains carbonates. On the surface of the monument to Yu.M. Yuriev, IR spectroscopy found copper and zinc carbonate aurichalcite (Cu, $Zn)_5(CO_3)_2(OH)_6$, which was not detected by X-ray phase analysis.

The frequency of copper chloride occurrence, whose presence on the surface of monuments made of copper and its alloys (Table 4.6) indicates different stages of the "bronze disease", on the monuments of the Necropoleis significantly varies. Most often the basic copper chloride atacamite $Cu_2(OH)_3Cl$ is found, its solubility being significantly lower than that of other chlorides occurring on the surface of bronze

Fig. 4.19 Non-uniform distribution of colored patina (as vertical streaks of gray-green color) on the surface of the monument to P.Z. Andreev

monuments. Generally, chlorides are registered at a low height, which may indicate a significant role in the incidence of "bronze disease" of monuments in St. Petersburg of solid particles with hygroscopic properties, including particles of table salt that get on the surface of the monuments in the winter. It can be assumed that in the spring chlorides are present in insignificant quantity on the surface of all monuments. The most common paragenetic minerals of the salt layer, according to XRD data, are brochantite, antlerite; brochantite, malachite and brochantite, atacamite.

According to the data of the studies, there are three types of corrosion film on the surface of the monuments in the museum Necropoleis, which successively transform into one another (Table 4.5):

1. Single-layered dark patina, consisting of copper oxides.
2. Double-layered young patina, which can be either dark or colored. It consists of oxides (the lower layer) and copper salts (sulfates, carbonates, chlorides), with predominant oxides. The salt layer is thin, and often incomplete.
3. Two or more layers of mature, colored (all shades of green and blue) patina. The content of salts and copper oxides is comparable or there are more salts than oxides.

Single-layered dark patina forms a dense film on the surface of the monuments, which has good adhesion to the bronze surface, suggesting that it has good protective ability. In the Necropolis of Masters of Art there are monuments completely covered with such patina (to G.A. Tovstonogov, I.N. Pevtsov, A.S. Dargomyzhsky, N.I. Utkin and N.K. Cherkasov), which were erected 20 to 50 years ago. Together with other, later forming types of patina, single-layer patina was found on many monuments of the Necropoleis, which may have spent up to 160 years in the urban environment.

Formation of young double-layered patina on the monument to V.V. Stasov (transition from the first type of patina to the second) began less than four years after the first survey. In 10 years there was no transition to the third type of patina. On the monument to A. Bozio, formation of mature double- or multiple-layered patina (transition from the second to the third type) was recorded after 4 years, and on different parts of the monument to V.F. Komissarzhevskaya—after four years and ten years, respectively.

The degree of crystallinity of the patina, regardless of the type of the corrosion film, varies considerably. The presence of a large amount of X-ray amorphous phase in many cases indicates intensive crystallization and recrystallization processes accompanying atmospheric corrosion of copper alloys, which does not subside.

Table 4.4 Copper minerals of corrosion origin on the surface of the bronze monuments of the Necropoleis

Compound type	Name	Formula
Oxides	Cuprite	Cu_2O
	Tenorite	CuO
Sulfates	Brochantite	$Cu_4SO_4(OH)_6$
	Antlerite	$Cu_3(SO_4)(OH)_4$
Carbonates	Malachite	$Cu_2(CO_3)(OH)_2$
	Auricalcite	$(Cu, Zn)_5(CO_3)_2(OH)_6$
Chlorides	Nantokite	$CuCl$
	Atacamite	$Cu_2(OH)_3Cl$
	Calumetite	$CuCl_2 \cdot 2H_2O$

Table 4.5 Change in the mineral composition and structure of the corrosion component of patina on bronze monuments of the Necropoleis from 1999 to 2010 (according to XRD)

Monument (color of the patina)	Phase composition (type of corrosion film)		
	1998	2002	2008
A. Bozio (dark)	Cuprite, brochantite—substantial; antlerite-little; malachite-traces (type 2)	Brochantite—substantial; cuprite-little (type 3)	Brochantite—much, antlerite-little, cuprite-traces (type 3)
V.V. Stasov (dark)	Cuprite—substantial (type 1)	Cuprite—basic phase; antlerite-little (type 2)	Cuprite—very much, brochantite—little (type 2)
V.F. Komissarzhevskaya (dark)	Cuprite—much; malachite, atacamite, nantokite—little; brochantite, antlerite—traces (type 2)	Cuprite—basic phase; malachite—little (type 2)	Brochantite—much; cuprite—little (type 3)
V.F. Komissarzhevskaya (greenish-blue)	Cuprite—much; malachite, brochantite-substantial (type 2)	Malachite—basic phase; brochantite—much; cuprite —little (type 3)	Malachite—very much; brochantite—much; cuprite- substantial; calumetite—traces (type 3)

Table 4.6 Copper chlorides on the surface of Bronze monuments in the Necropoleis

Monument	Necropolis	Year of detection
Atacamite		
E.S. Karneeva[a]	18th century	1999, 2007, 2010
A.F. Turchaninov	18th century	2010
V.F. Komissarzhevskaya	Masters of Arts	1999
A. Maghir	18th century	1999
A.G. Rubinstein	Masters of Arts	1999
A.G. Beloselskaya-Belozerskaya	18th century	1999
Nantokite		
M.I. Avilov	Masters of Arts	2008
V.F. Komissarzhevskaya	Masters of Arts	1999
Calumetite		
M.I. Avilov	Masters of Arts	2008
A.I. Kuindzhi	Masters of Arts	2008
V.F. Komissarzhevskaya	Masters of Arts	2008
E.S. Karneeva[a]	18th century	1999, 2007, 2010
Unknown (N-18 No. 1066)	18th century	2007

[a]The sculpture is made of copper

The facts that the primary patina, consisting of copper oxides, can last from two to 160 years, and that all types of patina are often present on the surface of the same monument (Fig. 4.20), indicate that the influence of internal factors (composition and uniformity of the alloy, surface quality, etc.) and the existence and quality of the protective polymer coating on the rate of corrosion is great, often exceeding the impact of the environment.

The results of the work showed that the natural patina on the surface of bronze monuments of the Necropoleis is not sufficiently resistant to the corrosive effects of the ambient air and does not ensure preservation of monuments.

Monuments afflicted with the «bronze disease» and requiring restoration (to E.S. Karneyeva, A.G Rubinshtein, V. F. Komissarzhevskaya) have been identified (on the monuments to E.S. Karneeva and A.G. Rubinshtein the work has already been done). It was shown that minor foci of the bronze disease are probably present on most bronze monuments in the Necropoleis. In order to prevent their further development, it is necessary to monitor. The composition of the patina regularly and to continue the practice of washing monuments (at least twice a year, above all in spring).

It was established that in many cases the internal factors (composition and homogeneity of the alloy, surface quality,

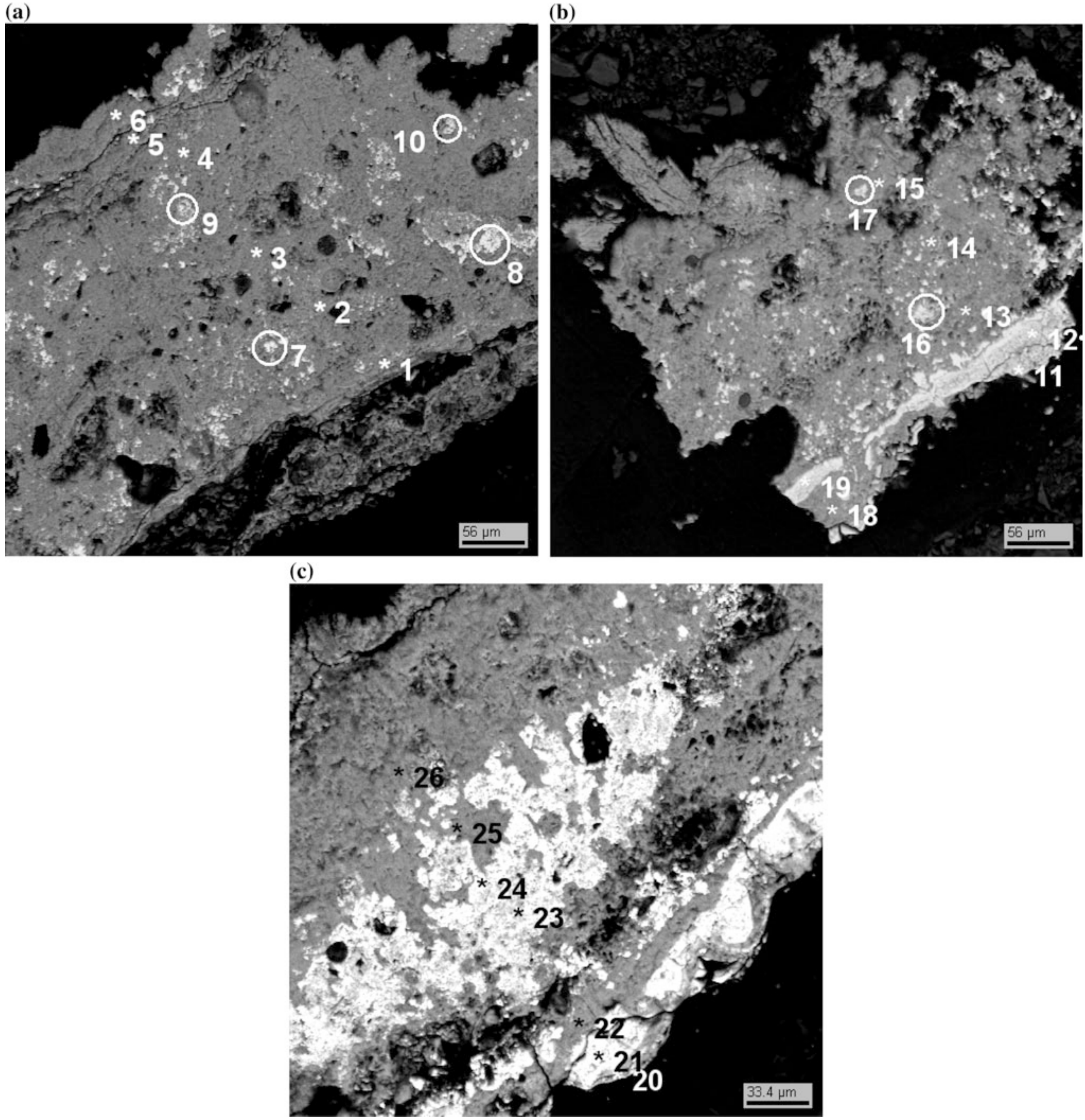

Fig. 4.20 SEM images of patina on the surface of the monument to V. F. Komissarzhevskaya in the Necropolis of Masters of Arts: **a** copper salts (light spots) interspersing the oxide layer (type 1), **b** two-layer patina (type 2), **c** multi-layer patina (type 3). The figures indicate the points where elemental composition was identified

etc.), as well as the presence and quality of protective polymer coatings, affect the corrosion rate to a greater extent than the environment. Therefore, when creating and placing new monuments, it is necessary to put forward inexorable demands in regard to the quality of the alloy and the surface treatment of the monument.

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5 Changes in the Necropoleis Monuments' Status Over Time

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Abstract

The history and temporary changes in the condition of outstanding artistic monuments in the museum Necropoleis, made of various materials, are surveyed: those to A.I. Kosikovsky (Paolo Catozzi and A.I. Terebenev, sculptors, 1840), E.A. and V.N. Kochubey (A. Costoli, sculptor, 1856), A.Ya. Okhotnikov (F. Thibaut, sculptor, 1800s), M.V. Lomonosov (J. Stälin, author of the design, 1766), V.V. Stasov (I.Ya. Ginzburg, sculptor, I.P. Ropet, architect, 1908), P.V. Kindyakov (Paolo Catozzi, sculptor, 1828), N.M. Karamzin (of unknown authorship, 1820s) and E.A. and E.N. Karamzin (of unknown authorship, 1850s), A.Ya. Potemkina (of unknown authorship, 1830s). The materials of the monuments are described, the results of restoration work and dated materials science analyses are given.

Keywords

Monument state • Expert survey • Monitoring • Qualimetric evaluation • Restoration • Conservation • Current care

5.1 Monument to A.I. Kosikovsky

Sculptors P. Catozzi (Paolo Catozzi) , A.I. Terebenev (author of the portrait), Master I. Aleshkov. 1840, Marble

The monument to the merchant of the first guild, Andrei Ivanovich Kosikovsky (1768–1838), a St. Petersburg tax farmer who supplied victuals to the Russian army during the Patriotic War of 1812 and the military campaign of 1813–1814, occupies a special place in the ensemble of the

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Necropolis of Masters of Arts. The eight-columned portico with the sarcophagus is located at the entrance to the Necropolis (Fig. 5.1), catching the eye of each museum visitor not only because of its artistic merit but also by its dimensions (4.10 × 4.33 × 4.12 m)—it is the biggest marble monument in the St. Petersburg necropolis.

The polystyle portico was made in the workshop of the "monument man" I. Aleshkov, as the inscription on the stylobate says: *Master I. Aleshkov*. The sarcophagus under the roof of the portico, with splendid ornamental carving on its body, was sculptured in Paolo Catozzi's workshop in 1840 (inscription on the pedestal of the sarcophagus: *Paolo Catozzi F. 1840*).

A bas-relief profile portrait of A.I. Kosikovsky, remarkable for its poignant treatment of the character, is on the eastern side of the sarcophagus. The portrait was carved by sculptor A.I. Terebenev, the author of the famous atlantes of the New Hermitage portico. The restoration of the gravestone made by the museum in 2004–2005 was, apparently, the first in its history, as can be judged from the state of the marble surface before restoration (Figs. 5.1 and 5.2).

Fig. 5.1 Monument to A.I. Kosikovsky (view from the south side) 2000

5.1.1 Expert Survey of the Monument Status Before the Restoration

The photograph of the monument, made around 1910, clearly shows that the whole surface of the sarcophagus has already turned black (in this connection, the ornament was clearly seen), but has no serious losses. In the 1970s, the sarcophagus was already in a critical condition. On the greater part of the surface black gypsum crusts (see Sect. 4.3) formed. As a result of detachment of the crusts accompanied by extensive crumbling (marble sugaring occurs under them), significant fragments of the sarcophagus were lost, in particular, reliefs on the scroll legs and the feet in the form of lions' paws, some parts of the ornament. Many "hanging" crusts could fall off at any time, and in the areas where it occurred emerging secondary crusts were observed. It should be noted that there was a clear boundary of contamination on the columns: black dense buildups covered only half the circumference, namely the surface facing inside the portico.

A detailed examination of the state of the monument was carried out in 2000–2001 (by experts N.F. Lepeshkina, M.S. Zelenskaya) and 2009–2010 (by experts M.I. Ivanova and M.S. Zelenskaya) (Lepeshkina 2004, Ivanova 2012). The analysis of elemental composition of the patina on the surface of A.I. Kosikovsky's tomb was made by I.V. Esipova (Esipova 2006).

The examination of 2000–2001 (before the restoration) revealed that the monument was in a catastrophic condition (Figs. 5.1 and 5.2).

The sarcophagus was almost entirely covered with gypsum-rich patina, which was extensively exfoliating with the marble (Fig. 4.12c). The thickness of gypsum crusts on A.I. Kosikovsky's tomb varied from 150 to 1350 μm, which was associated with a complex surface relief of the sarcophagus. Electron microscopy showed numerous tabular gypsum crystals forming a complete cover (Fig. 4.13a, b). The beginning of a secondary gypsum crust formation was registered in the areas where the primary gypsum patina had flaked off (Fig. 4.12d).

In addition to sulfur and calcium, the following elements were present in the gypsum-rich patina: silicon (0.15–15 wt %), aluminum (0.2–5 wt%) and iron (0.3–3 wt%), also Na and K in substantially smaller amounts (not more than 1.2 wt%).

In thin dense crusts with a thickness of 100–200 μm, the maximum content of Al and Si was near the surface, gradually decreasing closer to the rock (Fig. 5.3a), which indicated that these elements had come from the environment. The iron content either remained unchanged, or was at the minimum in the central part of the crust. Probably, such distribution means that iron came both from the environment and from the rock. In thicker and porous crusts, 200–400 μm

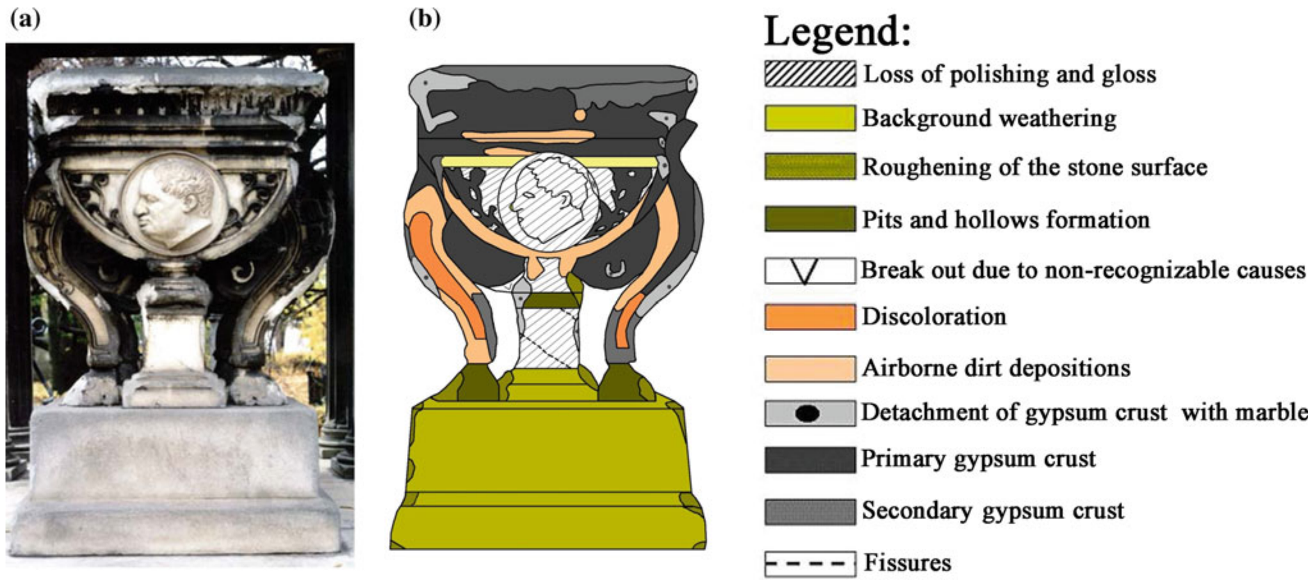

Fig. 5.2 Fragment of the sarcophagus of the monument to A.I. Kosikovsky (east side): **a** photograph, **b** map of marble deterioration types. Examination of 2001(Lepeshkina 2004)

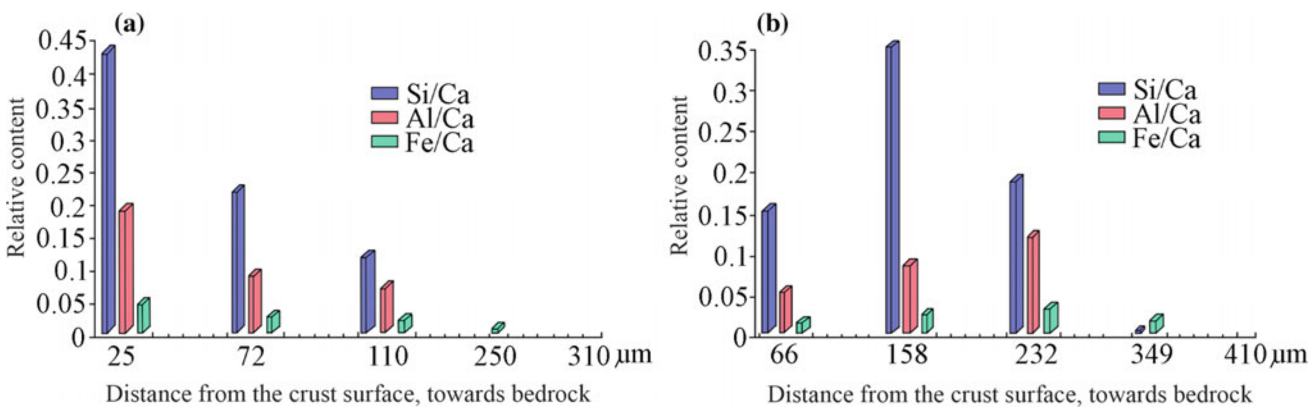

Fig. 5.3 Distribution of Si, Al, and Fe in crusts of thickness: **a** 100–200 µm; **b** 200–400 µm (Esipova 2006)

thick, the maximum concentration of silicon always, and that of aluminum in most cases, was inside the crust (Fig. 5.3b). The iron content either remained constant, or increased towards the center of the crust. It can be assumed that the selective penetration of elements deeper into the crust is due to the activity of microorganisms, which, penetrating the rock, perform biogenic transport of silicon and iron. It is important to note that the maximum content of less important impurities (Na, K) always occurs at the center of the crust and does not depend on the type of the basic elements distribution.

As a whole, the results of the study of element distribution in the gypsum-rich patina on the surface of A.I. Kosikovsky's tomb indicate that the impurities get on the surface of the monument mainly from the environment. Migration of the elements deeper into the crust takes place with the participation of microorganisms. At the initial stages of crust formation, the basic microelements (S, Si, Al, Fe) are on its surface, only Na, K and other elements whose content does not exceed 1 wt% can penetrate inside. Then such elements as Si, Al, Fe begin to penetrate into the thickness of the crust. The change in the content of elements within the crust may be due to the accumulation of microorganisms (bacteria, algae and micromycetes) in depressions and cracks. Among them, the leading place belongs to microscopic fungi. As result of mycological studies 21 species of microscopic fungi were identified (Table 5.1), whose occurrence in the examined samples varied from 3 to 80%.

Most of the identified species are active biodeterioration agents. Among the dominant are species of the genera *Cladosporium, Aureobasidium, Alternaria, Penicillium, Candida*. Together with bacteria and algae, they can produce

Table 5.1 Species of Micromycetes on the Monument to A.I. Kosikovsky before and after the Restoration

2000 (before restoration)	2010 (after restoration)
Alternaria alternata	***Alternaria alternata***
Aspergillus clavatus	*Aspergillus niger*
Aspergillus ustus	***Aureobasidium pullulans***
Aureobasidium pullulans	***Cladosporium cladosporioides***
Candida sp.	*Cladosporium herbarum*
Cladosporium cladosporioides	***Cladosporium sphaerospermum***
Cladosporium sphaerospermum	*Coniosporium* sp.
Cryptococcus capsulata	***Epicoccum nigrum***
Cunninghamella japonica	*Fusarium solani*
Epicoccum nigrum	***Fusarium* sp.**
***Fusarium* sp.**	*Hormonema dematioides*
Mucor racemosus	*Phaeococcomyces exophialae*
Paecilomyces sp.	*Ulocladium chartarum*
Penicillium expansum	
Penicillium sp.	
Phaeosclera sp.	
Phoma glomerata	
Rhizopus stolonifer	
Sclerotinia sclerotiorum	
Scytalidium lignicola	
Sporotrichum laxum	
Trichoderma viride	

Note Dominant and frequently occurring species are highlighted in bold

a destructive effect on the material of the monument due to chemical and physical action on the substrate. It has been established that as marble decays and the gypsum crust is formed, the count of fungi species inducing biodeterioration in the affected areas of the monument increases (Table 4.3). The maximum diversity of micromycetes species was observed where the surface layer of marble had crumbled and the secondary gypsum crust began to form.

The motion for urgent restoration of the monument was made in the late 1970s. In the file on the monument there is a statement that in October 1979 “during the preparation of the gravestone for restoration, experimental consolidation of fragments with significant sugaring and decay” was made by conservation experts M.N. Lebel (using the Hermitage technology, with a solution of poly (butyl methacrylate) in ethanol) and E.N. Ageeva (using the technology of the All-Union Central Research Laboratory of Conservation and Restoration, with silicone materials). In the statement drawn up a year later, it was noted that consolidation according to the techniques of the Hermitage «yielded a positive result».

A detailed examination of the condition of the monument 20 years later, in 2001, showed that Kosikovsky’s gravestone is in a critical state and it is no longer possible to delay restoration. However, the Museum of Urban sculpture was able to start this work only in 2004, and the reason was not only the lack of sufficient funds. In the St. Petersburg there was no experience of scholarly restoration of marble sculpture of a similar nature and scope of decay.

5.1.2 Restoration of the Monument

The author of the restoration method was Sergei Alekseevich Shadrin, a reputed Petersburg specialist in the technique of marble and limestone restoration. In 2004, the restoration of the eight-columned portico was carried out, requiring great effort, time and extraordinary patience in view of the size of the monument, whose surface was for the most part fouled by dense layer of pollutants. Compresses with sodium carboxymethyl cellulose gel were effectively used, much attention was paid to the control of biological damage. Under the layers of pollutants deposited from the air and biological contamination, magnificent white marble with bluish veins revealed itself, the festoons on the roof of the portico. The expressive masks of acroteria took a new lease on life. The restorers strengthened the stone structure, performed masticing of cracks and minor losses and surface hydrophobization.

The technique for the restoration of the sarcophagus in 2005 was developed after a thermal imaging survey to determine the extent of marble decay under the crusts and how far it had spread. Following the survey, structural strengthening of the stone was performed in the areas of deterioration by means of injections through the crusts. This method allowed not only to strengthen and preserve the «spalling plastic artwork», but also provided guidance for the further effective removal of contaminants in areas with crusts.

Large lost fragments of the sarcophagus were not reconstructed on principle; the tasks of the restoration were to control the process of intensive weathering of marble and preserve the plastic decoration of the monument. The voids under the crust were filled up and the areas where the crust had peeled off were protected with a finely dispersed lime plaster. The installation of a bronze gilded cross on the roof of the portico was the finishing touch.

5.1.3 Expert Survey of the Monument Status in 2009–2010

The examination of A.I. Kosikovsky's tomb (5–6 years after restoration) showed that its condition significantly improved (Figs. 5.4 and 5.5).

The results of the survey showed that on the surface of the monument to A.I. Kosikovsky here and there biofilms of green color are formed, in which algae dominate (of Chlorophyta division) (Fig. 5.6). Local disintegration of stone is observed on the surface of the sarcophagus due to crumbling. In addition, on marble surface a dark dirt deposition is formed in which microscopic fungi accumulate and develop (Fig. 5.7).

Fig. 5.4 Monument to A.I. Kosikovsky after the restoration (view from the east side) 2010

The number of micromycete species decreased from 21 (before restoration) to 13 after restoration (Table 5.1). However, the dominant species remained the same as before the restoration. On the surface of the monument dark-colored micromycetes predominate. In affected areas, the count of fungi turned out to be quite high, reaching 6000 CFU per 1 g of sample In general, the state of the stone is that of the initial stage of gypsum-rich patina formation. To slow down sulphation, regular conservation of the marble surface is required (removal of fouling and biocidal treatment). In addition, it is necessary to strengthen the marble surface on the sarcophagus.

5.2 Monument to E.A. and V.N. Kochubey

Sculptor A. Costoli. Florence. 1856. Marble

Monument to E.A. and V.N. Kochubey (Fig. 5.8) occupies an exceptional place in the ensemble of the Necropolis of the 18th century. The monument is made of white, fine- and medium-grained homogeneous marble; the rectangular foundation—of dark-gray fine- and medium-grained polished amphibolite. The winged figure of an angel elevated onto the pedestal, giving rise to a feeling of sweet sorrow and peace, is an expressive plastic accent in the space of the Necropolis and is clearly visible from Nevsky Prospekt. The upper part of the high pedestal, with an exquisitely carved ornament, is made in the form of a sarcophagus, on the north side of which there is a medallion with a portrait of a young woman, and on the south side – of her little daughter. The portraits are framed with wreaths of leaves and flowers, snakes twining around them. The lower part of the pedestal is adorned with the heads of putti and the coats of arms of the famous Kochubey and Stolypin noble families.

Ekaterina Arkadyevna Kochubey (1824–1852), née Stolypina, was a relative of M.Yu. Lermontov, and her maternal grandfather was Admiral, Count N.S. Mordvinov. The young woman died in Italy shortly after the birth of her daughter Vera Nikolaevna (1851–1852), who was buried together with her mother in her homeland.

N.A. Kochubey ordered the funeral monument to his wife and daughter from the Florentine sculptor Aristodemo Costoli (1803–1871) in 1856, whose signature is preserved on the plinth of the sculpture: *A. Costoli. Firenze. 1856*. A. Costoli was considered a master of artistic gravestones, memorials created by him are in the church of Santa Croce in Florence, in Genoa and Pisa.

The monument to Kochubey has long attracted the attention of researchers studying the processes of marble deterioration. In particular, the portrait of E.A. Kochubey was used as an illustration to the article by E.N. Ageeva «The deterioration of marble sculpture in the open air».

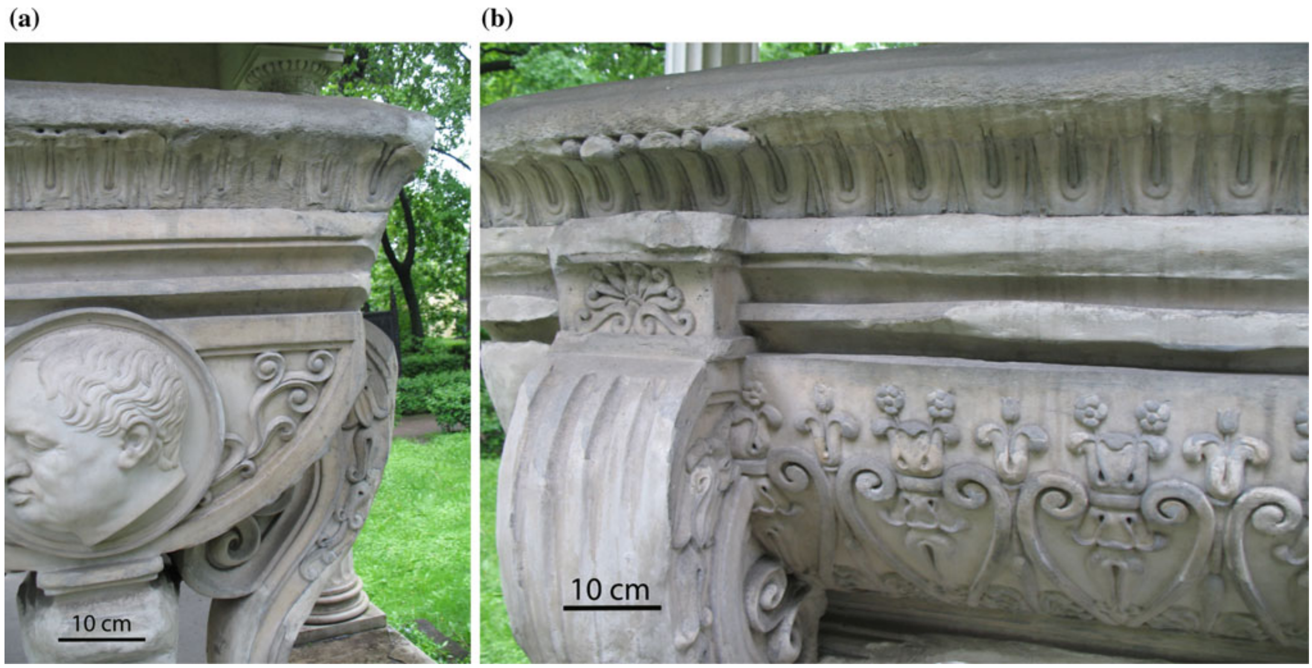

Fig. 5.5 Fragments of the sarcophagus of A.I. Kosikovsky's tomb after the restoration (2010): **a** eastern side, **b** southern side

Fig. 5.6 Biological buildup. The north side of the pedestal. May 2010

In the photographs from the second half of the 1970s the formation of gypsum crust as globular buildups on the left side of the portrait protected from the flowing water by a relief wreath (the border passing through the parting in the hair and the middle of the forehead) and on the nose was fixed. The same type buildups can be seen on other parts of monument (for example, on the volute supports of the sarcophagus, inaccessible to rainwater).

Fig. 5.7 Roughening and fouling of marble on the lid of the sarcophagus. The eastern side of the monument. May 2010

5.2.1 Restoration of the Monument

In 1979–1980 restoration of the angel figure with re-creation of the lost fragments of the wings was performed.

In 2006, a complete restoration of the monument was made (it should be noted that the pedestal had not been restored before). In view of the forthcoming work, the state of the portrait of E.A. Kochubey, and, more precisely, the results of the removal of crusts, caused major concern. Trial cleanings were made using compresses with gel of sodium salt of carboxymethyl cellulose. The crust is flaked, under it there was dense, fairly smooth marble compared with rough eroded marble on the surface of the monument.

The full cycle of restoration works included removal of dirt and crust detachments, biocidal treatment, stone strengthening, masticing of small losses and hydrophobization treatment (Loginova 2012), Beside the little fingers of hands and the tips of the wings of angel were recreated on the base of the old photographs.

In the portrait of Ekaterina Arkadyevna after restoration a part of the hair, forehead and nose, formerly concealed by the crust, are distinguished by the whiteness of the marble, making it possible to imagine what it looked like originally.

The monument was born anew, surprising us with the beauty of the stone, permeated with bluish veins, its exquisite perfect ornament, joining us to the high culture of Italy with its centuries-old traditions of creating memorial compositions and artistic treatment of marble.

5.2.2 Expert Survey of the Monument Status

Examinations of the state of the monument were made in 2002, 2009 and 2013. The expert examination of 2002 (expert N.F. Lepeshkina) found numerous types of deterioration (Fig. 5.9): intense airborne pollutant depositions (Figs. 5.10a and 5.11), formation and beginning of detachment of gypsum-rich patina (Fig. 5.10a), abundant development of colonies of dark-colored microscopic fungi (Fig. 5.11b, Table 5.2) and algae (Fig. 5.11a).

According to qualimetric calculations, the degree of marble deterioration, in general, was 32% (Lepeshkina 2004). Following the examination, a conclusion was made that the monument is in a critical condition, and restoration is required.

The results of the 2009 inspection (expert M.S. Zelenskaya) showed that three years after the restoration of the monument, initial stage of the deterioration of stone material is observed. Mud running on the surface of the relief portraits (Fig. 5.10b), a slight crumbling of marble and the start developing colonies of dark-colored fungi on the surface of the stone (Fig. 5.12) are the prerequisites for the development of process of marble sulphation. The mycological examination (Table 5.2) identified 6 species of micromycetes. Based on the results of the inspection of 2009 a complex of measures for current care was recommended to slow down the processes of stone deterioration.

The results of the 2013 examination (expert M.S. Zelenskaya) showed that seven years after the restoration the

Fig. 5.8 Monument to E.A. and V.N. Kochubey (view from the south-west side) 2013

monument state has little changed. On the surface of the statuary marble there was an uneven layer of airborne pollution (Figs. 5.13 and 5.14). Peeling and crumbling resulting to roughening of the marble surface occurred on decorative elements on the southern and northern sides (Fig. 5.13b). The dark-colored fungi colonies continue to develop, mainly on horizontal surfaces (Fig. 5.13). On the northern side of the pedestal rusty patches were discovered (Fig. 5.14a). On the south side, traces of rust from coins were found on the pedestal, which resulted in discoloration of the stone material (Fig. 5.14b). No gypsum-rich patina was found. As a result of mycological examination, 7 species of microscopic fungi were identified, among which dark-colored micromycetes—active agents of stone deterioration dominated (Table 5.2). Their count in the samples is quite high (up to 2600 CFU-colony-forming units). According to the qualimetric calculations, the degree of marble destruction was 5%.

The stone material of the base of the monument (dark gray amphibolite) is covered with a thin layer of dust. On the vertical sections of the stone from the northern and southern sides, small dents and chips of unknown origin were found (Fig. 5.15a). On the horizontal surfaces on all sides the areas of stone peeling were found (Fig. 5.15b). The degree of amphibolite destruction was 4%.

The results of the examination demonstrated the effectiveness of restoration made in 2006 and measures of scheduled maintenance recommended in 2009. The stone materials of the monument to E.A. and V.N. Kochubey (statuary marble, amphibolite) are in good condition. No gypsum-rich patina, leading to irreparable loss of fragments of marble artwork, was found on the surface of the monument. A gradual increase in the amount of microscopic fungi was revealed. The continuation of ongoing maintenance is recommended: seasonal removal of contaminants (washing of the monument) and biocidal treatment.

5.3 Monument to A.Ya. Okhotnikov

Sculptor F. Thibaut. The 1800s. Marble, granite, cast iron

In the Necropolis of the 18th century, on one of the main paths, the monument to Horse Guardsman Alexei Yakovlevich Okhotnikov (1781–1807) invariably attracts visitors of the museum by its romantic appearance (Fig. 5.16). On the stones of a high grotto a sad figure of the mourner leaning on an urn sits at the foot of a broken tree with a lush crown (meaning "life cut off in its prime"). The poetic mood is enhanced by such details as a cross and an anchor in the depths of the grotto, as well as a marble relief depicting a grieving Genius at the sarcophagus with a "weeping" tree.

It should be noted that in the literary sources the early death of Alexei Okhotnikov is explained by his romantic relationship with a person of a higher social standing (according to legend, she commissioned F. Thibaut to make the monument).

The granite blocks of the grotto of A.Ya. Okhotnikov's memorial, as well as the plinth where there is a cross and an anchor, are made of pink, coarse-grained, porphyry-like granite. The sculptural composition with the figure of the mourner at the broken tree is of white fine- and medium-grained homogeneous marble. The archive of the museum does not contain information about the story of the monument. Okhotnikov's tomb, undoubtedly, was previously restored. On the sculpture of the mourner there is masticing with PBMA—poly (butyl methacrylate).

The issue of restoration of the gravestone was repeatedly raised over many years. The major concern was the sculpture of the mourner, whose features had been long effaced by time. Cracks, black crust and colonies of microorganisms formed on the weathered marble.

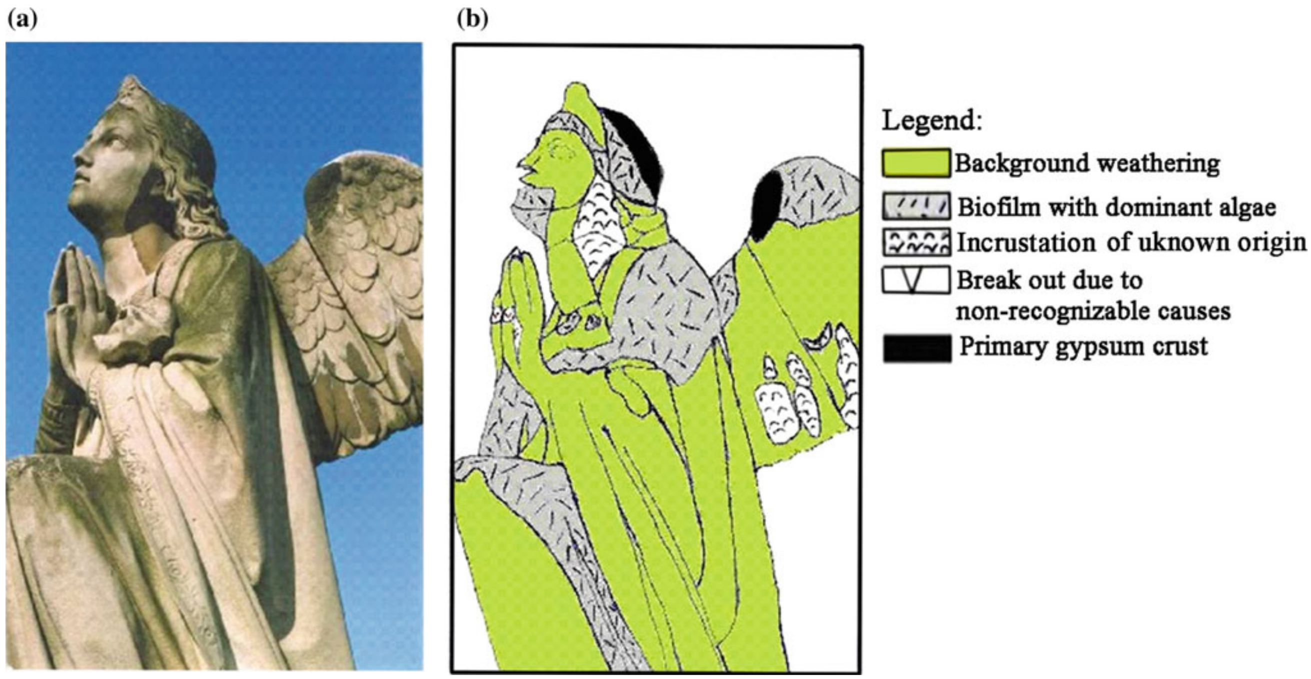

Fig. 5.9 Fragment of the angel sculpture on the monument to E.A. and V.N. Kochubey (Mironova 2000): **a** photo; **b** map of the types of marble deterioration. Examination of 2002

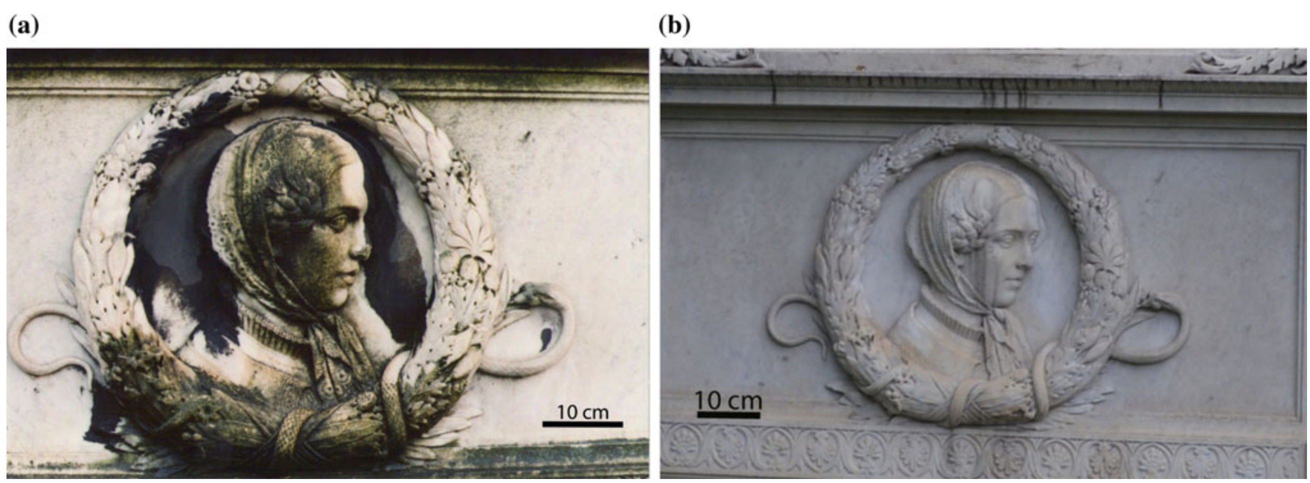

Fig. 5.10 Bas-relief portrait of E.A. Kochubey: **a** before restoration (2002), **b** after restoration (2009)

5.3.1 Restoration of the Monument

The restoration of A.Ya. Okhotnikov's memorial began in 2010. The grotto, whose basement had sunk into the ground, was raised and, after strengthening the foundation, was installed according to new benchmarks. In the course of the work, the massive granite base of the cross with an anchor was recovered (the lost anchor was replicated during the restoration process).

The terms of reference for the restoration provided for dismantling the mourner figure and the tree of marble, replacing them with replicas of polyester resin with marble chips. However, the sculpture could not be dismantled. The joint seam (apparently, cement was used, the monument could have been under restoration in the late 1940s—early 1950s) resisted all attempts to remove it. The Restoration Council of the museum, taking into account the critical condition of the sculpture, decided to leave it in its place, to take a cast and keep the replica in the museum collection. Only the marble plaque with an epitaph was taken down and restored in the workshop.

(a) (b)

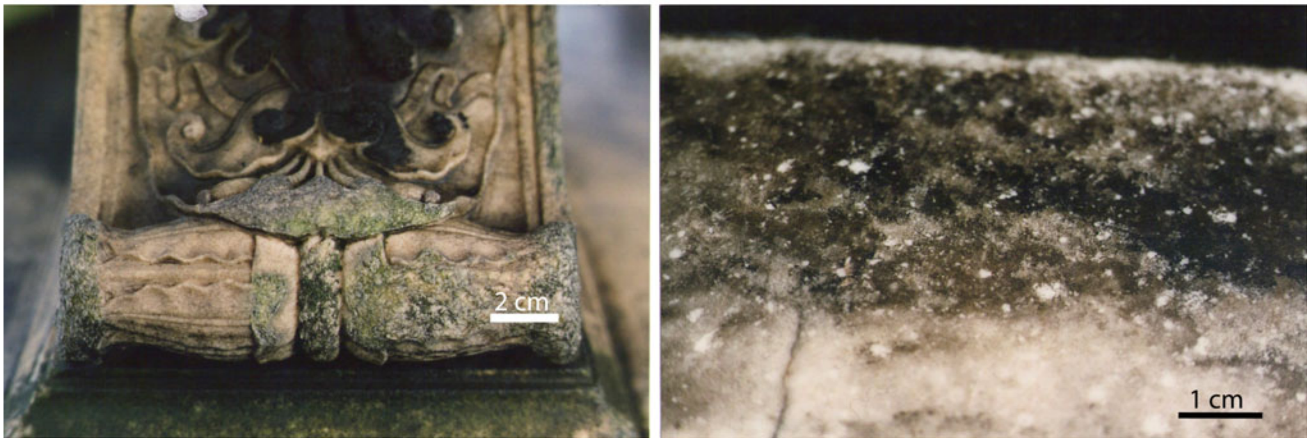

Fig. 5.11 Mud and biological deposits with the predominance of algae (**a**) and colonies of dark-colored fungi (**b**) on the horizontal surface of the marble pedestal 2002

Table 5.2 Species of microscopic fungi on the marble surface of the monument to E.A. And V.N. Kochubey on the base of mycological examinations of different years

2002	2009	2013
Acremonium strictum *Alternaria alternata* *Aureobasidium pullulans* *Cladosporium cladosporioides* *Cladosporium herbarum* *Cladosporium sphaerospermum* *Coniosporium* sp. *Fusarium oxysporum* *Hormonema dematioides* *Penicillium brevicompactum* *Phaeosclera* sp. *Ulocladium chartarum*	*Aureobasidium pullulans* *Cladosporium cladosporioides* *Cladosporium sphaerospermum* *Coniosporium* sp. *Hormonema dematioides* *Penicillium chrysogenum*	*Alternaria alternata* *Aureobasidium pullulans* *Cladosporium cladosporioides* *Cladosporium herbarum* *Coniosporium* sp. *Hormonema dematioides* *Phaeococcomyces exophialae*

(a) (b)

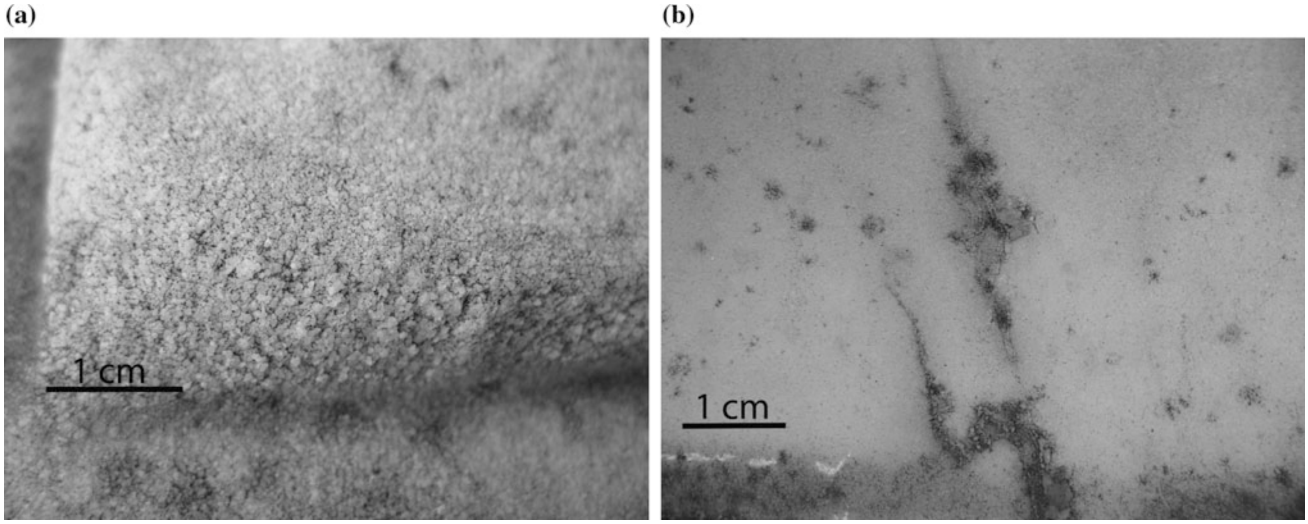

Fig. 5.12 Marble beginning to crumble (**a**) and the development of colonies of dark-colored fungi (**a**, **b**) on the surface of the monument 2009

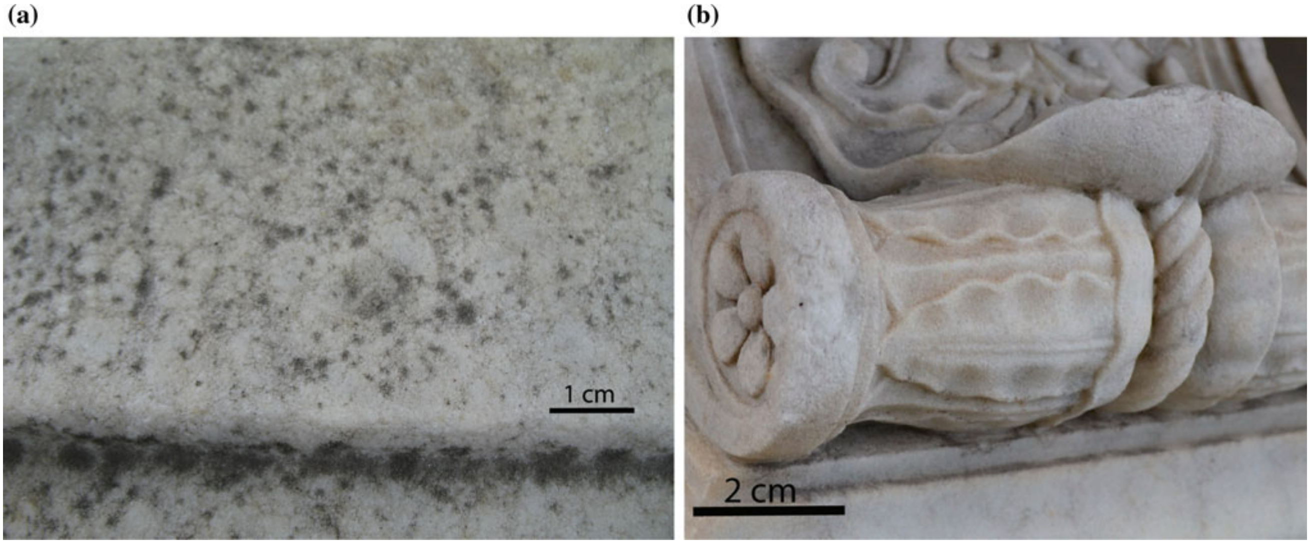

Fig. 5.13 Colonies of dark-colored microscopic fungi on the horizontal surface of the marble pedestal (**a**), peeling and crumbling of marble on the decorative elements (**b**) 2013

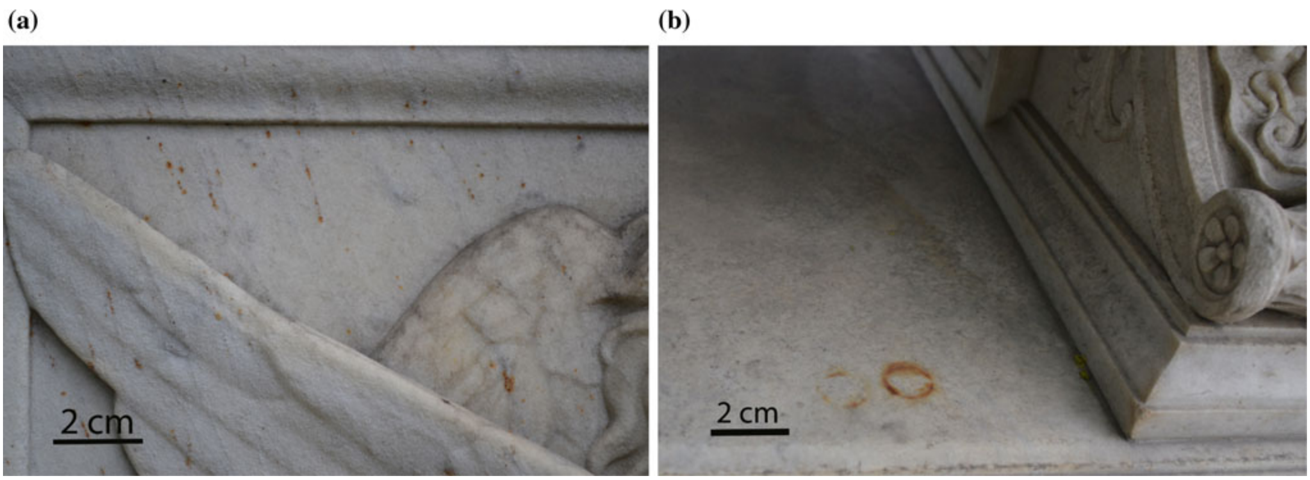

Fig. 5.14 Rusty patches on the vertical surface of the pedestal from the north side (**a**) and traces of coins on the horizontal surface of the pedestal on the south side (**b**) 2013

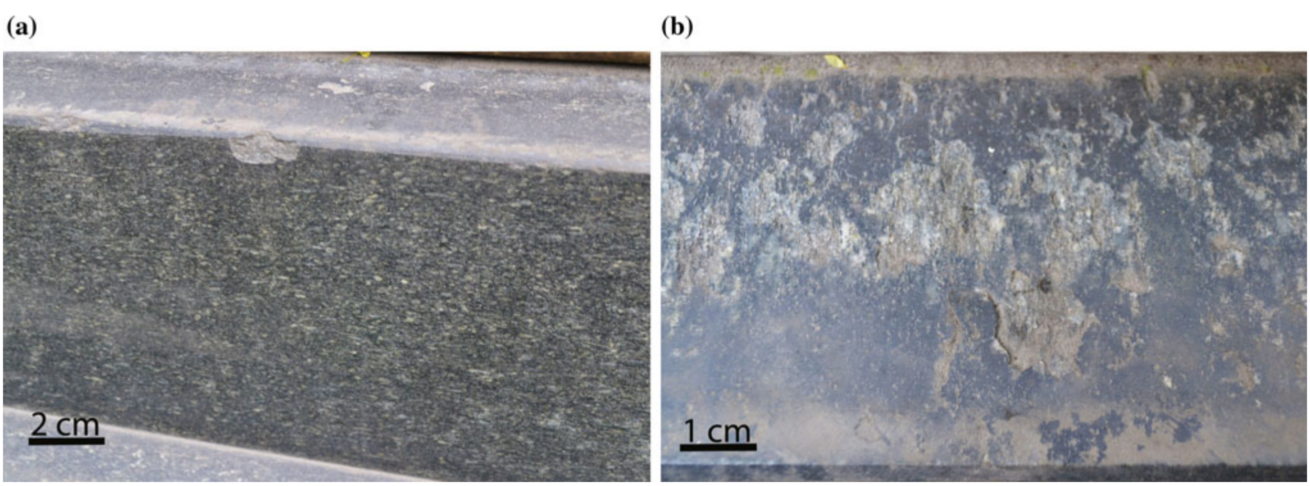

Fig. 5.15 Damage to the foundation of the monument: a chip of unknown origin on the north side (**a**), airborne mud deposits and stone flaking on the southern side (**b**) 2013

Fig. 5.16 Monument to A.Ya. Okhotnikov 2013

Restoration of marble was carried out according to the traditional method with the use of modern materials (Loginova 2012), including such measures as structural strengthening of marble, biocidal treatment and conservation (synthetic waxes were used). The ancient monument was transformed (Fig. 5.16). Now, as the restorers recommended, annual monitoring and routine maintenance (stone washing and renewal of the protective coating once every three years) were required to keep it in good shape.

5.3.2 Expert Survey of the Monument Status

Examinations of the state of the monument were made in 2002, 2009 and 2013 (three years after the last full restoration). In 2010, prior to the restoration to be carried out that summer, 3D laser scanning of the marble figure of the mourner was performed to create its electronic 3D model.

In 2002, N.F. Lepeshkina found extensive stone crumbling, development of colonies of dark-colored fungi (Table 5.3) on the entire surface of the marble sculpture, lichen and algae thalli (Fig. 5.17). On the neck of the sculpture and in the folds of the cloak (under the bent hand), the beginning of black gypsum crust formation was registered. Small fissures were found on the surface of the memorial marble plaques (on the western and eastern sides). The degree of marble deterioration, in general, was 15%. The results of the work prompted a conclusion that urgent restoration was needed.

The results of the 2009 expert examination (expert M.S. Zelenskaya) showed that intensive deterioration of the marble sculpture continues (Fig. 5.18a). Stone crumbling, development of colonies of dark-colored fungi, thalli of lichens and algae (Fig. 5.19), formation of gypsum-rich patina. During the mycological examination of the monument, 13 species of micromycetes were identified (Table 5.3), among which dark-colored microscopic fungi dominated. At the same time, their number in the samples was high (from 3500 to 6800 CFU). After the examination, it was again recommended that restoration should be carried out as soon as possible, as well as biocidal treatment of the monument.

Laser scanning surface of the mourner figure helped to identify on the electronic 3D-model such forms of marble weathering as cracks and scratches, and one of the primary gypsum crusts in the folds of the cloak (under the bent left arm) (Fig. 5.20). This made it possible to calculate the surface area covered by gypsum crust, which turned out to be equal to 60.85 cm^2, and the areas of other types of marble deterioration (Table 5.4).

The total area of the documented deteriorations (without taking into account the areas of soot and dust contamination and of colonies of microscopic fungi and algae) was 85.23 cm^2, which corresponds to 1.3%.

Table 5.3 Species of microscopic fungi on the marble surface of A.Ya. Okhotnikov's tombstone according to mycological examinations of different years

2002	2009	2013
Alternaria alternata	*Alternaria alternata*	*Alternaria alternata*
Aureobasidium pullulans	*Aureobasidium pullulans*	*Aspergillus niger*
Cladosporium cladosporioides	*Cladosporium cladosporioides*	*Aureobasidium pullulans*
Cladosporium herbarum	*Cladosporium sphaerospermum*	*Cladosporium cladosporioides*
Coniosporium sp.	*Coniosporium* sp.	*Cladosporium herbarum*
Fusarium oxysporum	*Fusarium oxysporum*	*Coniosporium* sp.
Hormonema dematioides	*Fusarium solani*	*Epicoccum nigrum*
Penicillium chrysogenum	*Hormonema dematioides*	*Fusarium oxysporum*
Phoma herbarum	*Penicillium brevicompactum*	*Fusarium solani*
Sclerotinia sclerotiniorum.	*Penicillium oxalicum*	*Penicillium brevicompactum*
Scytalidium lignicola	*Phoma herbarum*	*Penicillium herqueri*
Trichoderma viride	*Scytalidium lignicola*	*Phaeococcomyces exophialae*
Ulocladium chartarum	*Ulocladium chartarum*	
Asporogenous dark-colored fungus		

Fig. 5.17 Fouling of biological origin, crumbling of marble and black gypsum crust on the figure of the mourner on the monument to A.Ya. Okhotnikov 2002

The examination of the monument made in 2013, three years after the restoration (experts V.V. Manurtdinova, M.S. Zelenskaya), showed that the marble was covered with a thin uneven layer of airborne pollutants, which were mainly located on surface irregularities and in depressions (Fig. 5.18b). On the sculpture of the mourner, on the southern and northern sides, one can see the beginning of scaling and crumbling, which results in slight roughening of the marble surface (Fig. 5.21). On the marble slabs numerous small fissures and beginning of development of colonies of dark-colored fungi can be observed (Fig. 5.22).

On the granite blocks a layer of airborne mud can be seen (the thickest in the lower part of the grotto) and crumbling (Fig. 5.23)

The mycological examination detected the development of colonies of dark-colored fungi on the marble and granite surfaces. In total, 12 species of microscopic fungi were identified (Table 5.3), among which dark-colored micromycetes—active agents of biological deterioration of the stone dominated. Their count in the samples was low (from 650 to 800 CFU, in one case only it reached 2500 CFU). No algae or lichens were found on the surface of the monument.

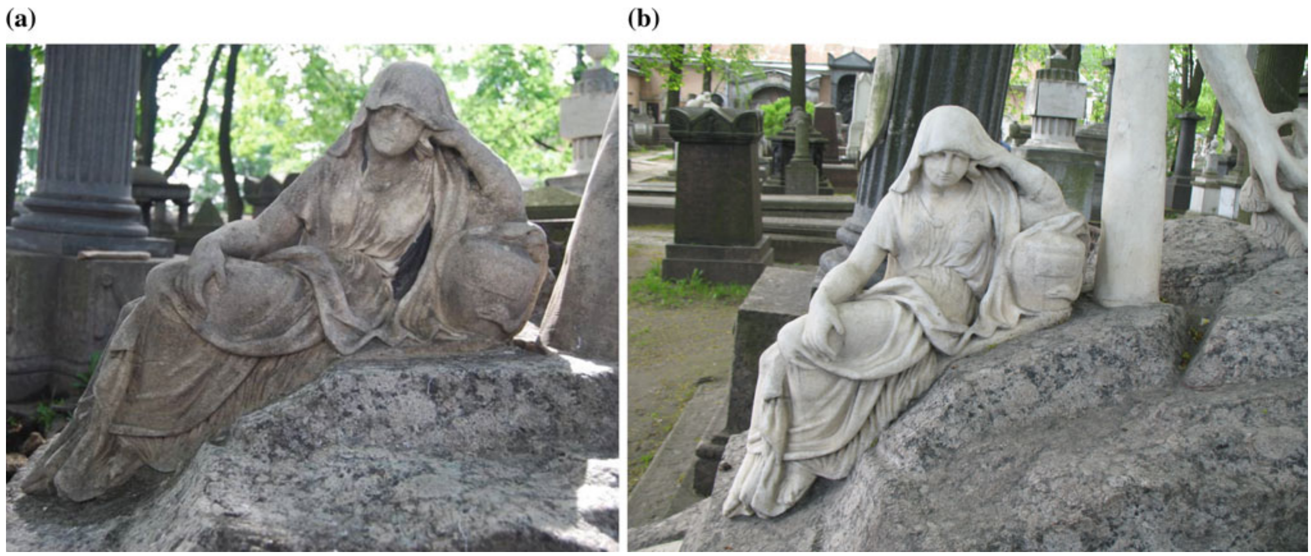

Fig. 5.18 Sculpture of the mourner of white marble: **a** before restoration (2009), **b** after restoration (2013)

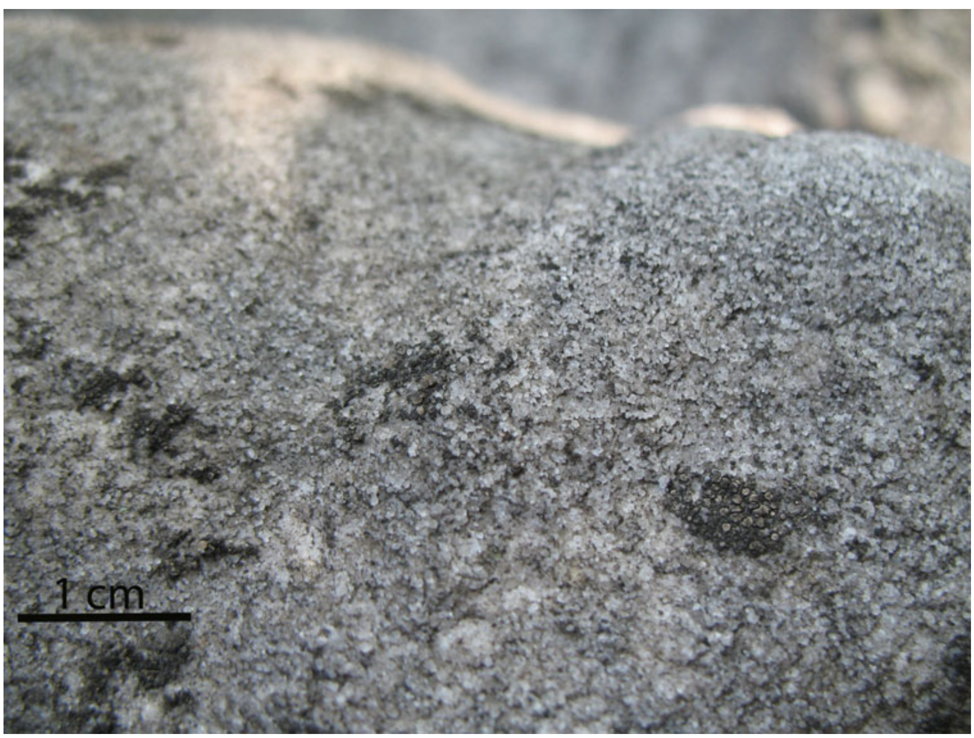

Fig. 5.19 Marble crumbling, microcolonies of dark-colored fungi, thalli of crustose lichens on the monument to A.Ya. Okhotnikov 2009

On the whole, the degree of marble destruction was 9%, that of granite—5%.

The results of the examination confirmed the effectiveness of the restoration. Three years after the restoration, the state of the stone materials of A.Ya. Okhotnikov's tombstone was good (the degree of deterioration was under 10%). No formation of gypsum-rich patina, causing irreparable loss of monuments from carbonate rocks, was detected. The number of microscopic fungi developing on the surface of the stone, decreased. As a preventive measure, it was recommended to monitor the state of the monument, and to remove contaminants (to wash the monument) each season, plus biocidal treatment.

(a) (b)

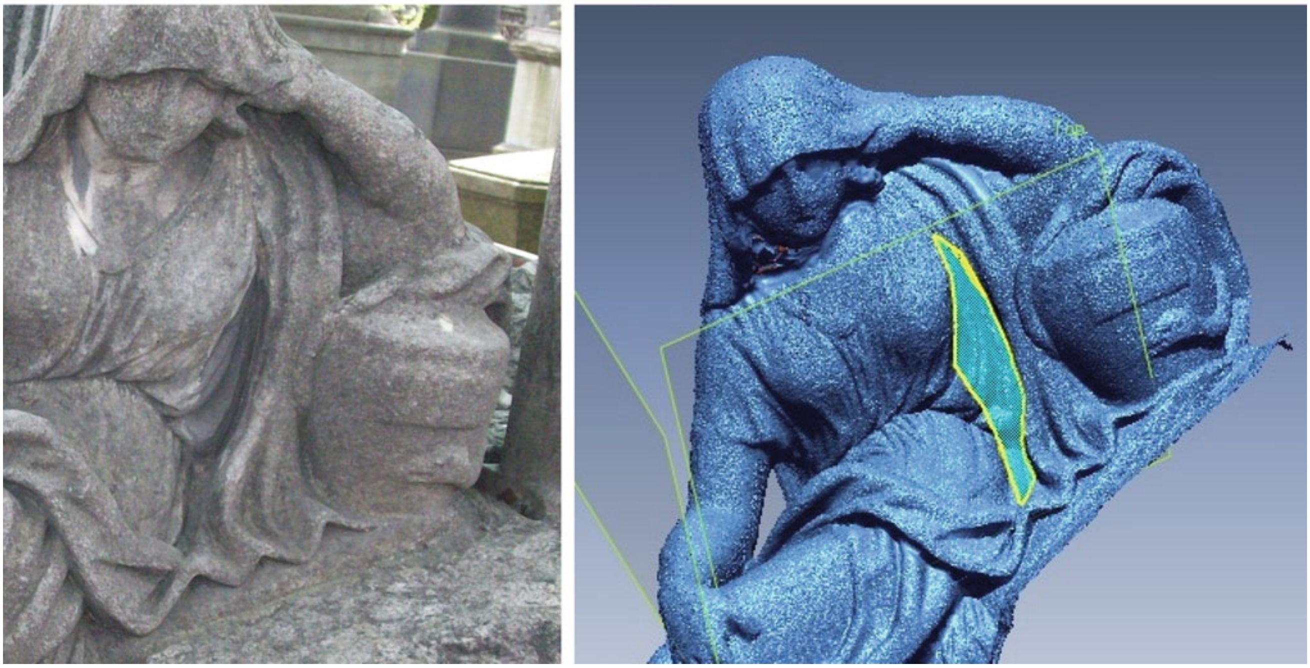

Fig. 5.20 Fragment of the mourner sculpture with gypsum crust in the folds of the cloak: **a** photograph, **b** electronic 3D-model, on which the area of the gypsum crust is highlighted (Leonova 2012)

Table 5.4 Surface areas of the mourner sculpture affected by deterioration of different kinds

Kind of damage	Affected area (cm^2)
Fissure 1 (left shoulder and back)	16.8
Fissure 2 (cloak over the left leg)	3.09
Scratch 1 (right elbow)	0.87
Scratch 2 (the cloak over the right knee)	0.6
Scratch 3 (the cloak over the right leg)	1.53
Scratch 4 (folds of the cloak over the right thigh)	1.16
Scratch 5 (folds of the cloak over the right thigh)	0.38
Primary gypsum crust in the folds of the cloak in the left armpit	60.8
	Total: 85.23

5.4 Monument to M.V. Lomonosov

J. von Stäehlin (author of the design), master F. Medico (Carrara). 1766
Marble, gilding (stele), limestone (socle); wrought iron (fence)

Mikhail Vasilyevich Lomonosov (1711–1765) was buried in the St. Lazarus cemetery of the Alexander Nevsky Monastery near the northern wall of the second wooden church of Annunciation, with a huge crowd of people. His contemporaries remembered the «magnificent burial», «with a rich ceremony at the Emperor's expense» (Lomonosov 1962).

The story of M.V. Lomonosov's tomb was described in a memo by J. Stäehlin (1709–1785), the author of the design of the monument (Stäehlin writes about himself in the third person): «Some time after Lomonosov's death, Chancellor Count Vorontsov, highly respecting his services to the fatherland, wanted to erect a monument to him of white marble, and put it on his grave in the Nevsky Monastery; He entrusted state councilor Stäehlin to write an epitaph and make a drawing for it in Florentine style. The Count sent both to Livorno, and the following year the monument of Carrara marble was received, made exactly to the drawing, as it is now in the cemetery of the above-mentioned monastery» (Lomonosov 1962) .

The exact date of the erection of the gravestone remains unknown. This is why J. Stäehlin's testimony that the monument was "received the following year" is important,

Fig. 5.21 Scaling and crumbling of Carrara marble on the details of the mourner's cloak on the south side 2013

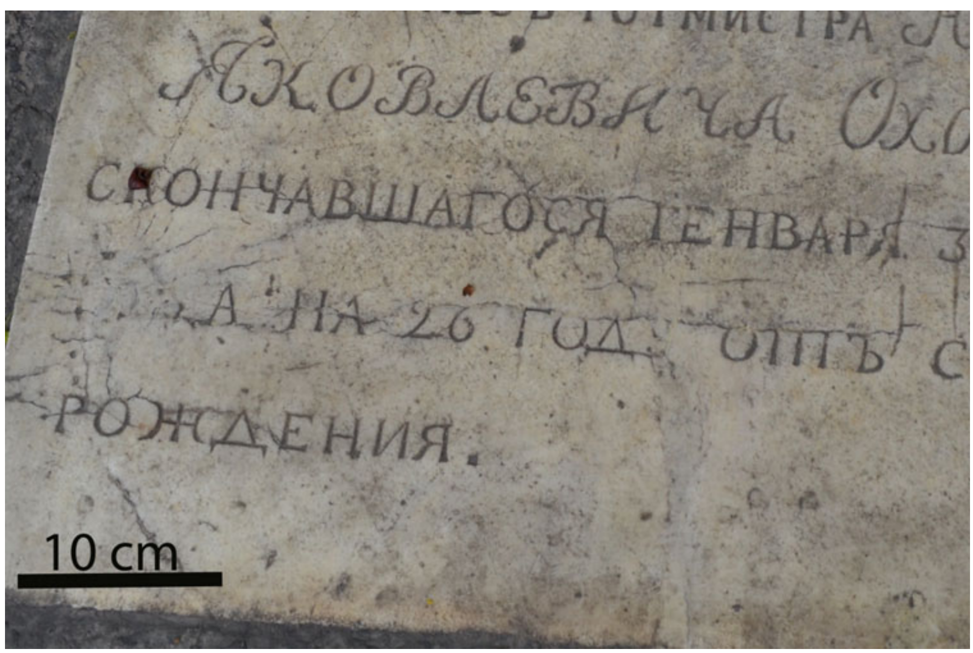

Fig. 5.22 Fissures, airborne pollution and colonies of microscopic fungi on the plaque of Carrara marble 2013

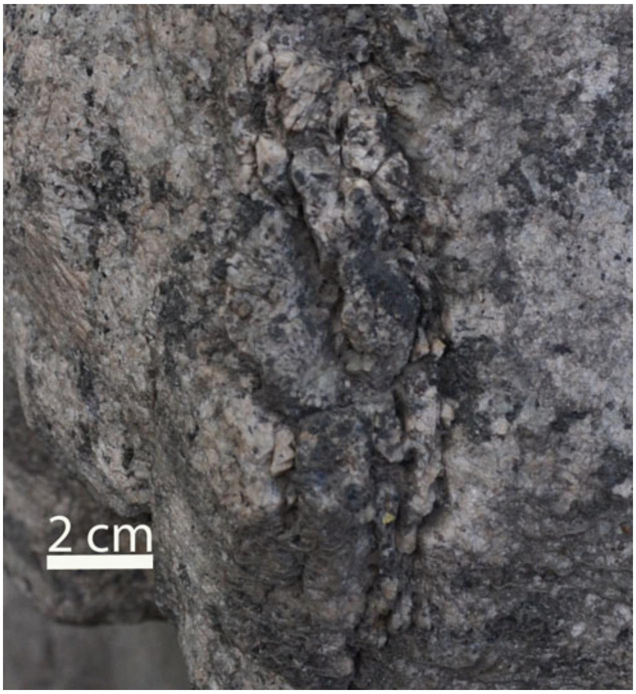

Fig. 5.23 Dents, hollows and airborne pollution on a block of pink-gray coarse-grained granite 2013

Fig. 5.24 Monument to M.V. Lomonosov in the Necropolis of the 18th century. The western side 2004

because then the memorial can be dated 1766 with sufficient certainty.

The tombstone of Lomonosov, made, as the author of the drawing emphasized, "in Florentine style", is a white marble stele topped with an urn in the shape of a sarcophagus (Fig. 5.24). On the stele there is an epitaph: on the west side, in Latin, on the eastern side in Russian:

> IN MEMORY / OF THE GLORIOUS MAN / MIKHAIL LOMONOSOV. / BORN IN KOLMOGORY / IN 1711. / FORMER STATE COUNCILOR. / PROFESSOR / OF ST. PETERSBURG ACADEMY OF SCIENCES. / MEMBER / OF STOCKHOLM AND BOLOGNA [ACADEMIES]. / EXCELLENT IN REASON AND LEARNING. / AN ILLUSTRIOUS ADORNMENT OF THE HOMELAND. / ELOQUENCE / VERSIFICATION AND RUSSIAN HISTORY / TEACHER / THE FIRST IN RUSSIA INVENTOR OF MOSAIC WITH NO GUIDANCE / SNATCHED BY THE PREMATURE DEATH / AWAY FROM THE MUSES AND HIS HOMELAND / IN THE DAYS OF HOLY EASTER 1765. / COUNT M. VORONTSOV ERECTED THIS TOMB / GLORIFYING THE HOMELAND WITH SUCH CITIZEN AND GRIEVOUSLY MOURNING / HIS DEMISE.

Under the epitaph on both faces of the stele reliefs are carved, designed to bring to light the multifaceted nature of Lomonosov's work: around the caduceus - the staff with wings, "entwined by snakes staring at each other", there are a lyre, a compass, a scroll and pen, as well as laurel and palm branches and a laurel wreath—impressively arranged symbols of glory and eternal memory. The winged staff, the attribute of Roman god Mercury, is polysemic; at the funeral stele of Lomonosov the caduceus is perceived as a symbol of penetrating the secrets of nature, reminding of his brilliant discoveries in the natural sciences.

Garlands, wreaths and drapes are placed on the sides of the epitaph and on the sarcophagus. Down on the northern side of the monument there is an inscription: FAIT EXECUTER PAR LE COMTE FRANCOIS / ANT. DEL MEDICO DELA / UILLE DE CARRARA EN TOSCANE (executed by Count F. Medico from Carrara in Tuscany).

Half a century later, the tombstone of Lomonosov was found, as we would say now, in an emergency condition. "This monument is threatened with a fall," wrote in the "Sorevnovatel Prosvescheniya i Blagotvoreniya" (Champion of Enlightenment and Charity) magazine in 1822, "and is barely noticeable among the magnificent tombs." It was also noted there that the "concern" about the renewal (the term "restoration" was not used at that time) of Lomonosov's memorial was displayed by the President of the Russian Academy of Sciences, A.S. Shishkov (Rytikova 2011).

The letter of A.S. Shishkov, addressed to D.P. Tatishchev «about the dilapidation of the monument over Lomonosov's grave»: «Dear Sir Dmitry Pavlovich. In the past sessions of the Russian Academy, it was said about the monument erected over the grave of Lomonosov, that it had already come askew, might fall soon, and needs putting in repair. The Academy would have paid attention to the preservation of the memorial sign of the man so famous, but since the monument was erected by Count Vorontsov, the Academy refrains to proceed to that without the consent of Count Vorontsov's family, and as it is aware that you are closely related to the House of Vorontsovs, it asks you, as its member, to take the trouble to communicate with whom it may concern from the Vorontsovs, whether they will be willing to renew the monument themselves, or to leave this to the Russian Academy. … January 17, 1822» (Rytikova 2011).

Having received this letter, D.P. Tatischev addressed the President of the Academy of Arts, A.N. Olenin (quoted from the draft letter): "The President of the Russian Academy referred to me … in its recent meetings it was considered necessary to mend the falling into disrepair monument over the grave of Lomonosov, which had been erected by the late Chancellor, Count Mikhail Larionovich Vorontsov.

> <…> In fulfillment of my duties, appealing to Your Excellency as the head of the Russian Academy and a well-known lover of our national literature, I humbly ask you to oblige the artists who are subordinate to you at the Academy of Arts, to examine the tomb of Lomonosov on the site in the Nevsky Monastery and make an estimate of how much <…> the repairs needed for that may come to. I should be notified accordingly <…> (Rytikova 2011).

5.4.1 Restoration of the Monument

Restoration of Lomonosov's tombstone was made in 1832, as evidenced by the inscriptions on the side faces of the stele. On the north side: "RENEWED / BY COUNT MIKHAIL / SEMENOVICH / VORONTSOV, 1832."; On the south side, the same inscription in Latin: «RENOVATUM A COMITE / MICHAELE / FILIO SIMONIS / WORONZOW. / ANNO 1832».

M.E. Glinka in the article "Monuments to Lomonosov", referring to the mentioned publication in the magazine "Champion of Enlightenment and Charity", believes that the work on "restoring" the gravestones was done in 1822, and in 1832 the "gilding of existing inscriptions on the monument" was renovated with the funds donated by M.S. Vorontsov (Glinka 1960).

55 years later the restoration of the gravestone was already performed on the initiative of one of Lomonosov's descendants, Grigory Ivanovich Nostitsa. On the side faces, under the lines telling of M.S. Vorontsov's participation in the renovation, is engraved: "G. N. / in 1887" (on the north side, and on the south side in Latin: C. N. / in. 1887 an.). In 1893, a wrought-iron fence was installed around the monument.

During the Second World War, the tomb of the scientist was in a shelter. The protective structure was a wooden case wrapped in tar paper, buried underground. In the summer of 1947, the construction was removed and the monument was "cleaned", and in the following season a complete restoration was made, including that of the lost fragments of marble garlands located on the sides of the texts of the epitaphs.

Beginning in the autumn of 1948, and for a number of years, in wintertime the monument to Lomonosov was sheltered by a wooden case, which is an old and effective measure to protect marble.

In 1949 inscriptions in Russian and Latin, wreaths, garlands and rosettes were gilded anew. By the 275th anniversary of Lomonosov's birth in 1986, the monument was again restored with gilding of the texts and relief details. In 2003, the marble was cleaned: contaminants were removed using compresses of hydrogen peroxide. The last restoration of the monument was in the summer of 2011, before the 300th anniversary of the birth of M.V. Lomonosov. Contaminations and masticing from old restorations were removed, marble structure strengthened, cracks, seams, small losses masticed, inscriptions, wreaths and garlands underwent conservation and were gilded using gold leaf. The fence was also restored: it was cleared of corrosion products with subsequent application of protective and decorative coating (Loginova 2012) .

5.4.2 Expert Survey of the Monument Status

Examinations of the monument was carried out in 2002 and 2003 (prior to its restoration in 2003) (by expert N.F. Lepeshkina). Small fissures were found on the surface of the stele on the western and eastern sides, as well as small quantities of various microorganisms (microscopic fungi, algae and lichens). According to the qualimetric calculations, the degree of marble deterioration was 6%, and that of flaglike limestone at the base of the monument—13% (Lepeshkina 2004).

A detailed examination of the state of the monument, made in April 2011–8 years after the restoration of 2003 (experts V.V. Manurtdinova, M.S. Zelenskaya), showed that the condition of the monument to M.V. Lomonosov changed for the worse significantly (Tables 5.5 and 5.6; Figs. 5.25, 5.26, 5.27, 5.28 and 5.29).

Marble is covered with an uneven layer of airborne contaminants (Fig. 5.25b). On the southern side of the marble stele, rusty streaks from the coins left by the visitors are visible (Fig. 5.26). The surface of marble is seriously contaminated with biogenic formations (Fig. 5.27). The development of colonies of dark-colored fungi (Fig. 5.27a) is observed almost over the entire surface, the sarcophagus being most severely affected. A coat of algae (Fig. 5.27b) covers the lower part of the stele (at the socle) from the north

Table 5.5 Results of qualimetric evaluation of the state of marble in 2002 and 2011

No.	Type of deterioration	Intensity of manifestation (on a 5-point scale)	
		July 2002	April 2011
1	Background weathering	1	2
2	Roughening of the surface	1	3 (at the edges)
3	Formation of pits and hollows	1	2
4	Break out due to non-recognizable causes	1	2
5	Detachment of stone	1	2 (in the central part on the east side)
6	Detachment of the primary gypsum crust with stone material	1	1
7	Detachment of the secondary gypsum crust with stone material	1	1
8	Primary gypsum crust	1	1
9	Secondary gypsum crust	1	1
10	Biofilm with dominant micromycetes	2 (mostly on reliefs)	3 (in places on the sarcophagus)
11	Biofilm with dominant algae	2 (on allegorical reliefs on the eastern and western sides)	2 (a thin coat on the lid of the sarcophagus)
12	Biofilm with dominant lichens	2 (on allegorical reliefs on the eastern and western sides)	1
13	Mosses and seed plants	1	1
14	Bird droppings	1	1
15	Airborne pollution	2 (on the text of the epitaph, reliefs)	3 (thin, uneven layer all over the surface)
16	Anthropogenic pollution	1	2 (traces of rust from coins)
17	Fissures	2 (East and West—lower and upper parts of the stele)	2.5 (on the surface of the stele from the west and east sides)
18	Deformation	1	1
Degree of deterioration (%)		6	18

and east sides. In addition, traces of peeling and crumbling) are clearly seen on the marble surface, leading to its roughening and emergence of small hollows (Fig. 5.28a. Most intensively, these processes are going on the lid of the sarcophagus and the edges of the monument. The initial stage of marble layer detachment was identified In the central part of the stele, on the east side, above the allegorical relief (Fig. 5.28b). In the lower part of the stele shallow fissures were found.

Comparison of the results of marble surveys of 2002 and 2011 (Table 5.5) showed that the increase in the degree of marble deterioration over the past eight years (from 6 to 18%, Table 5.5) was linked to physical and biogenic factors.

The examination of the monument base, made of flaglike Putilovo limestone, also revealed a significant increase in the degree of deterioration of stone material (from 13 to 30.5%, Table 5.6), which is associated with intensification of interrelated processes of mechanical and biogenic weathering (Fig. 5.29). There are flaking and exfoliation of the stone, leading to the formation of a corroded surface, primarily on the western and eastern sides. On the east side, there is a large cross crack, as well as a system of smaller fissures, which is also manifest on the south side. Fouling of biogenic origin (thalli of lichens, fungal colonies, algae stains) are distributed over the entire limestone surface.

The biological study of the samples from the surface of marble and limestone (Table 5.7) identified 15 species of microscopic fungi, among which dark-colored micromycetes, active agents of stone biodegradation, dominated.

The results of the monitoring in April 2011 showed that in order to prevent further decay of the monument, it is necessary to carry out partial restoration (surface strengthening and crack masticing). In addition, monitoring was recommended (control of the development of cracks and biofouling), as well as regular preventive measures (removal of contaminants, biocidal treatment).

5.5 Monument to V.V. Stasov

Sculptor I.Ya. Ginzburg, architect I.P. Ropet. 1908. Bronze, granite (monument); wrought iron, smalt, enamel (fence)

The monument to the outstanding music and art critic, art historian, mastermind of the Peredvizhniki artists and

Table 5.6 Results of qualimetric evaluation of the state of flaglike limestone in 2003 and 2011

No.	Type of deterioration	Intensity of manifestation (on a 5-point scale)	
		June 2003	April 2011
1	Background weathering	3 (moderate over the entire surface)	3 (insignificant over the entire surface)
2	Roughening of the surface	1	3 (at the edges of the stele)
3	Formation of pits and hollows	2 (shallow over the entire surface)	3
4	Break out due to non-recognizable causes	2 (south - pits at the top of the base)	2 (in a small amount)
5	Detachment of stone	1	2
6	Detachment of the primary gypsum crust with stone material	1	1
7	Detachment of the secondary gypsum crust with stone material	1	1
8	Primary gypsum crust	1	1
9	Secondary gypsum crust	1	1
10	Biofilm with dominant micromycetes	3 (all over the surface, a thin uneven coat)	4 (all over the surface, a thin uneven coat)
11	Biofilm with dominant algae	4 (all over the surface, a thin uneven coat)	4 (on the eastern side)
12	Biofilm with dominant lichens	2 (on the upper base slab)	4 (in places)
13	Mosses and seed plants	2 (north, south - at the bottom of the base)	2
14	Bird droppings	1	1
15	Airborne pollution	3 (thin, uneven layer all over the surface)	3
16	Anthropogenic pollution	1	1
17	Fissures	2 (south and north—a web of shallow fissures)	3 (east—a large cross crack)
18	Deformation	1	2
Degree of deterioration (%)		13	30.5

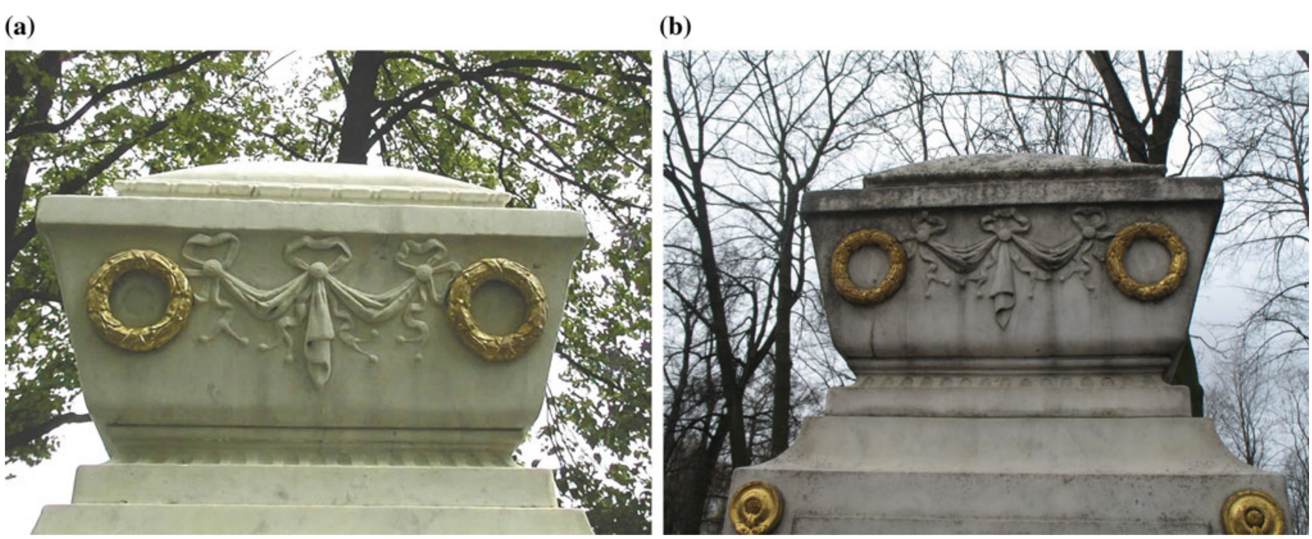

Fig. 5.25 Mud deposits on the marble surface of M.V. Lomonosov's monument: **a** 2004, **b** 2011

Fig. 5.26 Mud deposits, biological buildups and rusty streaks from coins on the horizontal and vertical surfaces of the stele under the sarcophagus. South side 2011

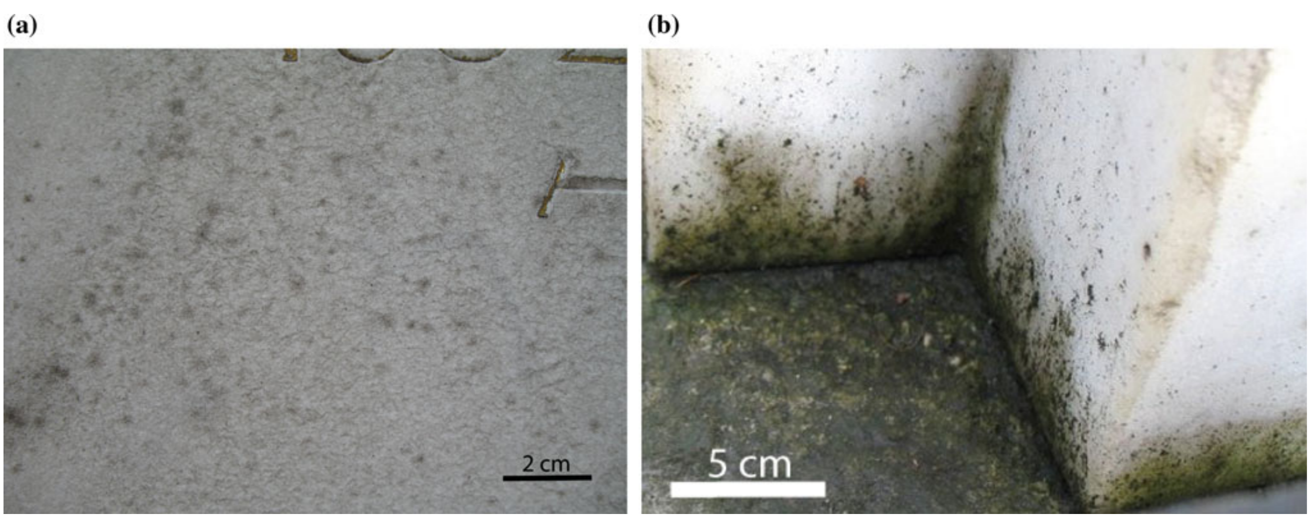

Fig. 5.27 Colonies of microscopic fungi **a** and algae **b** on the surface of the Carrara marble of M.V. Lomonosov's tomb 2011

composers of the «Mighty Handful» Vladimir Vasilyevich Stasov (1824-1906) is located at the southern wall of the Necropolis of Masters of Arts (Fig. 5.30). The bronze figure of Stasov, depicted in his favorite Russian national clothes: a traditional shirt, wide trousers and high boots, is set against the background of a granite block with the inscription: "To the Champion of Russian Art, V.V. Stasov. 1824–1906". The memorial is surrounded by a wrought-iron fence with an ornament in Russian style and round mosaic medallions with captions: «Painting», «Music», «Sculpture», «Architecture», «Archeology», «Literature», highlighting those spheres of artistic culture, with which the famous critic was involved. The door of the fence is adorned with Stasov's peculiar «coat of arms», with a monogram «B», goose quills, spurs and a burning glass (as is well known, Stasov was able to strike «a spark»

(a) (b)

Fig. 5.28 Peeling, crumbling (**a**) and detachment (**b**) on Carrara marble. Monument to M.V. Lomonosov 2011

(a) (b)

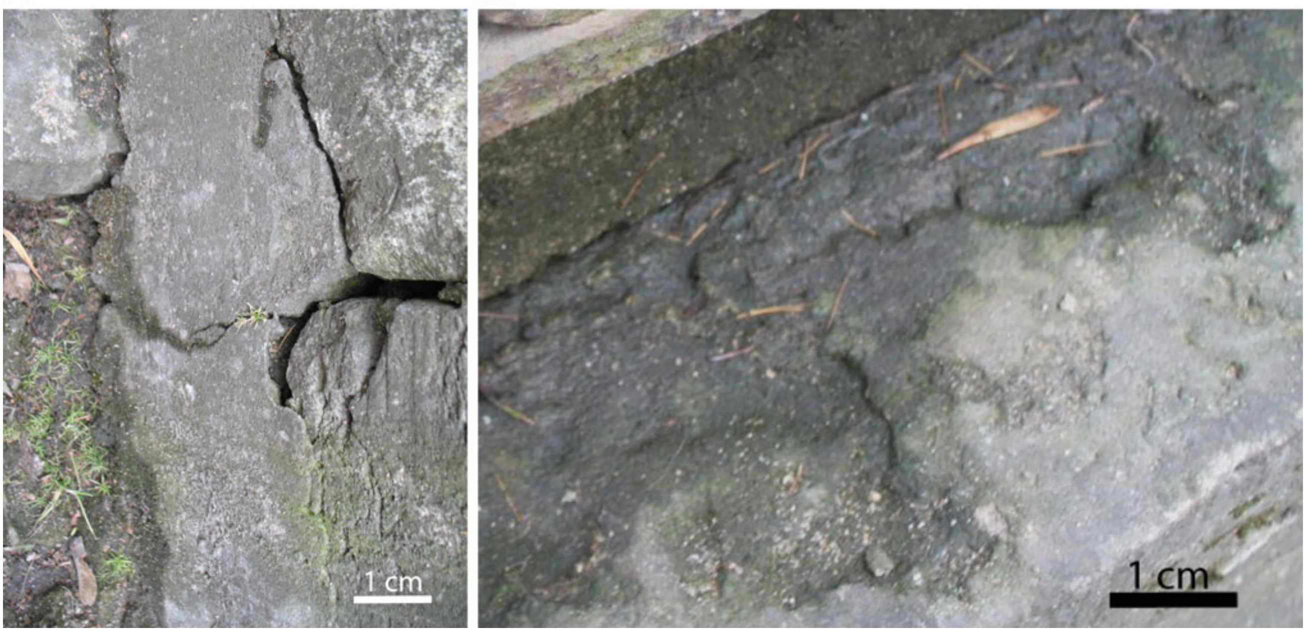

Fig. 5.29 Detachment (**a**) and the formation of areas of cracking (**b**) on Putilovo limestone. The base of the monument to M.V. Lomonosov 2011

out of his friends with new ideas and «spur» them at the right moment).

The design of the tombstone was made with the participation of V.V. Stasov's close friends, sculptor I.Ya. Ginzburg and architect I.P. Ropet who designed the wrought-iron fence. I.Ya. Ginzburg created a statue on the basis of a portrait he made in 1889. This statuette was in Stasov's study, and he liked it very much. «I would say that if I were some great historical person,» Stasov wrote to his daughter, "I would have never wished any other monument for myself, except this one: the combination of the natural posture … my usual one…—with an outfit not only national, but for me even the most beautiful of all existing ones" (Kudryavtsev and Shkoda 1986).

Table 5.7 Species of microscopic fungi and frequency of their occurrence on the stone surface of M.V. Lomonosov's tomb (2011)

Species of micromycetes	Frequency of occurrence (%)
Acremonium potronii	28.5
Alternaria alternata	**85.7**
Arthrinium phaeospermum	28.5
Aureobasidium pullulans	**85.7**
Cladosporium cladosporioides	**71.4**
Cladosporium herbarum	42.8
***Coniosporium* sp.**	**71.4**
Epicoccum nigrum	**57.1**
Fusarium oxysporum	**57.1**
Hormonema dematioides	**57.1**
Paecilomyces marquandii	28.5
Penicillium brevicompactum	14.3
Penicillium citrinum	14.3
Penicillium herqueri	14.3
Penicillium purpurogenum	14.3

Note The dominant species are highlighted in bold

Fig. 5.30 Monument to V.V. Stasov in the Necropolis of Masters of Arts

The monument to Stasov was erected with funds collected by his friends on a subscription, from an art lottery and concerts. By the spring of 1908, the construction of the tombstone had been completed, and on May 11, an opening ceremony was held. The monument made a great impression on the contemporaries. "We see not only an image of a person with a perfectly rendered likeness," noted the literary critic, S.A. Vengerov—"but as though it were a symbolic expression of the strength with which Stasov heroically advocated the views dear to him" (Hudozhestvennoe 2005).

In the history of Stasov's monument, as well as in many others' in the museum Necropoleis, a special page is associated with the years of the Second World War. The bronze figure of Stasov was dismantled and buried in the ground. In the beginning of August 1945, the statue had already been restored and installed in its place.

During the war, all display letters of the inscription on the granite block were lost, and the grave became unmarked. The famous inscription "To the Champion of Russian Art V. V. Stasov. 1824–1906" was recreated by the 125th anniversary of the critic's birth (the letters were cast at the *Monumentskulptura* factory). The anniversary was solemnly celebrated in Leningrad in the Grand Hall of the Philharmonic on January 17, 1949.

Immediately after that restoration of the mosaic medallions began. The medallion with the «Sculpture» caption was completely destroyed and had to be recreated. Three medallions, «Painting», «Music», «Architecture», were subject to restoration. These works were carried out in the Research Experimental Workshop at the Leningrad V.I. Mukhina Higher School of Art and Industry. The complete restoration of the wrought-iron fence was carried out in 1953–1954.

At the end of 1953, all the bronze display letters were again stolen from the granite block (they had been cast anew in 1957), and in 1976 the medallion with the «Architecture» caption was lost. Over time, mosaic crumbled from the medallions, some small details of the ornament disappeared (not without help of the museum's visitors).

In 2006, a complete restoration of fence of Stasov gravestone was performed. In the course of restoration, six new medallions were cast of cast iron, in which, on the base of available photographic materials, mosaic inscriptions were assembled: «Painting», «Architecture», «Archeology», «Literature». The mosaic in the medallions «Sculpture» and «Music» was disassembled and reassembled in the new medallions with the lost fragments replaced. The fence details were reconstructed: flame on the torch supports in cast iron and goose quills (iron). The fence was cleared of corrosion products, and protective decorative coating was applied.

At the same time, the bronze figure of Stasov, on the surface where of a picturesque green patina had formed, together with the block cut from pink, coarse-grained porphyry-like Rapakivi granite were washed.

5.5.1 Expert Survey of the Bronze Figure Status

Examinations of the bronze figure were made in 1999 (expert A.N. Nesterova), 2002 (expert E.V. Meschanova) and in 2008 (expert O.A. Vasilieva). The surveys showed that the surface of the monument is covered mostly with a single-layered black patina, adhering well to the bronze surface. The upper colored patina layer is very thin and uneven (Figs. 5.30 and 5.31).

According to the results of the X-ray study of the selected samples (Table 5.8), the dark single-layer patina and the lower layer of the two-layer patina consist of cuprous oxide cuprite Cu_2O. From among colored copper minerals in 2002 an insignificant amount of copper sulfate brochantite $Cu_4SO_4(OH)_6$ was found in the patina. In 2008, this mineral also was present, but either together with copper carbonate malachite $Cu_2(CO_3)(OH)_2$, or with malachite and another copper sulfate antlerite $Cu_3(SO_4)(OH)_4$. As in 2002, the content of copper salts in the crystalline state in the corrosion film is insignificant. The main component of the patina is an X-ray amorphous matter.

According to the results of the qualimetric evaluation made in 2008, the degree of deterioration of the bronze figure is 7%. Corrosion film and artificial coating perform their protective functions, deviations from the ideal state are related to airborne pollution, bird droppings and insignificant violations of the surface homogeneity

5.5.2 Expert Survey of the Granite Block Status

Examination of the block of Rapakivi granite was carried out in 2010–2012. The experts were A.D. Vlasov (bacteriological analysis), K.S. Kuruleva (qualimetric evaluation of the state of the stone), M.S. Zelenskaya (analysis of the species composition of micromycetes) and K.V. Sazanova (analysis of the chemical composition of surface buildups and the adjacent soil).

The main types of damage are shown in Fig. 5.32, 5.33, 5.34 and 5.35. The most noticeable type of fouling is green

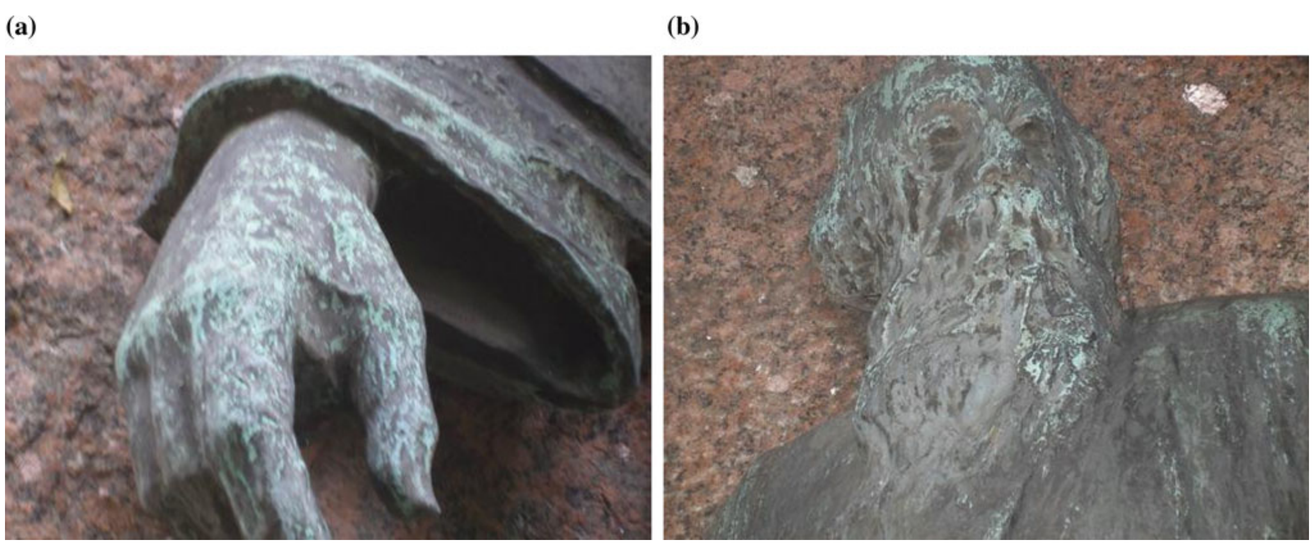

Fig. 5.31 Non-uniform distribution of bluish-green (**a**) and bluish-gray (**b**) patina on various parts of the surface of the monument to V.V. Stasov. The surface texture is beginning to decay

Table 5.8 Results of X-ray phase analysis of the patina from the surface of the monument to V.V. Stasov (Nesterova 2000, Meschanova 2004, Vasilieva 2011)

Year	Color and place of sampling	Mineral composition of the patina
1999	Black—from the right hand	Cuprite
2002	Black—from the toe of the right boot	Cuprite—very much, antlerite—a little
	Black—from the back of the right boot	Cuprite
2008	Black—from the right boot	Cuprite—very much, brochantite—a little
	Bluish-green—from the right hand	Antlerite, brochantite, malachite—in comparable amounts
	Bluish-gray—from the right boot	Cuprite—much, malachite, brochantite—a little

Note In all samples, an X-ray amorphous substance is present

Fig. 5.32 Organic buildup in the space between the monolith and the pedestal. Aerophilous algae and small turfs of moss develop

algae stains (Chlorophyta Division) (Fig. 5.32, 5.33 and 5.34). These stains cover a significant part of the monolith, although they are more developed on the south side of the monument. It should be noted that green stains are located mainly on the upper half of the granite block, while the lower part of the monument (closer to the ground) is predominantly covered by dark crust (Fig. 5.35). The densest buildups are found where the parts of the monument are joined, and enough room remains for accumulation of mud and biological contaminants.

Small turfs of mosses also develop there. The elemental analysis showed (Tables 5.9 and 5.10) that in the dark deposit the content of iron, magnesium and calcium is higher, whereas in the green stains there are aluminum, potassium and sodium. The silicon content in both types of buildups is practically the same.

Obviously, the nature of the damage to the monument is determined by the conditions of its location in the Necropolis—in fact, right on the bank of the Monastyrka river flowing nearby (Fig. 5.36), under the crowns of trees, resulted plant secretions deposit on the monument surface.

Higher humidity provides optimum conditions for colonization of granite by microscopic aerophilous algae. It is green biofilms with the dominance of algae that cover most of the monument. At the same time, the soil serves as a source of soil particles that contain spores of fungi. This explains the formation of a dark outgrowth on the pedestal closer to the ground. Granular disintegration of rapakivi granite is very poorly expressed on the monument; locally it may be possible to observe a weak delamination of granite with the separation of small flakes, not more than 1 cm in size.

The results of the bacteriological study of biofilms from the surface of the monument indicate a high bacterial content. The leading factors in the growth of bacterial communities are essentially air and soil pollution, secretion of vascular plants dropping on the monument, as well as abundant development of algae, which can provide nutrition

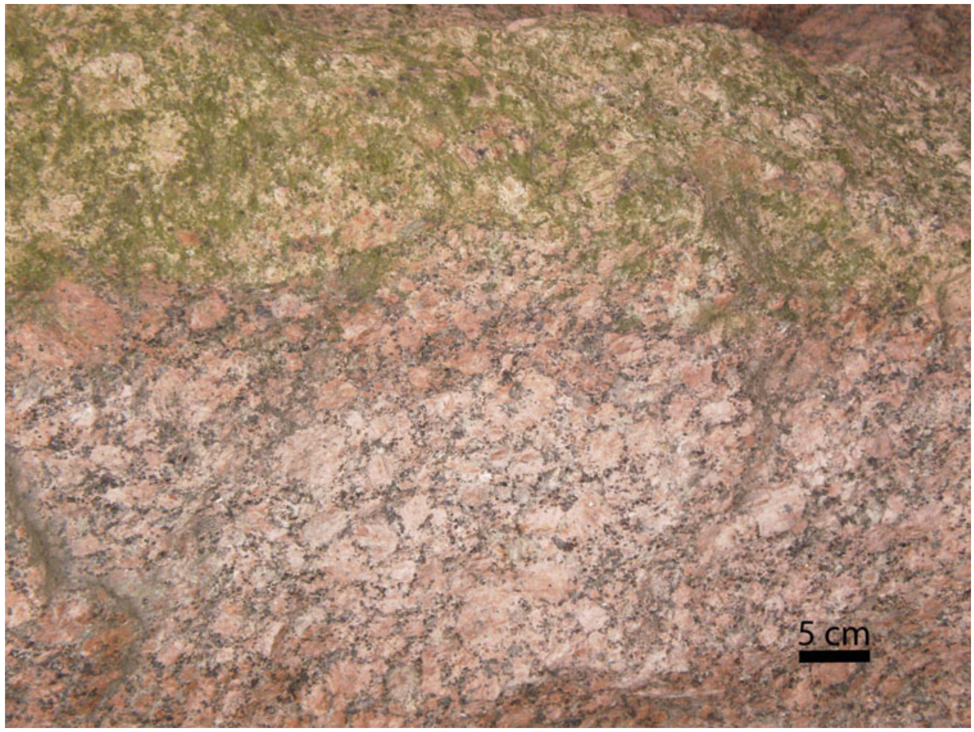

Fig. 5.33 Biological deposits on the granite surface. Biofilm of green color with dominant algae on the corner of the pedestal of the monument

Fig. 5.34 Ovoids of feldspar, surrounded by aerophilous algae

for bacteria. In springtime, the count of bacteria exceeded 10^6 CFU per 1 g of substrate. Heterotrophic mucous bacteria prevail, as well as spore-forming bacteria of the genus Bacillus, which can affect silicate minerals of granite, secreting organic acids. On the weathered surface of granite, pathogenic bacteria of the genus Leifsonia have been found. In autumn, the count of bacteria was significantly lower and amounted to 10^4 CFU per 1 g of substrate, which probably can be explained by the growth in this period of the amount of microscopic fungi that can suppress the development of

Fig. 5.35 Dark crust deposit on the pedestal (closer to the base of the monument) formed by mud layers and microorganisms (microscopic fungi dominate)

Table 5.9 Elemental composition of buildups on rapakivi granite (atomic absorption spectroscopy)

Element	Content of elements (wt%)	
	Dark crust	Green stains
Si	31.168	30.807
Al	6.951	9.055
Mg	0.788	0.435
Ca	1.474	0.254
Na	0.938	2.800
Mn	0.039	0.000
K	4.877	8.383
Fe	6.505	1.469
Ti	0.727	0.088

Table 5.10 Content of metals in mud buildups on granite and in soil (atomic absorption spectroscopy)

Metal	Concentration of metals, μg/g	
	Buildups on granite	Soil
Fe	32280.6	5025.6
Mn	501.8	106.9
Zn	502.2	446.8
Cu	500.9	467.8
Pb	125.1	173.1
Cd	15.5	10.9

bacteria. The composition of the microbiota of the soil near the monument and of the primary soil formations in the space between the parts of the monument are alike. This fact indicates that the soil can be a source of bacterial contamination of the monument.

To assess the possible influence of contaminants on the formation of biofilms, a study was made of the chemical composition of mud layers on the rapakivi granite, and also of the soil on the border of the monument (Table 5.10). The obtained data indicate the excess of MPC (Maximum

Fig. 5.36 River Monastyrka, flowing outside the boundary of the Necropolis of Masters of Arts

permissible concentrations) of such elements as Zn, Cu, Pb. However, it is known that microorganisms, especially dark-colored micromycetes, exhibit increased resistance to heavy metals, and therefore such concentrations cannot hamper their growth. It should be noted that the main differences in the composition of mud layers and the soil consist in the content of iron and manganese, which are several times higher in the mud on the monument. As shown in Sect. 3.3 this is due to biogenic accumulation of these elements.

Analysis of the composition of organic substances in mud deposits on granite (chromatography-mass spectrometry) showed their high content. In two samples from the surface of the monument to V.V. Stasov sugar alcohols, sugars, amino acids, organic acids were found. The total number of potential low-molecular carbon sources for the fungi varied from 3 to 5 mg/g of dry matter. The total amount of amino acids is 0.1–0.3 mg/g of substrate. These indices are quite sufficient for the active development of a heterotrophic microbial community including microorganisms with different metabolism types. The soil extract was significantly poorer in comparison with the mud layers on granite. Apparently, the higher content of organic substances on the surface of the monument is due to a lower rate of their decomposition than in the soil.

In general, the data obtained indicate a significant contamination of the surface of the monument under the influence of the environment. This leaves a noticeable imprint on the development of the lithobiont community. In particular, the mycological studies have made it possible to identify a significant diversity of species and a high count of micromycetes in the analyzed samples (Table 5.11).

In total, on the surface of V.V. Stasov's memorial 19 species of micromycetes were identified, most of which are known as active deterioration agents of stone substrates. The group of dominant species includes dark-colored micromycetes, found also on other monuments of the Necropoleis.

According to the results of the qualimetric examination performed in 2011, the degree of deterioration of the granite block as a whole is 6% due to the development of biological buildups, air pollution and minor crumbling.

According to the results of complex monitoring research, the monument is in a satisfactory condition. Corrosion processes on the surface of the bronze figure gradually evolve. Granular disintegration of the rapakivi granite is poorly expressed. However, the saturation of microbial films (with the dominance of micromycetes and algae) is quite high, which indicates a potential danger from microorganisms for the material of the monument. To prevent the development of corrosion processes and the deterioration of granite, seasonal preventive work is recommended.

5.6 Monument to P.V. Kindyakov

Sculptor P. Catozzi. 1828. Marble, garnet gneiss, granite

The tomb of Peter Vasilyevich Kindyakov (1768–1827) belongs to the few sculptures in the ensemble of the Necropolis of the 18th century, whose author is reliably known. The majestic allegorical figure of *Faith* with a veil over the head and a cross in the hand was sculptured by Italian sculptor Paolo Catozzi: on the plinth of the statue on the north side one can see the signature: fecit Paulus Catozzi

Table 5.11 Species composition of microscopic fungi and frequency of their occurrence on the surface of the monument to V. V. Stasov

Species of micromycetes	Frequency of occurrence (%)
Alternaria alternata	**57.1**
Aureobasidium pullulans	**92.8**
Cladosporium cladosporioides	**85.7**
Cladosporium herbarum	**64.3**
Epicoccum nigrum	42.8
Fusarium oxysporum	28.5
Fusarium solani	21.4
Fusarium sp.	7.1
Hormonema dematioides	**85.7**
Mortierella lignicola	14.3
Mucor racemosus	14.3
Penicillium brevicompactum	7.1
Penicillium citrinum	7.1
Phoma glomerata	7.1
Phoma herbarum	14.3
Scytalidium lignicola	14.3
Trichoderma viride	14.3
Asporogenous light-colored fungus	50.0
Asporogenous dark-colored fungus	28.5

Note The dominant species are highlighted in bold

in St. Peter. A 1828. The sculpture is mounted on a pedestal of a rare and beautiful rock—garnet gneiss (Fig. 5.37).

Major-General P.V. Kindyakov fought in the Patriotic War of 1812, lived an exacting life, for many years in Moscow, but died in St. Petersburg and was buried in the Smolensk Orthodox cemetery. In 1931, the monument to Kindyakov, in order to preserve this beautiful memorial sculpture, was moved to the Necropolis of the 18th century.

(a) (b)

Fig. 5.37 Monument to P.V. Kindyakov in the Necropolis of the 18th century: **a** before the conservation and restoration work (2007), the sampling sites are shown; **b** after restoration (2013)

The statue of *Faith* by that time was already damaged: there was no right hand.

Before the restoration of the monument, a research among the iconographic material was made for the reconstruction of the lost fragment of the sculpture. It was found that *Faith* had a chalice (a cup for communion) in the hand. For St. Petersburg Necropoleis, this iconography of the allegory of Faith was a great rarity, the parallels were found in Western European art.

The issue of restoration of P.V. Kindyakov's tomb became especially critical in the early 2000s, due to an extremely poor condition of the marble sculpture, with extensive black crusts, and disintegration of the stone.

Practically the restoration of the difficult, from the point of view of preservation, monument to P.V. Kindyakov was begun on the initiative of Vyacheslav Semyonovich Mozgovoy (1943–2012), who for many years had worked as a conservation professional at the State Museum of Urban Sculpture. In 2006, V.S. Mozgovoy participated in a major project to restore 15 artistic tombstones by Italian masters in the Necropolis of the 18th century. This work was the first instance of using lasers for cleaning the stone during the restoration of marble monuments in the State Museum of Urban Sculpture. The use of this method of cleaning, which was new to the St. Petersburg specialists at the time, was made possible within the framework of an Italian-Russian project organized by the Italian Institute of Foreign Trade (ICE). The project was coordinated by the association of Italian art restorers *Assorestauro* from the Italian side, from Russia—by the Committee for State Control, Use and Protection of Historical and Cultural Monuments of St. Petersburg.

5.6.1 Expert Survey of the Monument Status Before the Restoration

Expert examinations of the state of the monument were made in 2002 (by experts N.F. Lepeshkina, M.S. Zelenskaya), in 2007 (by expert I.V. Knauf) and in 2012 (by expert E.I. Makeeva)

Examination of the monument in 2002 showed that on the marble surface an intense formation and detachment of gypsum-rich patina was going on, and colonies of microscopic fungi were visible. On the figure of Faith on the east side, numerous small fissures were found, on the east side of the cross there was a deep crack. According to the results of qualimetric evaluation, the degree of deterioration of the marble sculpture was 34%. Recommendations were made for conservation and restoration work on the monument.

By the beginning of conservation and restoration work in 2007, the monument to P.V. Kindyakov had been in an extremely poor condition (Figs. 5.37a and 5.38a). Granulation, sugaring of marble, biological buildups could be observed (Fig. 5.38a). A black gypsum crust, the presence of which was confirmed by X-ray phase analysis (Fig. 5.39) and scanning electron microscopy (Fig. 5.40a), covered a significant portion of the sculpture (Fig. 5.38a). The surface of marble was affected by various types of biological deterioration agents, such as algae, colonies of lichens and

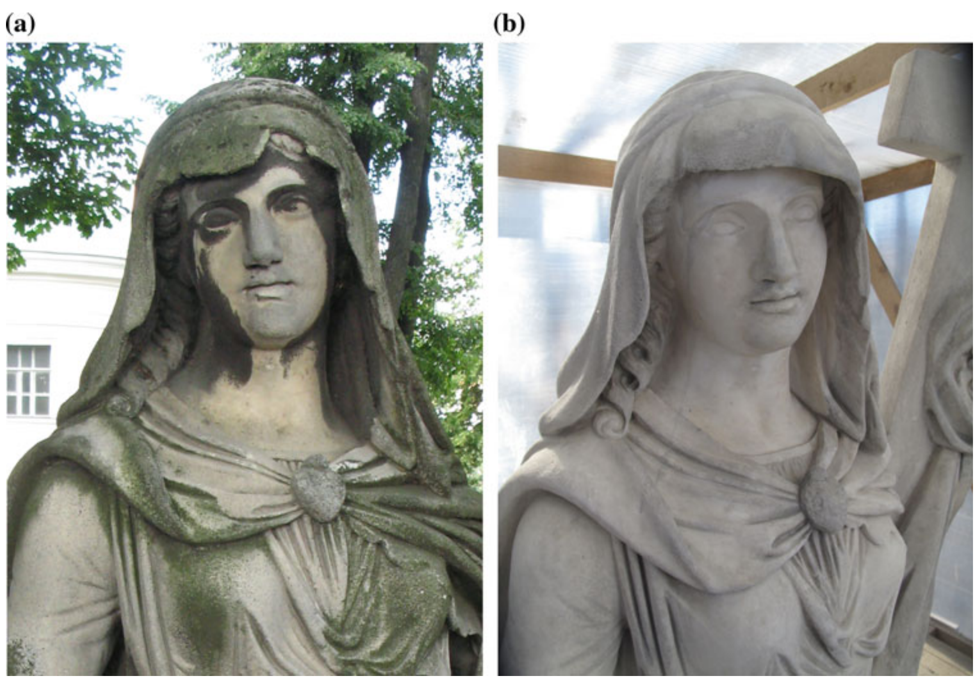

Fig. 5.38 Fragment of the marble sculpture: **a** before the beginning of conservation and restoration work (2007), **b** after restoration (2013)

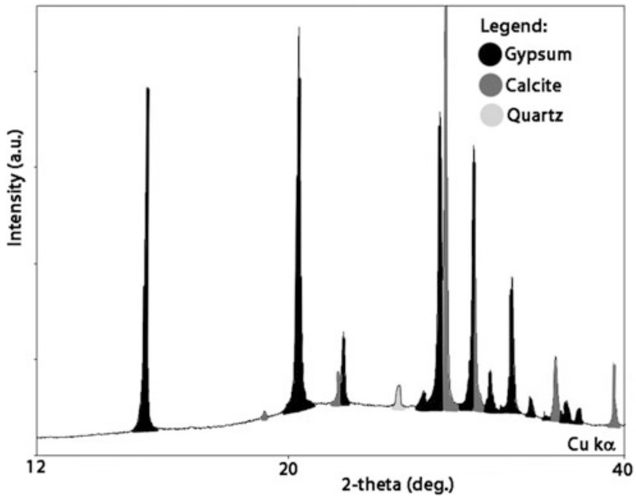

Fig. 5.39 Fragment of the X-ray pattern of the sample from the surface of the monument to P.V. Kindyakov. Results of X-ray phase analysis: calcite $CaCO_3$—very much, gypsum $CaSO_4 \cdot 2H_2O$—plentiful, quartz SiO_2—little, mica—traces (2007)

microscopic fungi: *Alternaria alternata, Penicillium sp., Acremonium strictum*. The right hand of the figure with the chalice was lost (Fig. 5.41).

The electron micrograph taken in 2013 shows a solid cover of gypsum crystals (Fig. 5.40b). Between them are numerous microorganisms (fungi, algae), which indicates their active part in marble deterioration.

5.6.2 Removal of Biofouling and Crust Layers with a Laser

Urgent measures for the conservation of the marble sculpture were taken in 2007. Trial cleaning of the monument was performed, using *Smart Clean II* laser device from *El.En*, Italy (for more details about this laser see Sect. 5.2.2), during which the main modes of laser cleaning of the monument from black atmospheric gypsum crusts and colonies of biodeterioration agents. V.S. Mozgovoy, a certified restorer of stone and gypsum sculpture supervised the work, which was performed by restorers of stone and gypsum sculpture S. L. Petrova and Yu.A. Loginova. Great practical and consulting assistance in the work was provided by an expert in laser restoration techniques VA Parfenov.

At the initial stage of work with the laser, the technique of removing colonies of biodeterioration agents from certain parts of the sculpture about 2.0 × 2.0 cm in size was tested. After carrying out test cleaning in all designated areas, using different combinations of the laser output parameters, it became clear that the laser cleaning is not very effective for the removal of biofouling from the surface of eroded marble. In view of this, it was decided to use *Rosima 110* biocidal preparation (*Acima*, Switzerland) to remove colonies of biodeterioration agents.

Later, the laser device was used to remove gypsum-rich patina (black gypsum crusts). Just as in the previous version of cleaning, the optimum output parameters of the laser were

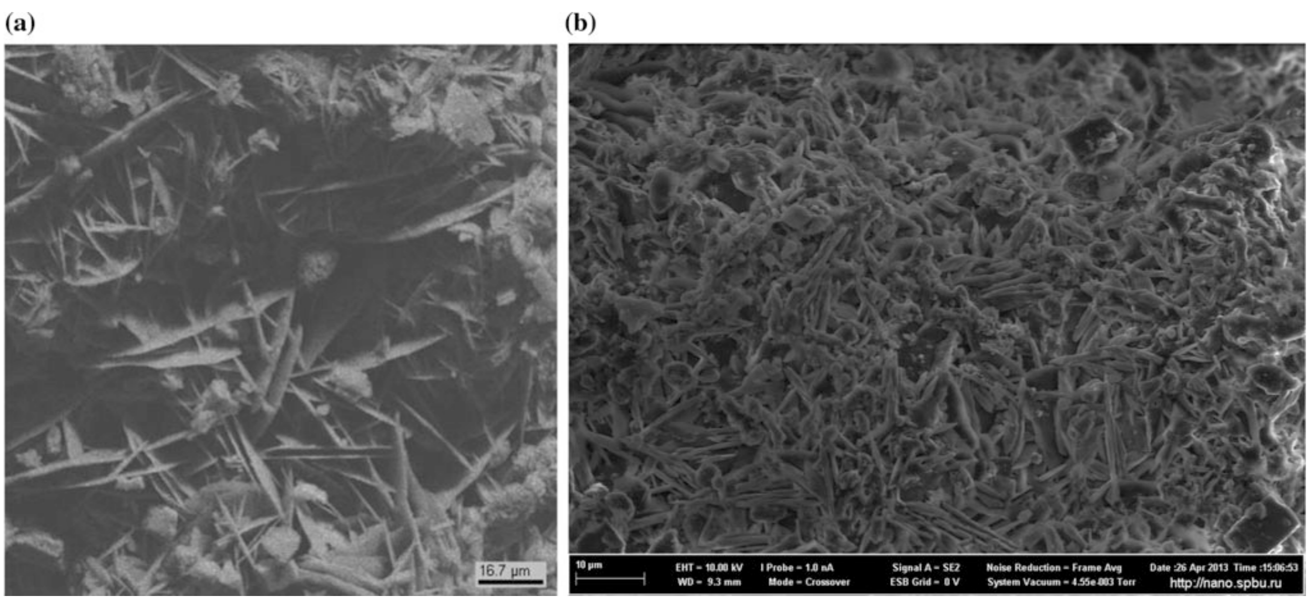

Fig. 5.40 SEM images of the marble surface of the monument to P.V. Kindyakov prior to restoration. Tabular gypsum crystals are visible: **a** 2007, **b** 2013

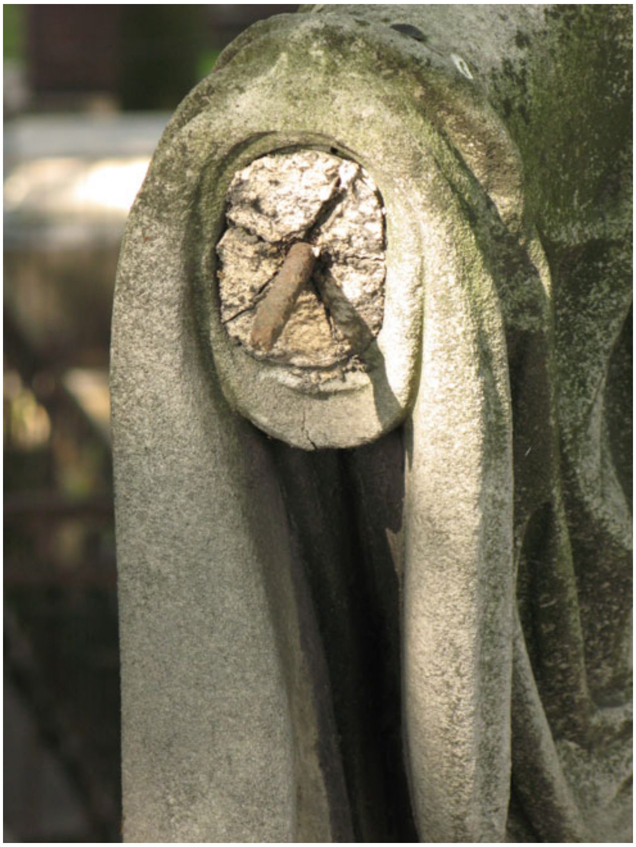

Fig. 5.41 Right arm of the Faith sculpture before restoration; the hand, previously fixed to a metal pin, is missing

experimentally chosen, to test the method of laser stripping. For this purpose, separate sections were selected, divided into squares of about 1.5 × 1.5 cm (Fig. 5.42).

First, the parameters for treating marble with a gypsum crust of the medium level of development (1–1.5 mm thick) were selected (Fig. 5.42a). For such areas of the sculpture surface, uniform stripping took place with the laser fluence of 6.0–7.0 J/cm^2 and pulse repetition rate of 7 Hz. The rate of crust removal was low (1 cm^2 in 4 to 6 min).

The next stage of the work was an empirical selection of the laser output parameters for removal of denser gypsum crusts (2–3 mm thick) (Fig. 5.42b). During trial cleanings it was established that thick crusts can be stripped layer by layer. The time for treating an area of about 1 cm^2 varied from 2 to 3.32 min. The optimum level of the laser fluence in this case was 8–11 J/cm^2. In the same way, the operating conditions were worked out for all parts of the sculpture with black crusts.

It is important to note that in the sample areas cleaned by the laser, the marble acquired a natural white color (Fig. 5.42). There were traces of polishing and the author's work. After laser cleaning, the stone structure was stabilized with KSE 300HV stone strengthener from *Remmers* (Germany).

In 2008, the restorers examined the sculpture, and additional strengthening of the marble surface in certain weakened areas was recommended, so another reinforcement of marble with the same compound was performed.

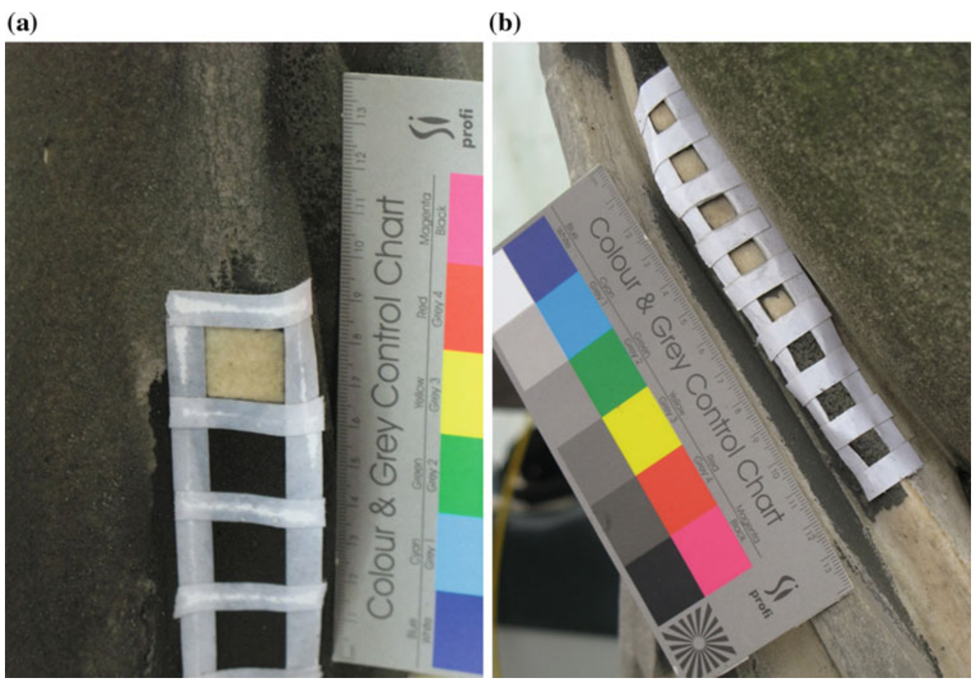

Fig. 5.42 Laser stripping of the gypsum crust of various degrees of development (2007): **a** medium, **b** intensive

Before the restoration (from 2007 to 2012) the monument was under a shed closed on the four sides. For one season only prior to restoration, the shed was removed, and in 2012 on the back of the figure and on the pedestal of the monument minor biofouling appeared, as well as a layer of atmospheric and soil contamination. The crack along the two sides of the cross was clogged with dust from the soil. The process of marble sugaring continued, not as intense as before, but significant in the areas where rainwater flowed and accumulated.

5.6.3 Restoration of the Monument

In 2012, work on the monument to P.V. Kindyakov was resumed by the *Naslediye* Restoration Workshop LLC. Restorer A.V. Chekalyuk and the restorer of the State Museum of Urban Sculpture, E.I. Makeyeva worked under the supervision of Yu.A. Loginova, the head of the Museum Service for daily maintenance and upkeep of the monuments. The main tasks of the work were to continue clearing the surface of marble of dense black crusts, structural strengthening of the stone and replacement of the missing right hand.

Structural strengthening of the stone made in 2007 and 2008 not only stabilized the crumbling marble, but also resulted in hardening of gypsum crusts and their stronger adhesion to the underlying marble. Therefore, it was necessary to make serious adjustments to the previously used laser stripping modes.

It turned out that to effectively remove black gypsum crusts it was now necessary to operate at much higher levels of laser fluence (up to 38 J/cm^2) and a higher pulse repetition frequency (up to 10 Hz). But even under such conditions, the removal of the gypsum-rich patina went very slowly. The treatment of an area of about 1 cm^2 took from 15 to 20 min. After all work on marble cleaning was completed, the structural strengthening of the monument material was carried out.

Restoration of the right hand of the Faith figure was made using photographs from the archives of the State Museum of Urban Sculpture. The measurements and examination of the remaining left hand of the figure enabled to calculate the proportions, taking into account the stylistic features of the fragment to be reconstructed. The study of iconographic material showed that there was a chalice in the right hand of the Faith. The missing hand with the chalice was remodeled with a composite material made of polyester resin with marble chips (Fig. 5.43).

In the process of restoration, the old corroded and split metallic pin was removed (Fig. 5.41). The restored fragment was installed on a ceramic pin. Masticing of the joint and the crack on the cross was made with Paraloid B-72 copolymer (by Kremer, Germany) with the maximum filling with marble chips of various fractions. The final stage of the work was to protect the surface of the monument with a solution of *Rosima 110* biocidal preparation (from *Acima*, Switzerland), and then *Funcosil AG* water repellent (from *Remmers*, Germany).

Fig. 5.43 Fragments of the Faith sculpture (the hand with a chalice) reconstituted from the stone substitute

The experience of restoring the tomb of P.V. Kindyakov is an example of many years of joint work of researchers and restorers, during which it was possible to conduct historical archival research and monitor the state of the monument in the process of conservation and restoration work for five years. The used laser method of cleaning the surface of the monument of black gypsum crusts has shown its effectiveness. It was possible to uncover the original marble surface that kept the traces of the author's work (Figs. 5.37b and 5.38b). In the future, for preservation of the sculpture, it is necessary to take preventive measures regularly—remove contaminants in time, treat the surface with biocides.

5.7 Monuments to N.M. Karamzin and E.A. and E.N. Karamzin

Unknown master, 1820s.(the monument to N.M. Karamzin); unknown master, 1850s. (the monument to E.A. and E.N. Karamzins); marble, granite (sarcophagi); bronze (wreaths); ormolu crosses; wrought iron (railing), limestone (foundation of the railing)

Outstanding writer and historian, author of the multi-volume "History of the Russian State", Nikolai Mikhailovich Karamzin (1766–1826) was buried in the Necropolis of Masters of Arts. The white marble sarcophagus on Karamzin's grave (Fig. 5.44) is crowned with a wreath of oak leaves, symbolizing loyalty to the Fatherland, on the western side there is an ormolu cross. The monument, made according to the will of the writer without "any superfluous ornaments", was popular (the tomb of the poet I.I. Dmitriev in Moscow was made on its model), it is described in the verses by V.A. Zhukovsky:

> The faithful son of Russia here comes to pray;
> Atop the marble of the grave a wreath is seen;
> Inspiring him for a bright and glorious day,
> That holy name: Karamzin.
>
> (English by I. Bekzadian).

In 1851, his wife Ekaterina Andreevna Karamzina (1780–1851) was buried next to N.M. Karamzin, known as the mistress of a literary salon, visited often by famous writers. The gravestone of Karamzina was created on the model of the sarcophagus on the grave of her husband with the only difference that a bronze wreath of roses was placed on it.

In 1891 on the same family plot the daughter of N.M. and E.A. Karamzins—Elizaveta Nikolaevna was buried (1821–1891), as evidenced by the text carved on the sarcophagus of Ekaterina Andreevna.

The monuments were restored many times. In 1949, the bronze wreath was remade that was lost earlier (in the first third of the 20th century) from the sarcophagus of E.A. Karamzina, modeled on the wreath of oak leaves on the monument to her husband, and not of roses, as before (apparently due to the lack of iconography). In 1972, a full restoration of the monuments was made. In 1982—the fence was restored. In 1992—both tombstones were restored, and the gilded crosses were placed on the butts of the sarcophagi instead of those lost in the first third of the twentieth century. Presumably, these are crosses from the late 19th and early 20th century, that were kept in the museum.

Restoration of the monuments with the fence and improvement of the site in 2016 were made on the eve of the 250 anniversary from the date of birth of N.M. Karamzin.

5.7.1 Expert Survey of the Monument Status Before Restoration

The qualimetric evaluation of the state of monuments to N.M. Karamzin and E.A. Karamzina, made by M.V. Ivanova in May 2011, showed that the degree of marble deterioration of both sarcophagi is close (23 and 20%, respectively). On both monuments, the stone was crumbling, leading to a significant roughening of the surface and the appearance of shallow pits (mainly on the edges of the

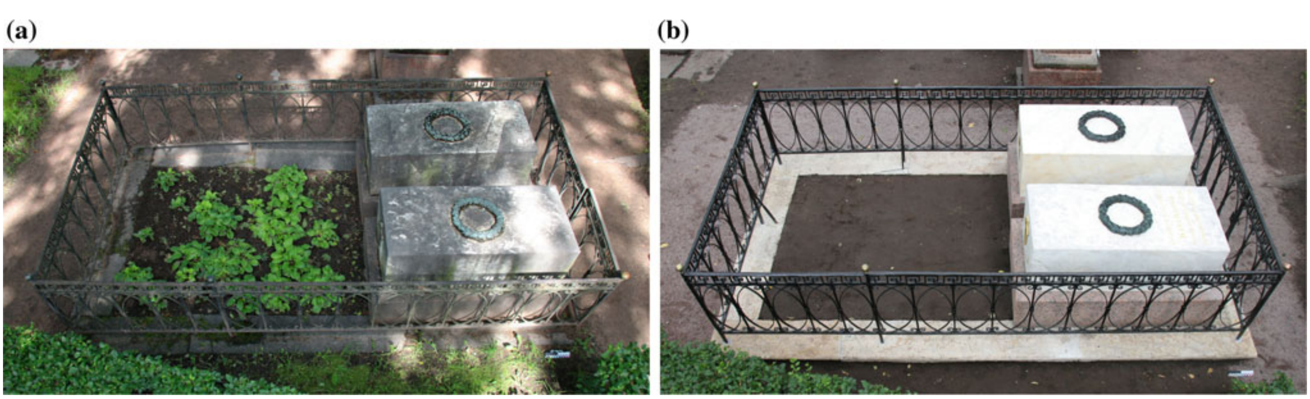

Fig. 5.44 The tombstones of N.M. Karamzin and E.A. and E.N. Karamzins in the Necropolis of Masters of Arts (a view from the south-western side): **a** before restoration (June 2016), **b** after restoration (August 2016)

sarcophagi), many fissures, mud layers, and the development of biological fouling with predominance of fungi and algae. On the south side of the sarcophagus of N.M. Karamzin's monument deep cracks were found. It was concluded that conservation work was necessary to strengthen the marble on the sarcophagi of both monuments.

In the summer of 2016 restorers H.V. Shumilova and V. V. Lebedev, biologist M.S. Zelenskaya and engineer A.E. Amosova performed a visual inspection and examination of the surface of the stone, non-ferrous and ferrous metal using a portable Micron Mobile microscope. In the process of inspection, localized marble deterioration, networks of cracks, chipping, intense contamination was discovered (Figs. 5.44a, 5.45, and 5.46).

On the surface of the tombstones and the metal fence, algae and colonies of dark-colored fungi were found (Fig. 5.45; Table 5.12).

The mycological examination of the monument revealed 16 species of micromycetes, most of which are known as active deterioration agents of rocky substrates and other materials. The group of dominant species includes dark-colored microscopic fungi, found also on other monuments of the museum Necropoleis. The amount of micromycetes in the samples was high (from 2500 to 7500 CFU). The results of the mycological examination were used to recommended biocidal treatment of the monument before restoration.

The surface of the bronze wreaths was covered with traces of loose emerald-colored patina, a microfissure is visible (Fig. 5.47). The gilding of the crosses was fragmentarily lost (Fig. 5.48). The stone foundation of the fence subsided in places and sank into the ground for a few centimeters. The surface of the wrought iron fence was corroded. Some of its fragments were lost.

During the stratigraphic analysis of the layer of paint from the surface of the fence, performed by A.E. Amosova, it was found that it was painted black once, and red lead primer was used for rust prevention (Fig. 5.49). Presumably, the paint was applied during the last restoration in 1982.

The energy-dispersive X-ray spectroscopy (EDX) analysis (Table 5.13) showed that the copper alloy from which the wreaths on both tombstones are made contains tin, nickel, iron and lead. A sample of the alloy from the wreath to E.N. Karamzina is characterized by a higher content of dopants (tin, nickel, lead). The alloy from the wreath on the monument to N.M. Karamzin contains silver. The presence of silver can be explained by the fact that the details of the wreath were soldered with a silver-containing solder.

Copper, from which the crosses are made, is characterized by a constant small admixture of nickel. On both crosses there are traces of gilding. In the gilding on the cross of N.M. Karamzin, mercury was discovered, which probably indicates that the amalgamation process was used. In the gilt on the cross from the gravestone of E.A. Karamzina, no traces of mercury were found, from which it can be concluded that gold electroplating was used for this monument.

Fig. 5.45 Mud buildups, algae growths, colonies of dark-colored fungi and cracks on the butt end of the marble tombstone of N.M. Karamzin (June 2016, shows the result of trial cleaning)

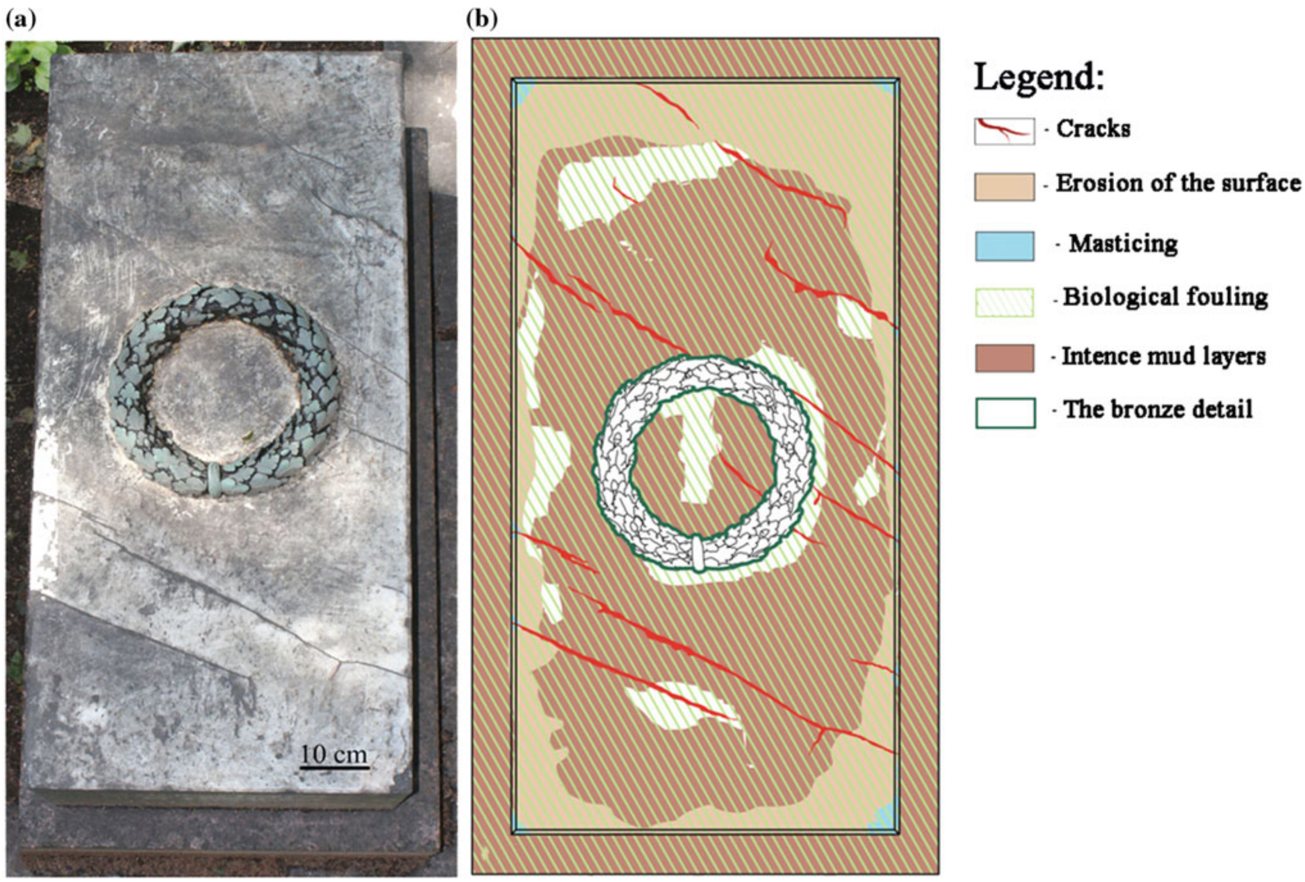

Fig. 5.46 The tomb of N.M. Karamzin (seen from above) prior to the beginning of restoration (June 2016): **a** photograph, **b** map of the forms of marble deterioration (the signatures on the picture: cracks, erosion of the surface, masticing, biological fouling, intense mud layers, the bronze detail)

Table 5.12 Species composition of micromycetes found on the tombstones of N.M. Karamzin and E.A. Karamzina (2016)

Species of micromycetes	Frequency of occurrence (%)
Alternaria alternata	50
Aureobasidium pullulans	100
Cladosporium cladosporioides	100
Cladosporium herbarum	16
***Coniosporium* sp.**	100
Epicoccum nigrum	16
Fusarium oxysporum	50
Hormonema dematioides	66
Mortierella lignicola	16
Penicillium citrinum	33
Penicillium decumbens	50
Phoma glomerata	33
Phoma herbarum	50
Scytalidium lignicola	16
Trichoderma viride	33
Non-spore-forming light-colored fungus	33

Note Dominant species are highlighted in bold type

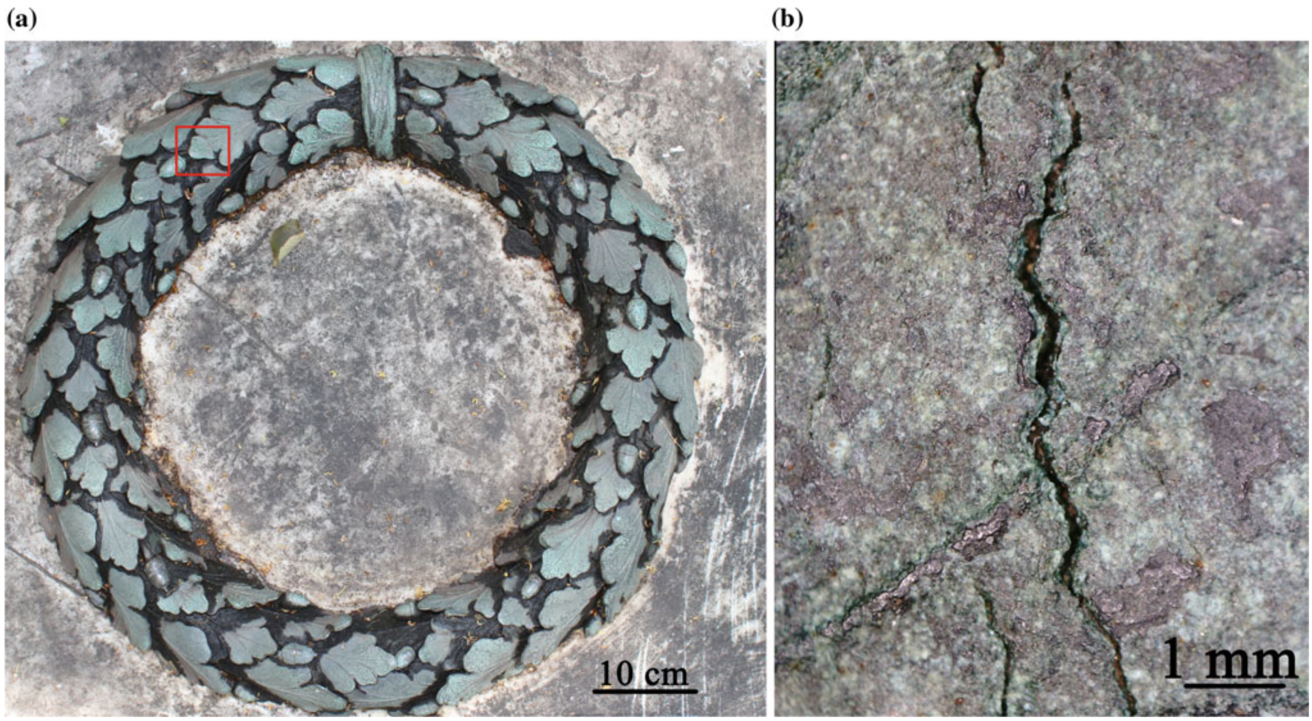

Fig. 5.47 Bronze wreath on the tomb of N.M. Karamzin: **a** general view, **b** microphotograph of the surface (a fragment, seen in the square in Fig. 5.47a)

Patina on the bronze wreaths and copper crosses has a heterogeneous composition. Its corrosion component is represented by oxides and sulfates of copper. In addition, quartz, phosphates and trace amounts of aluminosilicates (clay minerals) have been found.

5.7.2 Restoration of Monuments in 2016

The work on the restoration of the Karamzins' tombstones was started[1] in July 2016 with the disassembling of the fence, delivered to the workshop. The base of the fence, made of Putilovo limestone, was dismantled. The stone was in extremely poor condition: delamination was observed, and a network of cracks formed. The foundation was consolidated to eliminate subsidence and mobility of the base blocks. In parallel, work was begun on washing the surface of the marble monuments with subsequent structural strengthening of the stone (Fig. 5.50). The cracks on the marble surface were injected (Fig. 5.51), followed by masticing of stone defects (chips, pits, fissures) and applying a protective coating.

Of great interest is the wreath from the tomb of N.M. Karamzin: it is assembled on a ring and consists of 66 stylized oak leaves and 30 acorns (9 of which are fastening elements). Each leaf was made individually by stamping. During the restoration of the wreath, it was disassembled into the main elements for a thorough cleaning of all kinds of contaminants, and also for elimination of the fragment mobility. The wreath from the gravestone of E.A. and E.N. Karamzins was made relatively recently (in 1949), cast in a single block of bronze. Since it was in a satisfactory condition, the surface was washed.

During the visual inspection of the crosses deformations, dents, scratches were found. Probably, there were attempts to steal the crosses, using various tools. On the entire surface of the metal, spots of copper corrosion were observed, with patina formation, blue to green in color. After removal of all types of contamination, significant losses of gilding were found on the surface of the crosses (Fig. 5.48). The Restoration Council considered several options for their conservation. As a result, it was decided to apply tinted coating to the surface where the gilding was lost, thus preserving the existing historical gilding.

After the restoration, the condition of the monuments to the Karamzins substantially improved (Fig. 5.44b). However, white marble sarcophagi with large horizontal surfaces require constant care and maintenance: washing during the summer season and regular renewal of the conservation coating.

[1]The work was performed by the conservators of the *Naslediye* Restoration Workshop LLC.

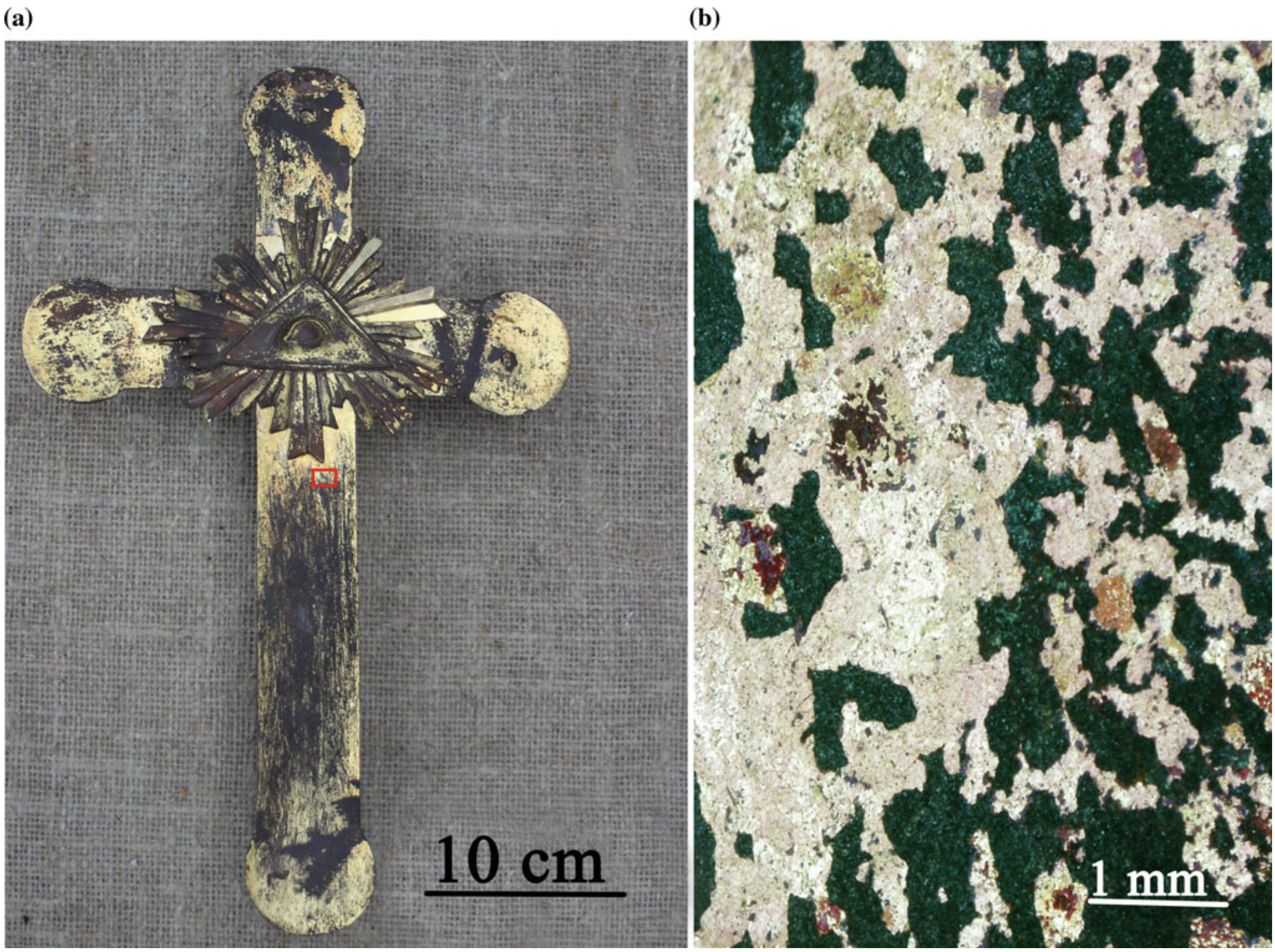

Fig. 5.48 Gilded cross on the tomb of N.M. Karamzin: **a** general view (after removal of contaminants), **b** microphotograph of the fragment of the surface seen in the square in Fig. 5.48a

Fig. 5.49 Microphotograph of a fragment of the paint layer from the fence

Table 5.13 Results of quantitative EDX-analysis of samples from the surface of wreaths and crosses (wt%)

Monument	No	CuO	NiO	ZnO	PbO	FeO	SnO	Al_2O_3	Ag_2O	Au_2O_3	Hg_2O	SO_2	PO_4	SiO_2
Wreaths														
To N.M. Karamzin	1	62	3	0	0	5	4	0	1	0	0	25	0	0
	2	80	3	11	2	0	4	0	0	0	0	0	0	0
	3	44	4	3	1	7	0	0	8	0	0	6	14	13
To E.A. and E. N. Karamzins	1	68	12	0	7	8	5	0	0	0	0	0	0	0
	2	66	2	0	0	5	4	0	0	0	0	5	8	10
	3	38	2	3	11	4	33	0	0	0	0	5	4	0
Crosses														
To N.M. Karamzin	1	85	2	3	0	0	2	0	0	0	0	5	0	3
	2	4	3	0	0	0	0	0	0	83	10	0	0	0
	3	23	3	2	0	0	0	0	0	61	11	0	0	0
To E.A. and E. N. Karamzins	1	67	3	5	0	2	1	0	0	0	0	15	2	5
	2	79	4	0	2	0	0	4	0	0	0	6	5	0
	3	21	4	5	4	0	0	0	0	55	0	0	3	8

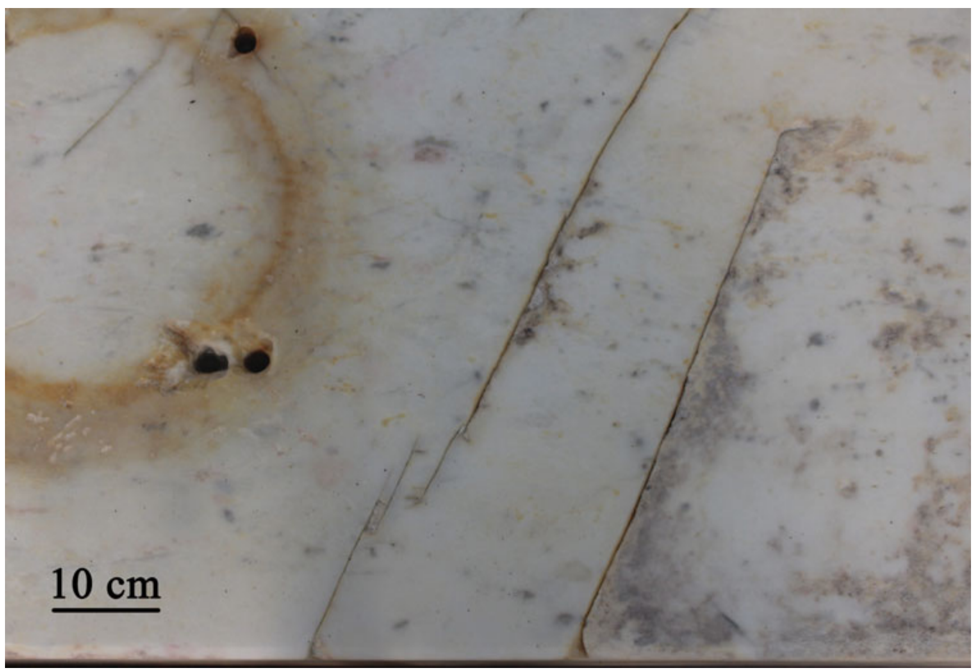

Fig. 5.50 Fragment of N.M. Karamzin's marble sarcophagus after washing. There are cracks and discoloration of the marble in the place where the wreath is fixed

5.8 Monument to A.Ya. Potemkina

Unknown master. 1830s. Limestone (the tomb with a portico a canopy), gabbro-diabase (sarcophagus), gilded brass (ornamental band on the sarcophagus), granite (base/socle), wrought iron (railing)

Monument to infant Alexandra Yakovlevna Potemkina (24.10.1830–17.11.1830), the third daughter of Adjutant General Ya.A. Potemkin (1781–1831), participant of the Patriotic War of 1812, is located near the eastern wall of the Necropolis of the 18th century, next to the tomb of the first wife of her father, V.I. Potemkina (1786–1810). These monuments are similar in form and material, but differ in the size and detail of the decor. Obviously, the tombstone of the infant, Alexandra, was made after the fashion of an earlier monument to V.I. Potemkina.

The monument to A.Ya. Potemkina (Fig. 5.52) is made of Putilovo limestone and is a portico on four Doric columns with a helm roof and triangular pediments, decorated with

Fig. 5.51 Injection of cracks on the marble with an adhesive compound

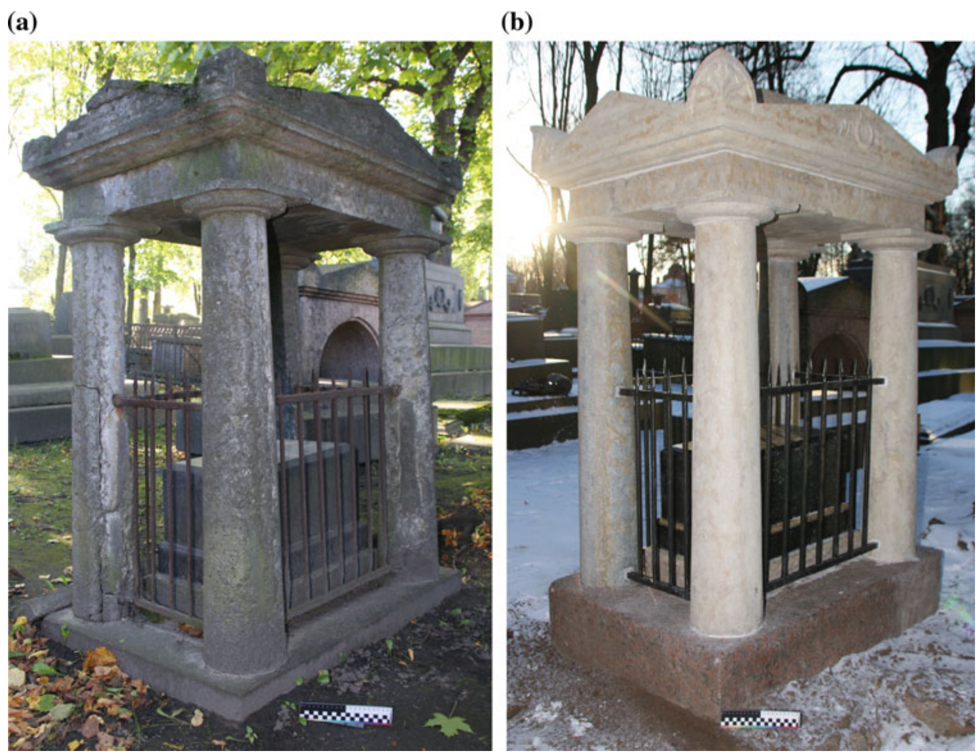

Fig. 5.52 Monument to A.Ya. Potemkina (view from the north-eastern side) **a** before restoration (September 2016), **b** after restoration (November 2016)

palmette acroteria. In the pediments there are reliefs: in the north one—a wreath with fluttering ribbons, in the southern one—a winged hourglass.

Under the roof/canopy there is a small one-piece sarcophagus with a carved epitaph, its lower part is decorated with a gilded brass ribbon. Between the columns of the portico there are wrought iron picket railings.

Originally, the portico was crowned with a cross, and on the western end of the sarcophagus was an embossed bronze coat of arms. These details have long been lost.

The tomb of A.Ya. Potemkina was never restored. For many years the state of the monument caused great concern, and recently it was called an emergency. Delamination of limestone in the southwestern column resulted in a large gap formed in the column between its two halves, in fact, the column broke in two. In 2016, a full restoration of the monument was made.

5.8.1 Expert Survey of the Monument Status Before Restoration

A detailed examination of the monument's condition, carried out by V.V. Manurtdinova and M.S. Zelenskaya in 2009 (August-September) showed that its condition was critical. Numerous cracks (including deep and through cracks) were registered on the surface of Putilovo limestone, the stone was flaking, gypsum-rich patina began to form, and bio-fouling of algae, thalli of crustose lichens and colonies of dark-colored fungi was actively developing (Table 5.14). On the roof of the portico the beginning of moss development was found (Fig. 5.53a). The qualimetric estimate of the limestone deterioration equaled 45%. After the expert examination of 2009, it was recommended to carry out restoration, and to take measures for biocidal treatment of the monument before it started.

Seven years later, in the summer of 2016, prior to the restoration, a second examination of the state of the monument was performed (by experts H.V. Shumilova, M.S. Zelenskaya, V.V. Lebedev), which confirmed that the gravestone was in a critical state (Figs. 5.52a, 5.54, and 5.55), and the extent of its deterioration significantly increased.

According to the visual survey, the tomb structure deviated from the vertical orientation, most of the granite base sank into the ground. The cross crowning the roof, the embossed bronze coat of arms from the sarcophagus, and the architectural elements of the roof—the upper fragments of the acroteria, were lost. A horizontal delamination of the architrave of the limestone portico, vertical delamination of

Table 5.14 Species of microscopic fungi found on the surface of the monument to A.Ya. Potemkina by the mycological examinations of different years

2009	2016
Alternaria alternata	*Alternaria alternata*
Cladosporium cladosporioides	*Aureobasidium pullulans*
Cladosporium herbarum	*Cladosporium cladosporioides*
Cladosporium sphaerospermum	*Cladosporium herbarum*
Coniosporium sp.	*Coniosporium* sp.
Fusarium oxysporum	*Epicoccum nigrum*
Hormonema dematioides	*Fusarium oxysporum*
Mucor hiemalis	*Fusarium solani*
Mucor racemosus	*Hormonema dematioides*
Penicillium brevicompactum	*Mucor racemosus*
Penicillium citrinum	*Penicillium citrinum*
Penicillium chrysogenum	*Ulocladium chartarum*
Penicillium herqueri	Non-spore-forming light-colored fungus
Scytalidium lignicola	
Ulocladium chartarum	

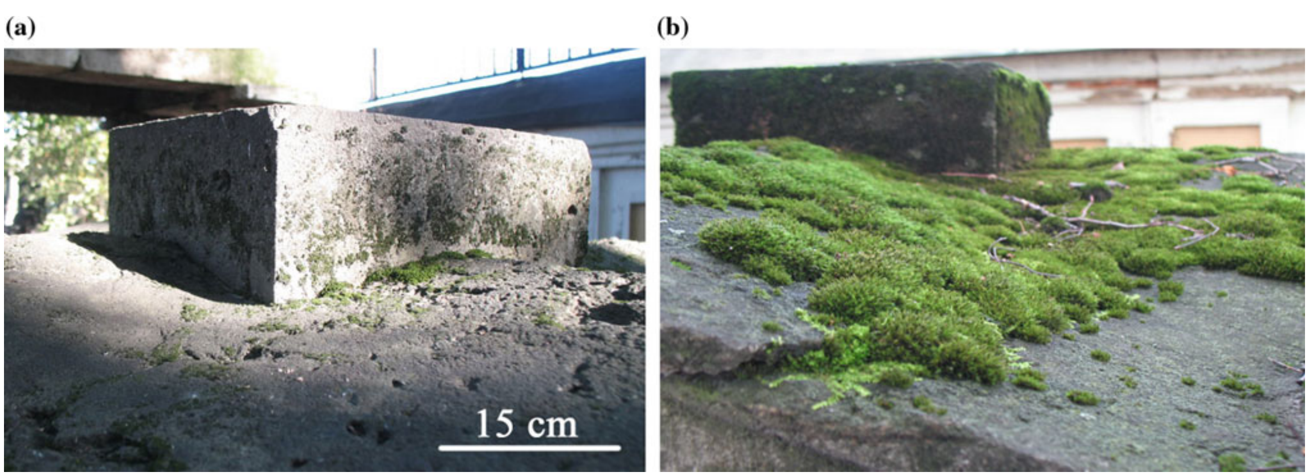

Fig. 5.53 Development of mosses on the roof of the portico of A.Ya. Potemkina's tomb before the restoration: **a** photo 2009, **b** photo 2016

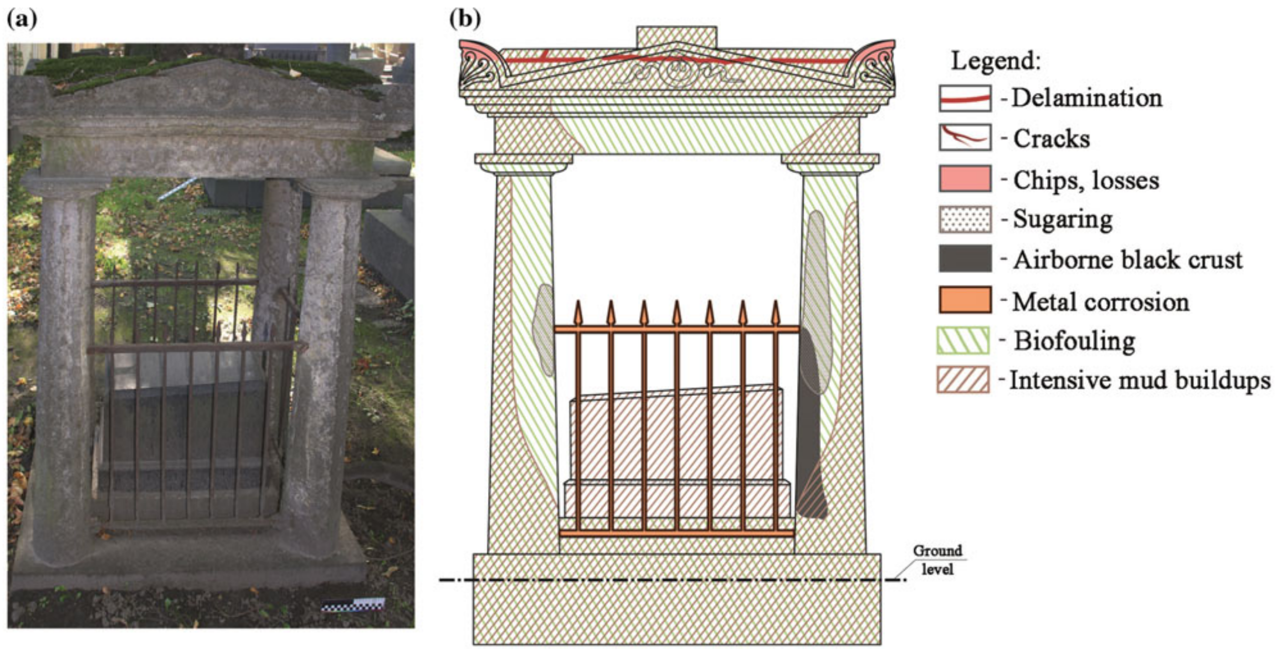

Fig. 5.54 State of the monument to A.Ya. Potemkina before restoration (2016, northern side): **a** photograph, **b** map (legend: delamination, cracks, chips, losses, sugaring, airborne black crust, gypsum crust, metal corrosion, biofouling, intensive mud buildups)

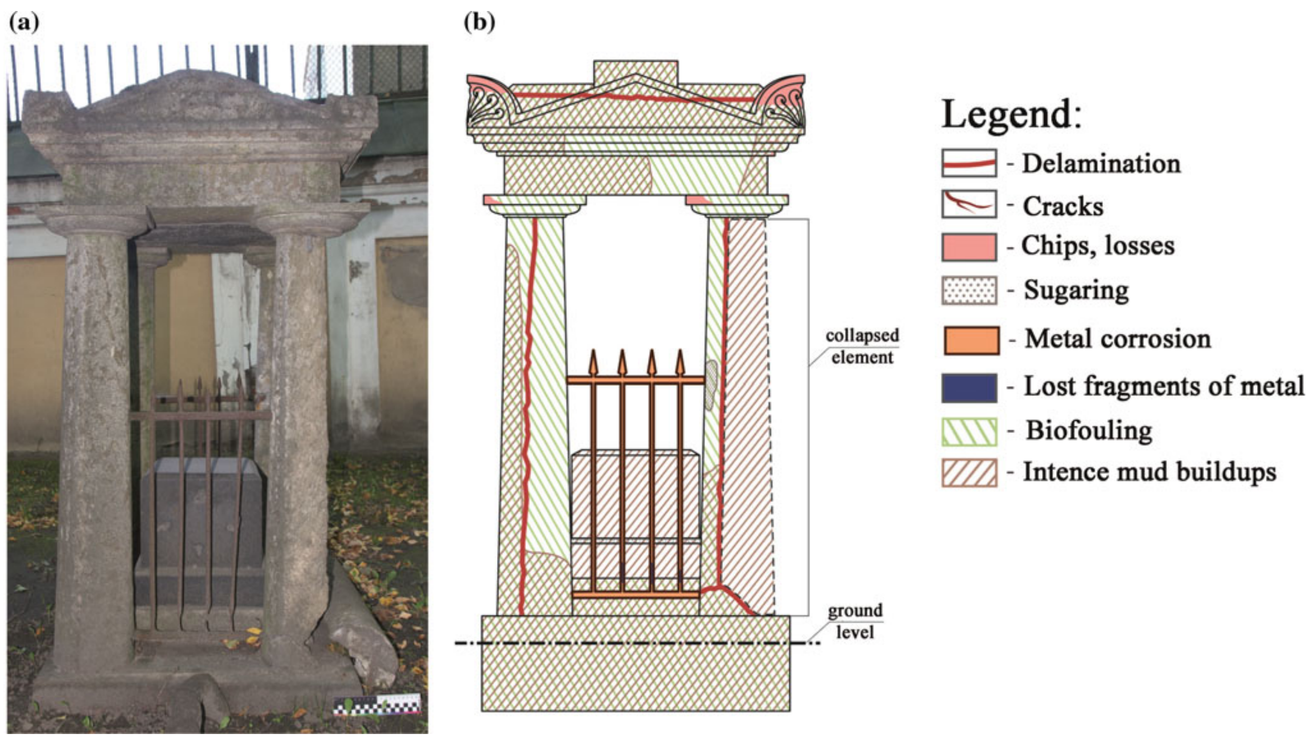

Fig. 5.55 The state of the monument to A.Ya. Potemkina before restoration (2016, the western side): **a** photo, **b** map (legend: delamination, cracks, chips, losses, sugaring, lost metal fragments, metal corrosion, biofouling, intensive mud buildups)

the columns were revealed (Figs. 5.55 and 5.56). The plinth of the limestone sarcophagus was split into two parts. The metal forged railing was entirely damaged by corrosion.

Using the Micron Mobile portable microscope, the specifics of the limestone destruction were studied. Numerous networks of multidirectional micro- and macro-cracks were

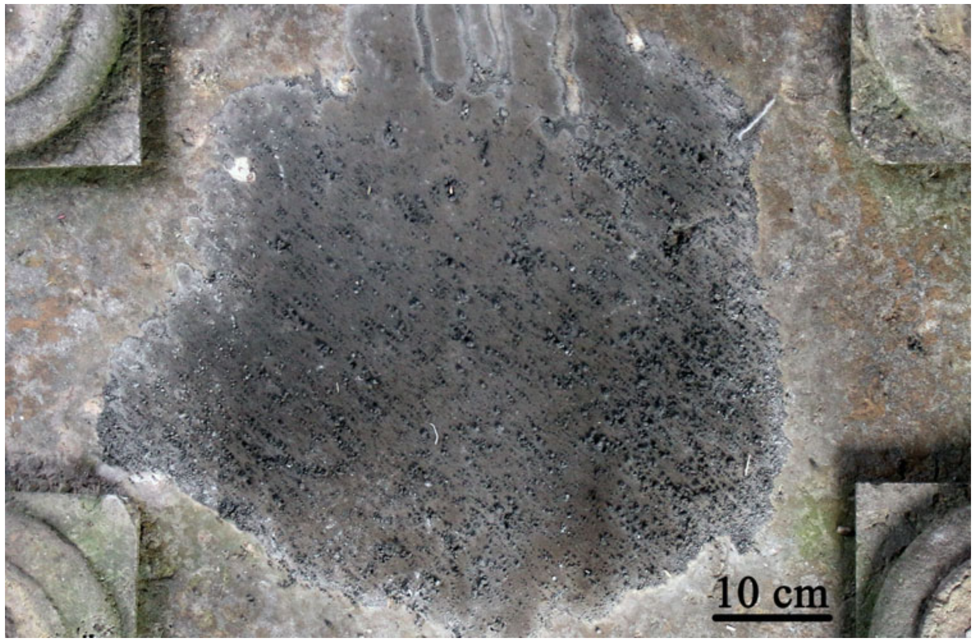

Fig. 5.56 Gypsum-rich patina on the inner surface of the roof of the canopy (before restoration, 2016)

registered, on the inner surface of the canopy roof and two columns (the southwest and northwest), black gypsum crusts formed (Figs. 5.56 and 5.57), which partially flake, which is accompanied by the sugaring of the stone. The presence of gypsum on the limestone surface was confirmed by X-ray powder diffraction (Fig. 5.58). The surface of the monument was covered by intense airborne and biological contaminants (Fig. 5.59). There is an intensive development of thalli of lichens, algal fouling, as well as colonies of dark-colored fungi (Table 5.14). A mycological examination of the monument identified 18 species of microscopic fungi (4800–6700 CFU in the samples), among which dark-colored ones dominated. On the roof of the canopy a continuous cover of moss formed (Fig. 5.53b).

A mineralogical and petrographic study of the stone material of the sarcophagus, conducted by A.I. Savchenok, allowed to establish that it is an intrusive magmatic mafic rock, which can be classified as gabbro-diabase (Fig. 5.60). The EDX analysis of the substance from the surface of the decorative metal band on the sarcophagus (Fig. 5.61) showed that it was made of a copper alloy containing zinc and trace amounts of tin, i.e. brass (No. 1–4, Table 5.15). The presence of an impurity amount of chlorine in the copper alloy (No. 3, 4, Table 5.15) indicates the initial stage of the "bronze disease" (Fig. 5.61b). The fact that the gilding covering the copper alloy contains an admixture of mercury (No. 5–7, Table 5.15), indicates the use of amalgamation (mercury fire gilding).

5.8.2 Restoration of the Monument

Restoration of the gravestone of A.Ya. Potemkina was performed in autumn 2016. The monument was dismantled, and all its parts were transported to the restoration workshop. The most labor-consuming work was connected with the restoration of the portico from Putilovo limestone—a material that is usually used for socles and foundations of monuments and rarely for vertical structures. The stone was washed, biological fouling and an extensive black gypsum crust on the ceiling inside removed. The restorers even called it "the queen of crusts" (Fig. 5.56). The further work was related to strengthening of the stone, masticing of chips and cracks and conservation. During the restoration, the lost fragments of acroteria were recreated. It was not possible to save the two columns, which were in extremely poor condition. By decision of the Restoration Council, they were replaced. The new columns were also cut from the Putilovo limestone, which is still mined in the same quarries near the village of Putilovo (Leningrad region, Fig. 2.31).

Fig. 5.57 Gypsum-rich patina and delamination of limestone (northeast column, before the restoration, 2016): **a** lower part of the column, **b** micrograph of the gypsum crust fragment

During the washing of the sarcophagus, a layer of paint was found on the surface of the decorative band of copper alloy (Fig. 5.61). After removal of contaminants from the surface of the sarcophagus, it became evident that the stone remained polished, and the gilding was preserved on the brass decorative band, with the ornament perfectly visible (Fig. 5.60b).

After the monument was assembled in its historical place in the Necropolis of the 18th century, it was possible to say that the main goal of restoration—to give the monument as much strength as possible and to preserve it for many years—was achieved (Fig. 5.52b).

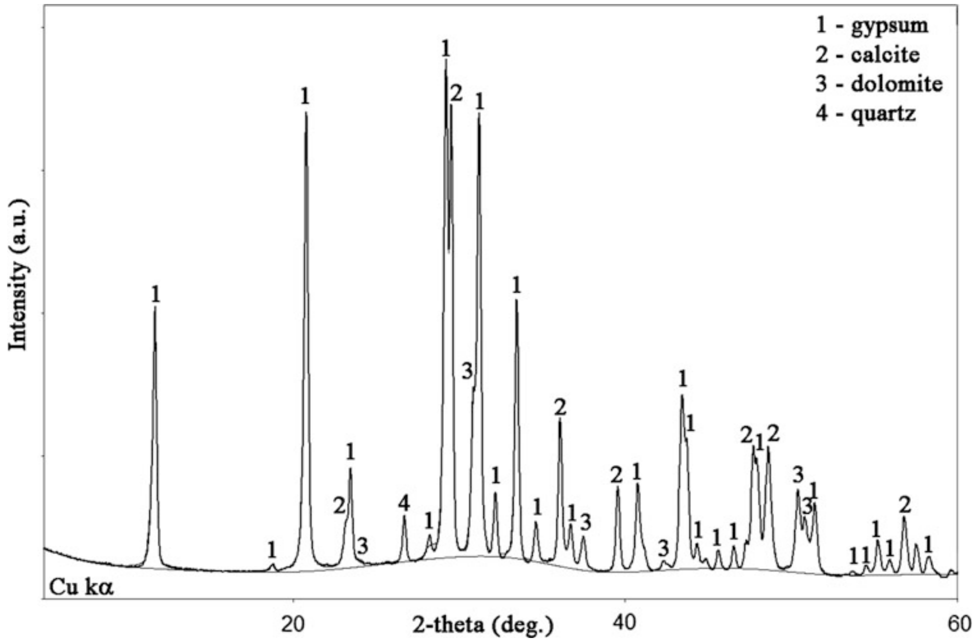

Fig. 5.58 X-ray pattern of the sample taken from the surface of Putilovo limestone prior to restoration (2016). XRD results: gypsum $CaSO_4 \cdot 2H_2O$—main phase, magnesian calcite $(Ca, Mg)CO_3$—much, dolomite $CaMg(CO_3)_2$—little, quartz SiO_2—traces

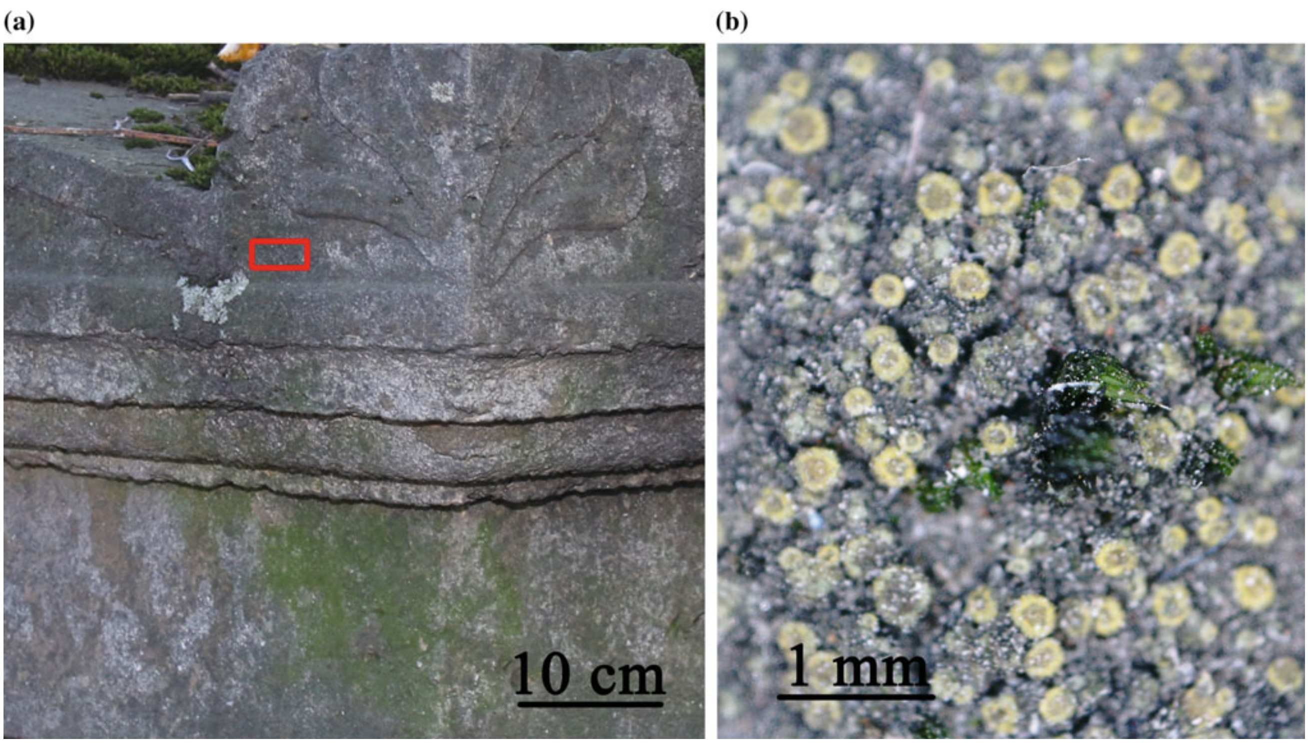

Fig. 5.59 Algae, lichens and mosses on the limestone surface (before restoration, 2016): **a** a fragment of the acroteria of the northeastern side, **b** micrograph of the thalli of crustose lichens and moss turf

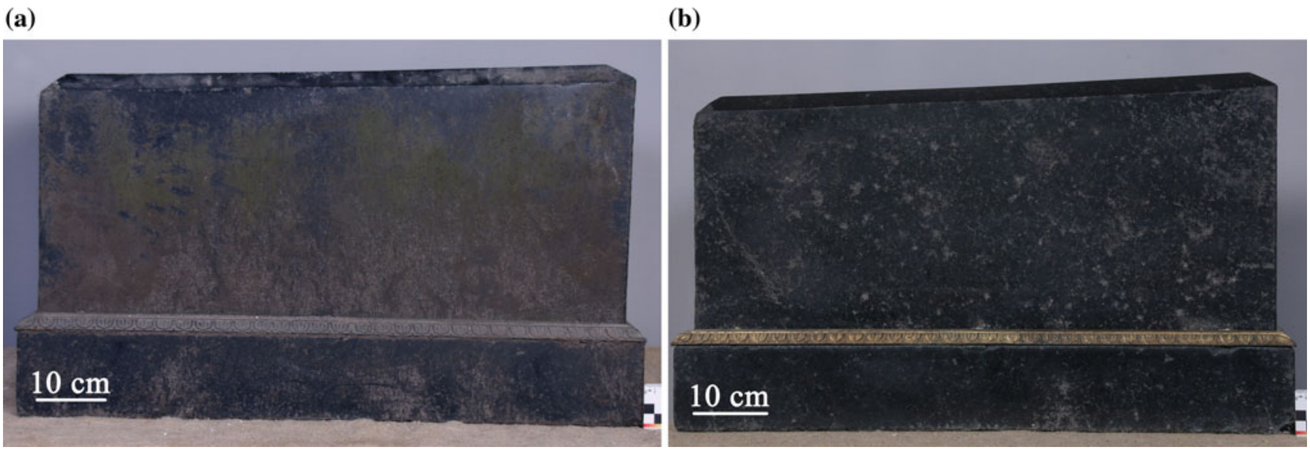

Fig. 5.60 Sarcophagus from the gabbro-diabase from the tomb of A.Ya. Potemkina (photograph of 2016): **a** before the restoration, **b** after the restoration

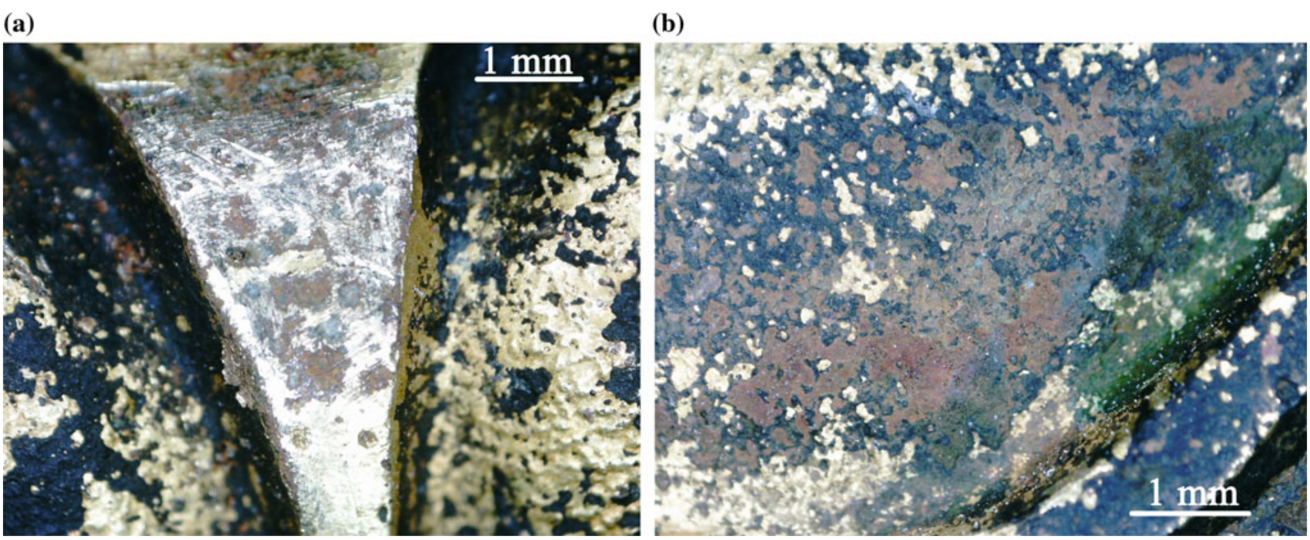

Fig. 5.61 Micrographs of the surface of the decorative band on the sarcophagus being cleaned during restoration: **a** the central part of the band, **b** the edge of the band

Table 5.15 Results of the quantitative EDX analysis (atomic %) substances from the surface of decorative band on the sarcophagus[a]

Surface	No.	Au	Ag	Hg	Cu	Zn	Sn	Fe	Cl	S	O
Of the copper alloy	1	0	0	0	90	5	0	0	0	0	5
	2	0	0	0	73	20	2	0	0	0	5
	3	0	0	0	30	3	2	0	3	2	60
	4	0	0	0	64	2	0	3	7	2	22
Of gilding	5	73	2	3	7	0	0	0	0	0	15
	6	42	1	4	28	7	0	0	0	0	18
	7	37	1	1	35	10	0	0	0	0	16

Note [a]all tests normalized to 100%

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6 Monitoring of the State of Stone and Bronze Monuments

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Abstract

Methods and approaches to be used in monitoring the monument condition are discussed. The main stages of materials science expert analysis are considered. The technique for qualimetric assessment of the integrated condition of the material and various options of mapping the forms of its deterioration are described: those based on the results of visual inspection, ultrasonic sounding, and also using computer technologies, including 3D laser scanning. The potential and efficiency of comprehensive laboratory instrumental methods for studying the material of the monument and the products of its deterioration are analyzed: polarization microscopy, X-ray powder diffraction, scanning electron microscopy, electron microprobe analysis, IR spectroscopy. The design of the database on the state of sculptural monuments in St. Petersburg, for the storage, analysis and structuring of the material gathered during the monitoring, is presented.

Keywords

Monitoring • Expert examination • Qualimetric evaluation • Mapping • Deterioration forms
Ultrasonic sounding • Computer technology
3D laser scanning • Instrumental methods
Polarization microscopy • Scanning electron microscopy
Energy-dispersive X-ray spectroscopy • X-ray powder diffraction • IR spectroscopy • Database

The system of measures for monument preservation (Frank-Kamenetskaya et al. 2003, 2010; Lepeshkina et al. 2005; Ekspertisa 2005; Prognozirovanie 2007; Razrabotka 2009; Kompleksnyi monitoring 2010, 2011, 2013; Nesterov et al 2011) was developed on the basis of complex monitoring, which, at the initiative of the Museum of Urban Sculpture, has been under way in the Necropoleis since 1998 by the joint efforts of scientists, scholars, post-graduates and students of the St. Petersburg State University and the Herzen State Pedagogical University of Russia (Mironova 2000; Nesterova 2000, Lepeshkina 2004; Meschanova 2004, Esipova 2006, Zolotareva 2008, Pamyatniki 2008, Sculptura 2010, Shahov 2011, Vasilieva 2011, Ivanova 2012, Leonova 2012, Muzei 2012, Kuruleva 2013). In this work the professionals of the Military Engineering Technical University, St. Petersburg State Electrotechnical University «LETI», JSC "OPTEC" and other institutions of St. Petersburg took also an active part. Inestimable consultations at various stages of the work were provided by the restorers and experts of the Committee for State Control, Use and Protection of Historical and Cultural Monuments of St. Petersburg.

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6.1 Main Stages of Expert Examination

Detailed materials research examination of the monument state included the following stages:

1. Visual inspection of the object. Photographic documentation. Sampling.
2. Qualimetric evaluation of the integral state of the monument material.
3. Mapping of the types of material deterioration.
4. Examination of the samples of material and products of its deterioration by instrumental procedures.
5. Examination of the species composition of the microbial community on the surface of the monument.
6. Developing a 3D model of the monument and a quantitative estimate of the types of destruction of its material by the results of laser scanning.
7. Archival research.
8. Creating and maintaining a database.

6.2 Visual Inspection of the Object. Sampling

During the visual survey of the monuments, preliminary diagnostics of the materials was carried out, the types of their destruction were identified and photographed, and the places of sampling were determined.

In the diagnosis of stone material, many features of the rock were taken into account; its color, fabrics, (homogeneity, banding, brecciation, etc.); granularity (fine- and medium-grained <1 mm, coarse-grained >1 mm, or inequigranular); presence and species composition of fauna, mineral composition including impurity minerals. The standard description of the types of rock destruction was brought in line with the classification of forms of stone weathering of monuments in St. Petersburg (Fig. 4.1), developed in the light of the international scale proposed by Prof. B. Fitzner (Technical University, Aachen) (Fitzner et al. 1995; Fitzner and Heinrichs 2002). A particular attention was paid to changes in the color and structure of the surface layer of the rock, registering deposits including biofouling of various colors, marked the cracks, micropits and hollows. The size of the hollows, their distribution and shape, usually help to distinguish the signs of weathering from the traces of vandalism.

During visual inspection of bronze monuments, attention was paid to the color of the patina, its density, adhesion to the bronze base and the pattern of its distribution. In addition, the wholeness (continuity) of the artificial protective cover was assessed.

When taking patina samples, we sought not to harm the appearance of the monument. For this, samples were taken in places hidden from the observer's eyes (mainly from the back of the monument). The fragments that have already peeled off from the surface of the monument, were predominantly used. Biological samples were taken from the monument surface using a non-destructive method - the sample from the surface was placed on agarized culture medium.

6.3 Qualimetric Evaluation of the Integral Status of the Monument

Periodic evaluation of the integral status of the monument material expressed in a single number makes it possible to estimate the relative rate of the monument deterioration and establishes a solid basis for planning conservation and restoration work and their priority. If this assessment is made before and after restoration, its results can be impartially evaluated.

When assessing the state of the monuments in museum Necropoleis, the qualimetric examination was applied (Frank-Kamenetskaya et al. 2003, 2010; Bulakh and Marugin 2009, 2013; Vasilieva et al. 2011; Bulakh 2012; Marugin and Bulakh 2014), which allowed to estimate the current state of the material Q using a single number changing from zero (total destruction) to one (ideal state).

Q was determined according to the formula:

$$Q = \prod_{i=1}^{n} q_i^{\alpha_i}, \qquad (6.1)$$

where Q is the required relative index of the overall state of the material; q_i - the i-th local parameter of the state of the material

$$0 < q_i \le 1; \qquad (6.2)$$

n—is the number of local parameters used for calculation at a certain level of detail; α_i—the weight coefficient of the i-th particular parameter

$$0 \le \alpha_i < 1, \qquad (6.3)$$

$$\Sigma_{\alpha_i} = 1 \qquad (6.4)$$

The degree of the monument deterioration was determined from the ratio:

$$\Delta Q = 1 - Q \qquad (6.5)$$

In an ideal state, $Q = 1$, $\Delta Q = 0$; with full destruction $Q = 0$, $\Delta Q = 1$.

Previously multilevel calculation models were designed to assess the state of stone and bronze monuments (Tables 6.1 and 6.2).

The choice of morphological particular parameters characterizing the deterioration of stone material (Table 6.1) was made according to the classification of anthropogenic forms of stone weathering (Fig. 4.1). For bronze monuments, the characteristics used in the pre-restoration expert examination of the state of the monument (mechanical damage, natural and

Table 6.1 Calculation model for qualimetric evaluation of the state of stone by morphological parameters (Expertise 2005)

I level of detail	II level of detail	III level of detail	
Local parameter			Weight of α_i, unit fractions
1. Stone loss	1. Background weathering	1. Background weathering	0.005
	2. Selective relief weathering due to crumbling and corrosion	2. Roughening of the surface	0.065
		3. Formation of pits and hollows	0.08
	3. Break out due to non-recognizable cause (anthropogenic, constructional etc.)	4. Break out due to non-recognizable cause (anthropogenic, constructional etc.)	0.003
	4. Detachment	5. Detachment of stone	0.09
		6.* Detachment of the primary gypsum crust with stone material	0.09
		7.* Detachment of the secondary gypsum crust with stone material	0.11
2. Deposits	5. Gypsum crust	8.* Primary gypsum crust	0.085
		9.* Secondary gypsum crust	0.10
	6. Biological colonization	10. Biofilm with dominant micromycetes	0.02
		11. Biofilm with dominant algae	0.02
		12. Biofilm with dominant lichens	0.02
		13. Mosses and seed plants	0.01
		14. Bird droppings	0.01
	7. Dirt depositions	15. Airborne pollution	0.03
		16. Anthropogenic pollution	0.002
3. Mechanical damage	8. Fissures	17. Fissures	0.13
	9. Deformation	18. Deformation	0.13

Note * - Parameters marked with an asterisk characterize the state of carbonate rocks only

Table 6.2 Calculation model for qualimetric evaluation of the state of copper and copper alloys by morphological parameters (Vasilieva et al. 2011)

I level of detail	II level of detail	
Local parameter		Weight of α_i, unit fractions
1. Deposits	1. Corrosion film	0.16
	2. Biological stains	0.02
	3. Airborne pollution	0.04
	4. Anthropogenic pollution	0.07
	5. Protective layer	0.13
	6. Bird droppings	0.09
2. Mechanical damage	7. Damage to surface homogeneity	0.11
	8. Dents	0.18
	9. Loss of fragments	0.20

synthetic buildups) were selected as morphological particular parameters (Table 6.2). The contribution of the particular parameters to the deterioration of the material was estimated on the basis of a field survey, first on a 5-point scale (5, 4, 3, 2, 1), and then passing on to the qualimetric one (from 0 to 1): 0, 0.25, 0.50, 0.75, 1 (if the degree of material preservation Q was calculated) and 1, 0.75, 0.50, 0.25, 0 (if the degree of material destruction ΔQ was calculated).

The relative area of a particular type of destruction was used as a measure for determining the development of various types of weathering. The values obtained were corrected for the depth of damage or the thickness of the

Table 6.3 Results of the evaluation of the state of the statuary marble of A.Ya. Okhotnikov's monument in the Necropolis of the 18th century by morphological parameters (2001)

Local parameter	Contribution to deterioration (on a 5-point scale)	Notes
1. Background weathering	2	Minor, found on the sculpture of the mourner
2. Roughening of the surface	2	On the chest of the mourner, in the folds of her robes
3. Formation of pits and hollows	1	None
4. Break out due to non-recognizable cause (anthropogenic, constructional etc.)	1	None
5. Detachment of stone	1	None
6. Detachment of the primary gypsum crust with stone material	1	None
7. Detachment of the secondary gypsum crust with stone material	1	None
8. Primary gypsum crust	2	On the left side of the neck and in the folds of the robes (under the bent arm)
9. Secondary gypsum crust	1	None
10. Biofilm with dominant micromycetes	3	On the mourner's robes, marble slabs
11. Biofilm with dominant algae	4	On marble slabs, the sculpture of the mourner, the broken tree
12. Biofilm with dominant lichens	2	In small amounts on the mourner's robes and marble slabs
13. Mosses and seed plants	1	None
14. Bird droppings	1	None
15. Airborne pollution	3	A thin, non-continuous coat over the whole surface
16. Anthropogenic pollution	1	None
17. Fissures	2	Numerous small cracks on marble slabs; a large crack extending from the left arm farther to the middle of the back
18. Deformation	1	None

Note According to the calculation results, the degree of marble deterioration is $\Delta Q = 14\%$

buildup. When assessing the state of a bronze memorial, the value of the particular parameter of the corrosion film was determined with account taken of its phase and elemental composition. An example of evaluation of the state of marble of one of the monuments of the museum Necropoleis is given in Table 6.3; that of bronze—in the Table 6.4.

6.4 Mapping of Forms of Deterioration of the Monument Material

Maps of the forms of deterioration of the stone material (Figs. 5.2 and 5.9), being visual representations of the results of the examination of stone monuments, are constructed from the photographs made during the visual survey, using graphics software.

In mapping, a special attention was paid to the evaluation of fracturing, which requires taking appropriate preventive and restoration measures in the shortest possible time. Ultrasonic sounding was used to detect heterogeneities of the rock material invisible from the surface (Chan et al. 2008; Nesterov et al. 2011). The promising nature of this method is due to the fact that the propagation velocity of ultrasonic waves in the material directly depends on its density. The lower the speed, the more significant is density inhomogeneity, the greater the probability of cracks, microcavities, micro-fracturing invisible from the surface.

Table 6.4 Results of evaluation of the state of the bronze of V.F. Komissarzhevskaya's monument by morphological parameters (2008)

Local parameter		Contribution to deterioration (on a 5-point scale)
1. Deposits	1. Corrosion film	4
	2. Biological stains	2
	3. Airborne pollution	2
	4. Anthropogenic pollution	1
	5. Protective layer	2
	6. Bird droppings	3
2. Mechanical damage	7. Damage to surface homogeneity	3
	8. Dents	1
	9. Loss of fragments	1

Note According to the calculation results, the degree of bronze deterioration is ΔQ = 34%

Ultrasonic sounding of the Necropoleis monuments was performed with *Pulsar 1.1* non-destructive testing device using two techniques (Table 6.5): (1) The sensors are located on different sides of the tested object (through-transmission sounding); (2) Sensors are located on one side (surface sounding). Surface scanning was performed if the shape of the object (slab, lid of a sarcophagus) or its position precluded through sounding. The measurements were taken along the profiles, spaced at intervals of 100–300 mm, depending on the size of the monument. The ultrasonic velocity was calculated dividing the distance between the emitter and the receiver by the measured time. Ultrasound propagation velocity maps were constructed using the *Surfer* software.

To assess the degree of density inhomogeneity of the material, the coefficient

Table 6.5 Examples of evaluation of mechanical damage to stone materials of the Necropoleis monuments by ultrasonic sounding

Monument	Method of sounding	Measurement results				
		V_{max} (m/s)	V_{min} (m/s)	K · 100 (%)	S (m)	ΔQ_{mech} (%)
Shokshinsky quartzite						
1. Unknown (N-18 No. 959)	Surface	6400	3600	44	0.2	35
Gray fine- and medium-grained granite, granodiorite						
2. E.M. Kozlovskaya	Surface	5200	4300	17	0.5	23
3. O.S. Pavlischeva		5980	5380	10	0.3	14
4. V.V. Vyazemsky		8000	3600	55	0.2	40
5. V.I. Panayev		7650	7050	8	0.2[a]	11
6. S.M. Yakovlev		6100	5200	15	0.5[a]	21
White homogeneous marble						
7. E.I. Zagryazhskaya	Through	3200	1200	62	0.2[a]	44
8. A.Ya. Okhotnikov		4872	1348	72	–	–
9. E.I. Kokoshkina		4900	2000	59	0.15	39
10. Unknown (N-18 No. 907)		5200	1400	73	0.20	49
11. Unknown (N-18 No. 984)		4800	2000	58	0.85	65
12. Unknown (N-18 No. 984/1)		5500	1600	71	0.25	52
Gray marble						
13. I.A. Apaischikov	Surface	5600	4000	29	0.25[a]	27
Flaglike limestone						
14. V.F. Velyaminov-Zernov	Surface	3400	1200	65	0.1	37
Calcareous tufa						
15. Unknown (N-18 No. 901)	Surface	3150	1650	48	–	–
16. Unknown (N-18 No. 958)		2800	900	68	0.4	58

Note [a]Based on the results of visual analysis of maps

$$K = ((V_{\max} - V_{\min}) / V_{\max}) \cdot 100 \quad (6.6)$$

was calculated, where $V_{\max,}$ $V_{\min}$ are maximum and minimum velocities of ultrasound transmission, respectively. The value of $V_{\max}$ characterizes the densest (trouble-free) zones of the rock, $V_{\min}$—the most heterogeneous, problem zones. For each object, ultrasonic velocity maps were plotted using the *Surfer* program (Figs. 6.1 and 6.2), where the transitions from dense zones with high speed to problem zones with low speed were clearly visible.

Evaluating the degree of mechanical damage of the stone material of the monument (ΔQ_{max}), the degree of its density inhomogeneity (K) and the relative area of the least dense zones characterized by the minimum ultrasound velocity (S) were taken into account. Calculation was performed by multiplying the values of these parameters, with the corresponding weight coefficients (α_1, α_2):

$$\Delta Q_{max} = K^{\alpha 1} S^{\alpha 2} \quad (6.7)$$

According to the above relation (6.4), used for qualimetric evaluation of the overall state of the object by the set of parameters, the sum of the weights was normalized: $\alpha_1 + {}_2 = 1$. Considering the fact that the contribution of the coefficient K predominates, α_1 was taken equal to 0.7; and α_2—to 0.3. The value of S was obtained from the finalized maps.

On the ultrasound transmission maps (Figs. 6.1 and 6.2), it is clearly seen that the inhomogeneous problem zones (with the minimum velocity of ultrasound) are confined both to the cracks observed from the surface and to the areas that seemed quite trouble-free during the field surveys. Thus, the approach used is reliable and provides additional information on the mechanical damage of stone materials of the monuments.

The maximum ultrasonic velocity in the examined stone materials (Table 6.5) varies from 8000 in hard rocks (quartzite, granites) to 2800 m/s in soft rocks (limestones). The degree of density inhomogeneity (K) is from 8 to 73%, mechanical damage of the rock (ΔQmech)—from 11 to 65%.

The degree of deterioration of monuments made of the same rock differs, which, in particular, is also related to their shape. Monuments of a more complex shape (sculptures, vases) are very vulnerable to the effects of aggressive factors of the environment and are usually in a poorer shape than monuments of a simpler design. From the data in Table 6.5 it follows that the monuments of a rather simple shape from homogeneous gray fine- and, medium-grained granites and granodiorites (ΔQmech < 20%) are least weathered. Those to deteriorate most strongly are monuments of limestone (ΔQmech ~ 60%) and sculptures of marble (ΔQmech = 39–65%).

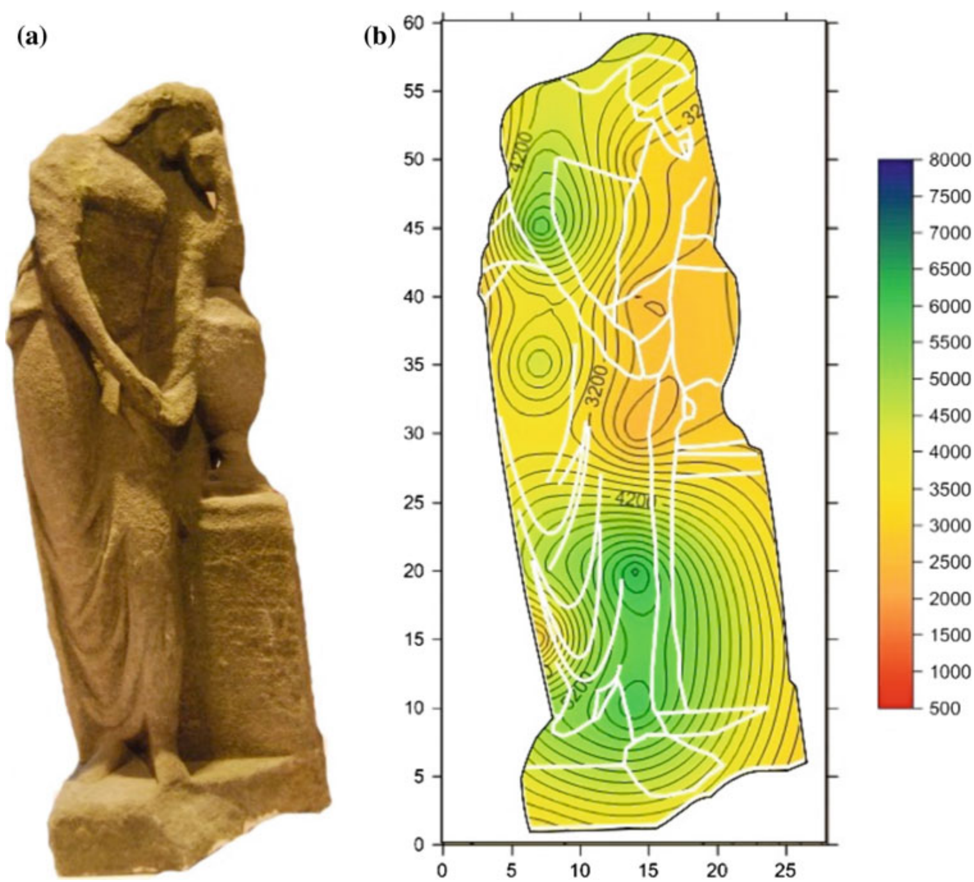


Fig. 6.1 Monument to the Unknown (N-18 No. 907) from marble in the Necropolis of the 18th century (Shahov 2011): **a** photo; **b** map of ultrasound velocity

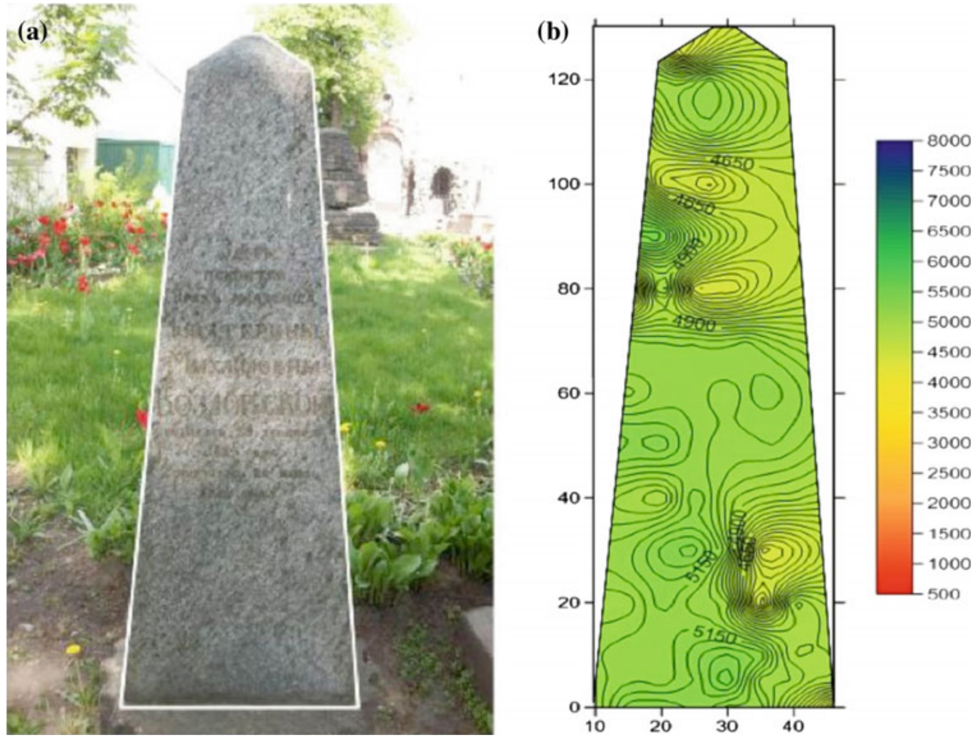


Fig. 6.2 Monument to E.M. Kozlovskaya from granite in the Necropolis of the 18th century (Shahov 2011): **a** photo; **b** map of ultrasound velocity

6.5 Mapping of Monument Biofouling Using Computer Technology

One of important practical tasks is the search for rapid methods of monument monitoring, allowing to assess their changes over relatively short periods of time. Obviously, in this case, the indicators should be chosen that could reflect such changes. Biological objects (biofouling) that develop on the surface of the monument causing damage to it can serve as such indicators. The rate of their development can be very high in the presence of favorable conditions. So, for example, in the conditions of St. Petersburg, during one vegetation period (from May to October) the extent of biofouling development changes very significantly. This can be observed on the monuments from various rocks (carbonate and silicate). The rate of development of biofilms with the predominance of aerophilic algae is particularly high. The marble sculptures get green in the humid years very fast. The same picture can be also observed on granite monuments, especially those under woody plants.

Development of a method for monitoring the biofouling of cultural heritage sites using computer technology (Shigorets et al. 2009; Grishkin et al. 2014) allows to register the areas of the most threatened biodeterioration sites, and the rate of changes in them, which is especially important for pre-restoration surveys.

This approach is based on the idea of identifying the main groups of macro- and microfouling by their spectral and color characteristics. The development of the CONSOLIDATOR-BIO software, which allows assessing changes of the stone monuments' surface based on the color characteristics of objects can be considered the first stage in the creation of such system (Shigorets et al. 2009). Then it was shown that the spectral characteristics are among the more informative indicators of biofouling of the natural stone (Shigorets et al. 2014). To assess the fouling of monuments, the images obtained in the visible (RGB) and near infrared (NIR) spectral regions are analyzed (compared). The photos can be made with a digital camera using special filters. For shooting in the IR range, the HOYA-R72 720 nm filter was applied. Photographs were taken with a CANON EOS 500D camera mounted on a tripod. Subsequently, the image analysis was carried out with a special software calculating the formal indices, such as NDVI, ENDVI and the like, which indirectly characterize the spectral properties of biological objects.

The main stages of the image processing and analysis are as follows.

The first step is to bring a series of images to a single camera angle. This function is necessary for the comparative analysis of images in a series, as well as for processing the images of an object photographed in the visible and near infrared ranges. Image alignment can be performed in both automatic and manual modes. The manual mode is for those images that cannot be automatically aligned. This operation can be performed if you bring all the images to the same base image in the series, selected by an expert. For each image in the series, a transformation matrix is calculated on the basis of the key (reference) points on it, which is used to align the current image with the survey point and the angle of the base image.

Another function of the preliminary processing is the separation of the image of the monument from the background (segmentation of the image). This procedure is performed once using interactive segmentation algorithms for the base image, after which the result is extended to other images in the series. As a result of segmentation, a series of images of the object of interest alone is obtained with no background.

The next stage of image processing involves the recognition and classification of biological objects using computer software based on modern mathematical algorithms built on the calculation of attribute vectors (Registration Certificate No. 2014662061 of 21.11.2014).

The attribute vector is a set of different vegetation indices. Calculations of each index are made from a combination of brightness values and their transformations in certain image channels. To recognize the types of biofouling, a previously "trained" classifier is used based on the on support vector machine (SVM). It is important to emphasize the role of the expert in the "training" of the classifier. The expert analyzes the images and points out the areas that belong to a particular type of biofouling, as well as the areas related to the material of the monument (free from biofouling). "Training" of the classifier can take place with several images of objects with typical forms of biofouling. The "training" process is going on using the cross-validation method, and the received data is accumulated in the database and can be used in the analysis of the forthcoming images.

As a result, processing the images, the software can map the biological fouling of monuments with a sufficiently high degree of reliability, showing the ratio of biological objects. According to the monument map, percentages are calculated of the areas occupied by one or other biological object. The changes in the status of the monument over the period that elapsed since the last inspection are determined by comparing the current map and its parameters with the map from the previous observation. With the help of these estimates, the expert can decide on the need for specific measures to preserve the monument.

This method is not without a certain error associated with the technology of photographic work, the illumination of the object, the presence of a shadow. However, this error is insignificant (usually not more than 5%) and does not affect the overall pattern of biofouling distribution. The reliability of the fouling distribution estimates is provided statistically due to the multiple (repeated) selection of standard fouling forms at the stage of "training" the software.

Let us list the advantages and disadvantages of the method:

Advantages:

- Low labor intensity (no special equipment is required, except for a digital camera and a set of filters);
- ability to monitor many monuments;
- the method is convenient for rapid assessment of the status of monuments;
- ease of use due to automation of image processing.

Disadvantages:

- dependence on the illumination of the object;
- dependence on the relief or shape of the monument;
- a relatively rough estimate of the state of the monument.

From 2014 to 2016, the developed method was used to assess the current status of monuments of the Museum Necropoleis (Tables 6.6), as well as to assess the effectiveness of conservation work on a number of monuments (Tables 6.7).

Using the example of the bas-relief on the monument to N.V. Smirnov in the Necropolis of the 18th century (Fig. 6.3), changes in the biofouled area (after protective treatment) over time were investigated. The estimates of biofouling development were made before cleaning, immediately after cleaning and 1 year after cleaning the monument (Table 6.7).

The obtained data indicate that as a result of cleaning the monument from biological damage, the biofilm with algal dominance was removed almost completely, while the biofilm with domination of fungi—only in part (17% decrease in color intensity) because of the persistence of dark pigments—melanins making up part of the cellular wall of microscopic fungi. In a year's time, a noticeable resumption of biofilm growth is observed (the area of those with algal dominance grew by more than 1%, and of those with the dominance of fungi—by 5.7%). The overall shrinkage of the clean stone surface after 1 year was almost 7%. These results point to the need for constant monitoring of the monument's status, as well as periodic protective treatments.

In general, the approbation of the proposed approach has shown its effectiveness in the recognition of biofouling of the monuments from various types of stone. Using computer technology, it is possible to classify (up to a certain level of detail) the types of biofouling, assess the stage of their development, determine the percentages of the main forms of biofouling, and compile maps of the deterioration of the monument. Further development of this method is associated with the expansion of spectral ranges, which can provide new information about biological objects.

Table 6.6 Assessment of the extent of biological deterioration of monuments using computer technology for mapping the biofouling

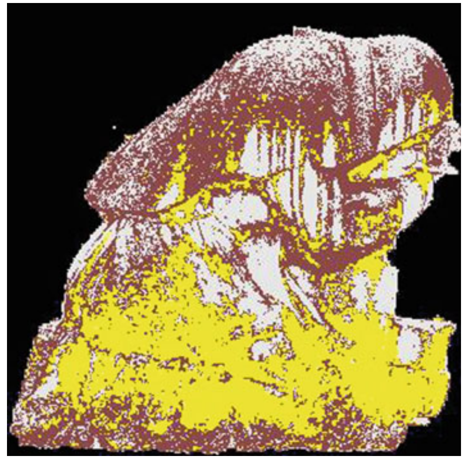
Image of the monument	Map of biofouling	Results of image processing (development of fouling, %)
The mourner (*Museum Necropolis of the 18th century*)		
		Biofilm with dominant algae (color yellow): 33.4 ± 1.4 Dark biofilm with domination of dark-colored micromycetes (color brown): 40.0 ± 1.9 Clean stone: 26.9 ± 2.1
Monument to A K. Haller (*Museum Necropolis of the 18th century*)		
		Biofilm with dominant algae: 59,0 ± 2,8 Clean stone: 41.0 ± 2.8

Table 6.7 Evaluation of the effectiveness of the protective treatment of the monument to N.V. Smirnov

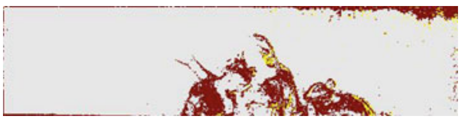
Cartogram of fouling	Development of fouling (%)
Before cleaning	
	Biofilm with dominant algae (color yellow): 25.8 ± 0.9 Black biofilm with dominance of micromycetes (color brown): 22.8 ± 1.1 Clean stone: 51.4 ± 2.1
After cleaning	
	Biofilm with dominant algae 0.1 ± 0.02 Black biofilm with dominance of micromycetes (color brown): 6.1 ± 0.9 Clean stone: 93.8 ± 2.9
1 year after cleaning	
	Biofilm with dominant algae (color yellow): 1.4 ± 0.08 Black biofilm with dominance of micromycetes (color brown): 10.9 ± 0.7 Clean stone: 87.7 ± 2.7

Fig. 6.3 Marble bas-relief of the monument to N.V. Smirnov with biofilms before biocidal treatment

6.6 Quantitative Estimate of Monument Deterioration with 3D Laser Scanning

3D laser scanning (Beraldin et al. 1998; Levoy et al. 2000; Fontana et al. 2003; Freydin and Parfenov 2007; Tishkin and Parfenov 2012; Parfenov 2016) is a new and very promising method for monitoring the monuments located outdoors. This technology makes it possible to create 3D computer models ("virtual copies") of monuments with accurate information about their size and geometric shape, and also allow for quantitative measurements of various kinds of damage to the monument materials. This is extremely important for both analyzing the state of monument conservation, and for planning and evaluation of the results of restoration (especially in case of damage to the monuments due to natural disasters or attempts by vandals). The accuracy of measurements of the modern laser scanners is on the order of fractions of a millimeter, which makes it possible to use these instruments for reliable documenting and detailed study of the condition of cracks, chips, scratches, gypsum crusts, corrosion spots (in the case of metal monuments), and other types of surface damage. For example, this offers a possibility to determine the length and width of cracks, the area of surface where partial crumbling of stone occurred, and in the case of monuments of marble and limestone, also the size of gypsum crusts.

In recent years, laser 3D scanning technology is increasingly being used abroad to monitor exterior monuments (Boochs et al. 2008), but in Russia it has not yet become widespread. Perhaps the only example of its use in this country is scanning of the figure of the mourner on the monument to A.Ya. Okhotnikov in the Necropolis of the 18th century (Fig. 6.4), performed in 2010 by a group of experts from the St. Petersburg "LETI" State Electrotechnical University and the St. Petersburg "Resstroy" Restoration Company.

In the course of this work, *Konica Minolta Vi-9i* scanner (manufactured in Japan) was used, which can offer the accuracy of measuring the relief of the examined surface at a level of 50–100 μm. Scanning was performed "in the field"—right in the Necropolis of the 18th century. The monument was scanned from a distance of about 1 m from its surface. The obtained set of scans was processed in the laboratory with special *RapidForm XOR3* computer software.

As a result, a high-precision 3D model of the figure of the mourner was created, containing exhaustive information about its dimensions and shape. After that, using the same software, the reconstructed surface areas of the sculpture were identified, where various forms of marble deterioration made themselves manifest (Fig. 5.20b) and the corresponding surface areas were evaluated (Table 5.5). The obtained results showed (see Sect. 5.3.2) that laser 3D scanning can be a good complement when analyzing the state of the material of the monument according to the qualimetric expertise. The reviewed approach allows to make a quantitative analysis of the surface defects of sculptures, in particular, to determine the length and average width of surface cracks to within a fraction of a millimeter, and the area of gypsum crusts to within a tenth of 1 cm^2.

The experience gained in this work allows us to draw some conclusions and formulate a number of practical recommendations on monitoring with 3D laser scanning:

1. To scan the sculpture, it is necessary to use laser or optical 3D scanners with the highest possible measurement accuracy (at least 0.05–0.1 mm) and resolution (at least 75–150 μm). To date, the greatest accuracy of measurements is provided by laser scanners of triangulation type or optical scanners which operate illuminating the object with structured white light (Sansoni and Docchio 2005).
2. In addition to the correct choice of the type of scanner used for measuring (i.e., with its accuracy taken into account), it is necessary to use multifunctional software in laser scanning, that should ensure high accuracy of combining individual scans at the stage of 3D model assembly and the necessary quantitative measurements in the analysis of the state of the monument surface. A great role in ensuring high accuracy of the created 3D-model is played by the professional skills of experts who perform scanning and subsequent "cross-linking" of individual scans into a single point cloud. This work should be carried out by technical personnel with extensive experience in scanning objects of cultural heritage.
3. Because in the course of scanning the information on small areas of the surface may be lost due to bright sunlight and the glare of laser radiation from the polished surface of monuments, it is desirable to do this work in the dark at night, or use special sunscreens.
4. The most labor-intensive operation in laser scanning is the creation of 3D model. Therefore, during the monitoring, it is not necessary to perform scanning and subsequent assembly of the 3D model of the whole sculpture every time. With repeat scanning, it is sufficient to do this work only on the «problem» areas of the monument's surface in order to identify changes that have occurred since the previous scan. Taking into account the high labor intensity, and, correspondingly, the cost of laser scanning, it is

Fig. 6.4 Laser scanning of the monument to A.Ya. Okhotnikov (2010)

advisable to do this work no more often than once every 1–2 years. However, in the case of severely damaged monuments or high erosion rates, scanning should be performed at intervals of several months.

It is important to note that in addition to 3D scanning, simultaneous high-quality digital photography of monuments can be useful in order to capture the state of their surface.

6.7 Study of Monument Material and the Products of Its Deterioration by a Complex of Instrumental Methods

In order to study the material of the monument and the products of its deterioration in the lab conditions, a set of sufficiently accessible instrumental methods was chosen.

For mineralogical and petrographic description of samples and thin sections of the stone material, ***binocular and polarization microscopy*** was used at the initial stage of the study. Thus, information was obtained on the main mineral composition of the rock, its homogeneity, grain -size composition and fabrics (for example, banding, brecciation, etc.). These data in many cases made it possible to redefine previous visual diagnosis of the rock and to tentatively determine its origin, comparing the samples to the reference ones (Figs. 2.3, 2.12, 2.15, 2.19, 2.30, 2.36, 2.40, 2.47 and 2.51). Microscopic methods were also used for the preliminary assessment of the mineral composition, structure and density of patina from the surface of bronze monuments.

Scanning electron microscopy was used for examination of the microstructure of the stone surface and assessment of its porosity. Using this method, the initial stages of deterioration of the monument's material invisible with a naked eye were discovered, and the structure of deposits on its surface, including biofilms, was studied (Figs. 4.11). In the case of carbonate rocks this is the only method allowing to penetrate into complex biomineral interactions occurring on the surface of the monument, to study the morphology of the crystals of the secondary minerals being formed (Figs. 4.13–4.16).

The elemental composition of rock-forming minerals and stone deterioration products was determined by energy-***dispersive X-ray spectroscopy analysis*** (*EDX*) (Fig. 5.3). Using this method, individual grains of impurity mineral phases were also detected, present in trace amounts.

The joint use of scanning electron microscopy and X-ray spectral microanalysis made it possible to study the laminated structure of patina from the surface of bronze monuments at the microlevel and, especially, the distribution of main minerals in it (Fig. 4.20).

Refinement of the diagnosis of the mineral composition of the stone material and the products of its deterioration, as well as that of the materials appearing on the surface of the monument as a result of previous conservation and restoration work was performed by ***X-ray powder diffraction*** (*XRD*) (see Chapter 2; Sects. 4.3, 4.4 and others). The agreement between the results of this method and petrographic findings was a reliable guarantee of their authenticity and made it possible to identify errors of both methods. The same approach was used to determine the basic phase composition of the crystalline component of the patina from bronze monuments.

When studying the phase composition of patina from the surface of copper and bronze monuments, ***IR spectroscopy*** was also used. This method proved to be very effective in determining the phase composition of X-ray amorphous patina from the surface of bronze monuments (see Sect. 4.4). In this way it was possible, for example, to establish that there are much more copper carbonates on the surface of the bronze monuments in the museum Necropoleis than it appeared following the results of X-ray phase analysis.

Identification of the species composition of the microbial communities on the surface of the rock substrate (fungi, algae, lichens, mosses) was performed by biological methods (Vlasov et al. 2001) using special identification guides.

6.8 Creating and Maintaining a Database

One of the most important stages in monitoring the state of the monuments was creating and populating a specialized database used to store, analyze and structure the accumulated factual information (Razrabotka 2009).

The *database* on the state of the sculptural monuments of St. Petersburg includes three major units (Fig. 6.5):

- the reference book "Materials of monuments and specifics of their deterioration",
- section "General",
- section "Results of Expert Surveys".

The reference book "Materials of monuments and specifics of their deterioration" provides data on the stone in the architectural and sculptural monuments of St. Petersburg and the processes of its deterioration. This reference book is very important, as it makes it possible to collect a lot of interesting knowledge published in various sources making it easily accessible.

In the database all monuments are divided into groups on an area basis. In the "General" section, historical background, the names of the sculptor and/or architect, a detailed description of stone and other materials, dates and scope of restoration and conservation work are provided for each

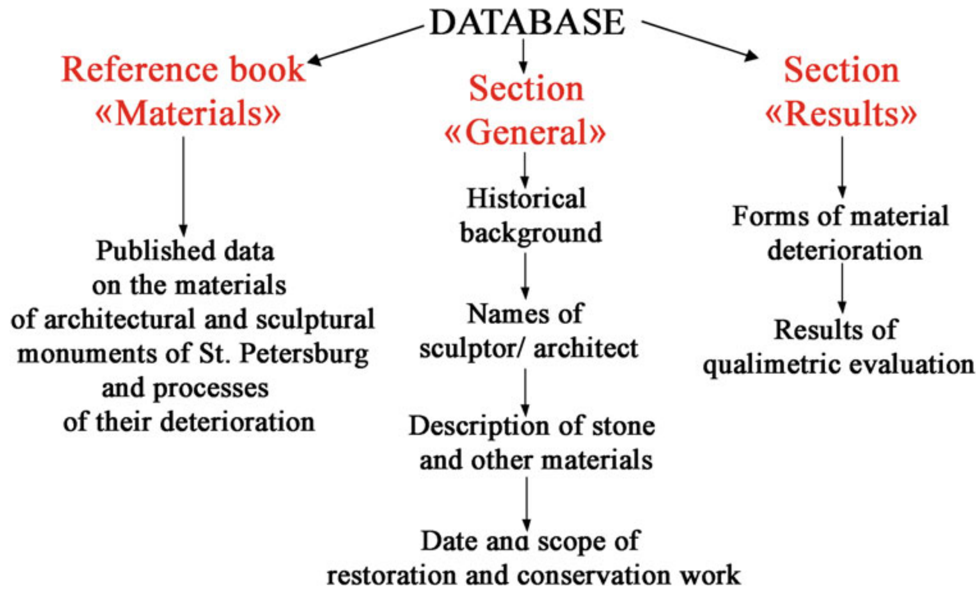


Fig. 6.5 Structure of the database on the state of the sculptural monuments in St. Petersburg

monument. The location of the monument is indicated with reference to the area and flagged on the sketch map.

In the section "Results of expert surveys", the information from dated expert analyses of the materials of each monument is presented. The state of each monument is described by tables and photographic documents that are arranged in the following order:

1. Forms of material deterioration.
2. Maps of the forms of deterioration. Maps of all visually observed forms of deterioration (seen on the surface), as well as the maps of internal density heterogeneities of materials, obtained by measuring ultrasonic transmission rates are presented.
3. Results of qualimetric evaluation of the integrated state of each of the stone materials and the material of the whole monument.
4. Results of laboratory studies of the material and products of its destruction. Descriptions of the samples and their location are given.

The results of the study are structured according to the following methods: light microscopy, X-ray phase analysis, microprobe spectral analysis, isolation of microorganisms by inoculating a nutrient medium with them, scanning electron microscopy, etc.

At the end of the summary of each examination there is the experts' opinion on the state of the monument and recommendations on the necessary conservation and/or restoration measures.

The database on the state of the sculptural monuments of St. Petersburg has been on the Web since 2007, now it is on the site: www.opticalcomponents.ru.

The database software allows for:

- the search for the given text in the specified field;
- the advanced search, over several fields and specified words simultaneously;
- search on the map;
- sorting in the specified field;
- quick links to the sections of the article (table of contents);
- managing/editing with the user's login/password.

Using an appropriate query, one can get information about each monument, select objects that match a specific criterion (material, author, year of creation, characteristics in the historical reference, number on the map) or a number of criteria.

The base is intended for museum staff and restorers, as well as professionals in various fields of knowledge (geologists, biologists, chemists, engineers, etc.) dealing with urban ecology and its influence on cultural heritage sites.

Currently, the database includes characteristics of the state of 650 stone and 40 bronze monuments in the Necropoleis of the Museum of Urban Sculpture and in other parts of St. Petersburg. Its organization allows to update the characteristics of the state of monuments as the new information becomes available, populate the bank with new objects. Creation of the database opened new opportunities for monitoring the state of urban monuments and studying the mechanisms of their deterioration. The researchers have got a perfect tool allowing to make scientific predictions of changes in the state of monuments and plan the performance, priority and frequency of conservation and restoration work. This approach makes it possible to assess the efficacy of measures to preserve cultural heritage monuments, reduce the costs of their restoration and avoid irreplaceable losses of unique objects.

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7 Methods of Monument Protection from Damage and Their Performance

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Abstract

The experience of the Museum of Urban Sculpture in chemical protection of stone monuments from biodeterioration is discussed. The effectiveness of various chemical biocides was compared. High efficiency of the three-stage treatment of monuments using a combination of different compounds in comparison with the known methods is shown. The effectiveness of the used protective compounds was assessed by the speed of the reinstatement of the microbial community over several years after the treatment of the monument. The potential of laser technologies for the restoration of monuments was proven experimentally. It is shown that the effectiveness of laser removal of biofilms from the stone surface is comparable, and in some cases even exceeds that of chemical treatment. In the case of intensive development of mosses and lichens on the surface of monuments, the effectiveness of laser cleaning significantly exceeds that of chemical biocides. Laser cleaning to remove gypsum-rich patina is also effective, but does not always result in the complete removal of gypsum crystals.

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Keywords

Monument protection • Biodeterioration • Chemical biocides • Laser cleaning • Gypsum-rich patina

7.1 Chemical Methods

The problem of protection and preservation of historical monuments is one of the most complex, and requires a comprehensive scientific approach. One of the ways to preserve monuments exhibited in the open air is to protect them from biological damage. Since the rate of biological degradation of the stone material is high, the challenge is to counteract this dangerous phenomenon. In order to address it, a good knowledge of the existing methods of controlling biodegradation agents is required, as well as the development of new, more effective ways of protecting the stone from deterioration.

The main methods of stone protection and conservation can be divided into mechanical, physical, chemical and biological. All of them are aimed at removal of various types of contaminants, surface crusts and deposits, biological films, microbial metabolites from the surface. The choice of treatment methods is determined after the preliminary analysis of the material, its fabrics, as well as the forms of stone weathering.

Today, the most widely used chemical method of protecting monuments from biodegradation is based mainly on the use of biocides—chemicals that kill or inhibit microorganisms colonizing a particular material. The main requirements for the modern biocidal products are:

- a wide spectrum of effect;
- prolonged duration of action;
- no adverse effect on the material (especially important when using biocides in restoration practice);
- penetrability (inhibition of microorganisms remaining in pores, cracks and structural cavities);
- low toxicity in relation to humans and environment.

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There is a wide choice of biocides, which belong to different classes of substances used to slow or stop the growth of microorganisms. Biocidal products are used to control fungi, algae, bacteria, lichens as well as mosses and seed plants. The efficacy of antimicrobial action depends on the correct choice of biocide, the method and conditions of treatment. The most important condition for the effective use of biocides is the preliminary analysis of the composition of biodeterioration agents on affected materials. In case a wide range of these agents is detected, a mixture of biocides can be used, significantly enhancing protective effect. Some modern biocides have water-repellent properties. The use of such substances not only leads to a better biological resistance of the material, but also to its lower moisture capacity.

Despite the widespread use of biocides for protection of materials from biodegradation, there is a lot of opposition to extensive reliance on them. First of all, there is an environmental hazard. Many products have high toxicity and, if mishandled, can pose a hazard to the health of the people and to the environment. Short duration of biocidal action in the open air leads to the fact that the treated surfaces can be recolonized by microorganisms. In this case, microorganisms may acquire resistance to the chemical components of protective compositions. Use of biocides can cause discoloration of the material and change its physical and chemical characteristics. In the case of inestimable cultural monuments, this is one of the main constraints on applying chemical methods of stone protection. All this indicates the need for a scientifically established justification for the use of biocidal products, as well as a continued research of environmentally safe and effective technologies for protecting stone monuments from biodeterioration.

For a number of years experts from the Faculty of Biology and the Institute of Earth Sciences of St. Petersburg State University, Herzen State Pedagogical University of Russia, the State Museum of Urban Sculpture have taken both research and practical measures to protect the monuments of the museum Necropoleis from biological deterioration (Razrabotka 2004, 2007; Konservaciya 2008–2013). This work is supported by the Committee for Culture of St. Petersburg. The following tasks were set before the team of scientists and the museum staff:

- evaluation of the efficacy of the recommended biocides for different groups of biodeterioration,
- search for new, highly effective and environmentally friendly protective compounds,
- testing of new products in laboratory conditions and on experimental sites on the monuments of the Necropoleis,
- practical work to protect monuments from biodeterioration (service and maintenance, biocidal treatment).

The monuments for testing protective compounds were selected jointly with the staff of the Museum of Urban Sculpture. The development and synthesis of new protective coatings were carried out at the Institute of Silicate Chemistry of the Russian Academy of Sciences. The laboratory studies of affected materials, identification of biodeterioration agents, obtaining pure cultures of micromycetes, primary tests of protective compositions were performed at the Laboratory of Mycology of the Faculty of Biology and Soil Science of St. Petersburg State University.

This work were initiated in 2004, when studies aimed at the selection of biocidal products for conservation of monuments and evaluation of their efficacy against a wide range of biodeterioration agents began (Frank-Kamenetskaya et al. 2008). The biocides of the QAC group (AquaDes, Surfanios, Nika-sept and Rocima 110) were included in the study. Preparations based on quaternary ammonium compounds showed approximately equal antimicrobial activity against microbial communities. The greatest toxic effect on all members of the microbial community (by the results of a microbiological analysis) was produced by preparation Rocima 110. Considering the data on the prolonged effect of this product on the destructive microbiota, it was suggested that it were used to reinforce the antimicrobial performance of the QAC group biocides. This technique was successfully used for conservation of monuments in the Necropoleis (Tables 7.1 and 7.2; Figs. 7.1, 7.2, 7.3 and 7.4). It is important to note here that most of the monuments of the Necropoleis are made of several types of stone, for example, a pedestal is of granite or the Putilovo limestone, and a sculpture is of marble. Each type of rock is vulnerable to specific forms of biological damage, and the efficacy of biocidal treatment may be different for different rock types. For this reason, the efficacy of preventive and conservation measures was assessed for each type of stone by the results of qualimetric evaluation (see Sect. 6.3), before and after treatment (Table 7.2).

Since the biocides were chosen empirically, according to the figures obtained during the experiments, the used compositions changed following the emergence of more effective products. Therefore, in 2007, the studies continued with the purpose of correcting the existing methods after new compositions had become available on the market. In order to select the most effective biocidal compounds, more than 10 promising chemicals capable to suppress biodegradation agents were tested. These included biocides based on quaternary ammonium compounds and polyguanidine, as well as the latest experimental compositions of photocatalysts and nanotechnologies. Biological samples from the trial areas and treated monuments were taken every year, which allowed not only to estimate the performance of protective

Table 7.1 Scope of preventive and conservation measures using biocides on monuments from various types of rock in the Necropolis of the 18th century (2004–2007)

Type of stone (elements of monuments)	Quantitative data on an annual basis (the number of treated elements of monuments)				Total elements of monuments
	2004	2005	2006	2007	
Marble	21	44	102	2	169
Flaglike (Putilovo) limestone	–	5	71	18	94
Travertine (Pudost stone)	–	–	1	1	2
Granite	5	12	135	6	158
Sandstone	–	–	–	1	1
Total monuments	26	61	144	28	287

Table 7.2 Evaluation of the integrated state of monuments from carbonate rocks before and after the maintenance

Monument to	Degree of deterioration (%)			
	Marble		Limestone	
	Before	After	Before	After
1. I.G. Amosov	28	19	–	–
2. P.V. Bakunin	22	16	–	–
3. A.G. Batasheva	21	17	24	21
4. A.L. Batasheva	18	9	–	–
5. A.V. Buturlina	24	18	25	21
6. N. Buturlin	18	14	–	–
7. Gavriil Georgievich	25	20	21	17
8. A.N. Golitsyn	19	10	25	17
9. A.B. Izmaylova	15	10	–	–
10. S.I. Kalashnikov	20	15	21	13
11. L.I. Kusheleva	18	12	–	–
12. M.V. Levashova	20	13	–	–
13. N.V. and A.V. Lukin	17	11	–	–
14. E.A. Mansurova	18	16	17	15
15. Maria Alexandrovna	20	15	27	19
16. S.V. Meshchersky	12	9	16	10
17. M.I. Mordvinov	15	11	–	–
18. E.L. Naryshkina	22	17	–	–
19. M.P. Naryshkina	22	15	–	–
20. S.V. Naryshkin	15	12	–	–
21. I.V. Chertov	21	14	24	19
22. Unknown (N 18 No. 1011)	17	10	–	–
23. Unknown (N 18 No. 795)	6	5	–	–

compounds, but also to assess the dynamics of the microbial growth resumed on the surface of the monuments. Observations showed that in all cases, the trial areas on the monuments looked better in comparison with the reference areas. However, the efficacy of the drugs was different. In particular, the ANTI-N protective compound showed maximum effectiveness in inhibition of mold fungi and penetration of the substance into the substrate. Impregnation of the material with this biocide prevented the formation of a surface biofilm while maintaining the natural porosity of the material, which subsequently allowed unimpeded restoration of the treated surface. In addition, this product has low toxicity to humans and no acrid odor.

Studies of nanocomposite biocidal compounds were started in 2007 (together with the Institute of Silicates Chemistry of the Russian Academy of Sciences). Under laboratory conditions, 8 experimental products were tested, including two mass-produced “nanotechnology enhanced”

Fig. 7.1 Monument to A.A. Borozdin (Necropolis of the 18th century): **a** before treatment, **b** after treatment. 2007

Fig. 7.2 Monument to P.P. Syrenkov (Necropolis of the 18th century): **a** before treatment, **b** after treatment. 2009

protective compounds: Nanoprotect® S, Kieselit-Nano Hydrophobierung. After the biological analysis of samples taken from the trial areas in 2008, a two-step treatment was recommended. According to the proposed procedure, QAC biocides were used for stone washing, and Kieselit-Nano-Hydrophobierung preparation—for fixing the biocidal effect (Figs. 7.2 and 7.3).

Despite the fact that ongoing maintenance of the stone monuments in the State Museum of Urban Sculpture was performed according to the technology proven over the years, monitoring of the composition of biofilms on previously washed and treated monuments showed that an additional step is needed in the technique—waterproofing. So, in 2010, during washing and protecting the monuments from

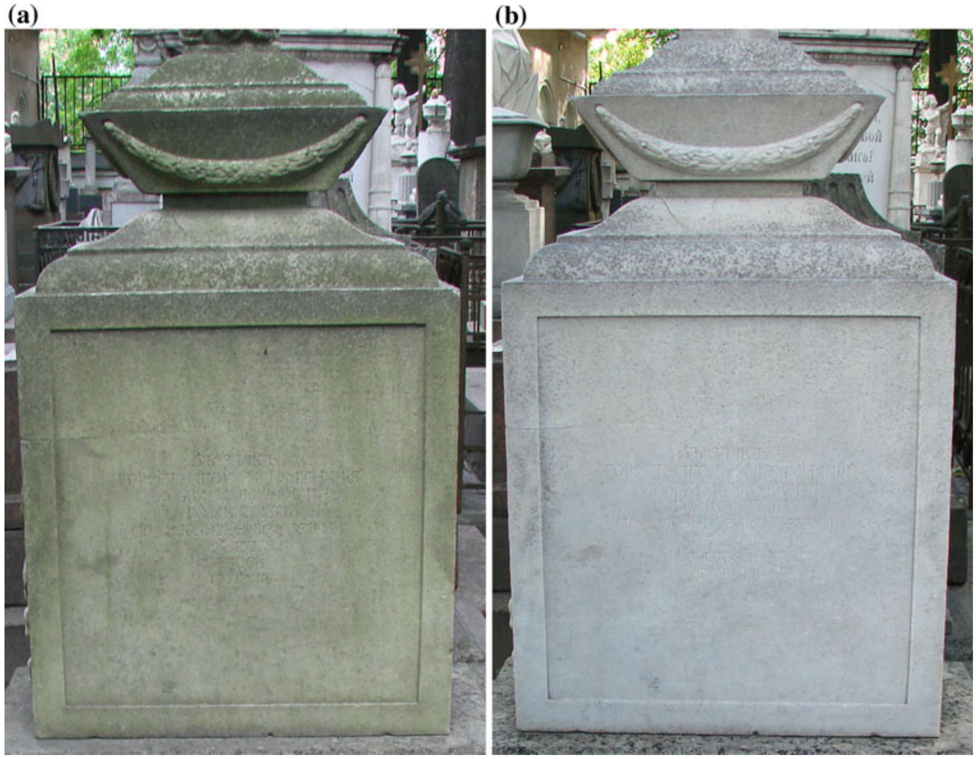

Fig. 7.3 Monument to A.G. Batasheva (Necropolis of the 18th century): **a** before treatment, **b** after treatment. 2009

Fig. 7.4 Monument to G. Trofimov (Necropolis of the 18th century): **a** before treatment, **b** after treatment. 2012

biodegradation, a three-step procedure was experimentally tested. The monuments were first washed with detergents for the stone, then the surface was impregnated with biocidal primers, and waterproofing of the stone was the final stage. In 2010 the aim of the studies was to determine the effectiveness of this three-step treatment as compared to the existing method, and to compare the protective performance of combinations of different compounds.

The mycological analysis of samples taken from the monuments in 2011 showed the effectiveness of this treatment. Washing the monument with LEM 3 composition, followed by priming with BFA and ANTI-N and waterproofing with Kieselit and Remmers Funcosil AG compounds (Gulenko 2012) proved to be the best. At that, the development of fungi, algae and other biological objects is inhibited on the surface of the treated areas (Fig. 7.4a, b).

Though good results were achieved with the three-stage method of protecting monuments from biological damage, in 2011–2013 testing and practical experiments with "nanotechnology enhanced" protective compounds continued. Various substances capable of inhibiting the development of aggressive microbiota were used as the basis of nanocomposite materials. Numerous experiments were staged during this part of the work, which can be divided into three groups:

- experiments to fine-tune the methods, efficacy criteria and test conditions;
- experiments on the effect of photocatalysts on cultures of destructive micromycetes (using special light installations);
- tests of "soft" biocides of non-photocatalytic action;
- tests of laboratory samples of protective nanocomposite coatings with various biologically active components (dopants) obtained by the sol-gel process.

The data obtained are reflected in a series of publications (Marugin et al. 2005; Vlasov et al. 2008; Vlasov 2012; Frank-Kamenetskaya et al. 2012; Khamova et al. 2012) .

In 2012, nanocomposite coatings with epoxy-silicate matrices were tested, which contained biocidal substances (detonation nanodiamonds—DND, and titanium dioxide).

Experimental protective compositions were synthesized at the Research Institute of Silicate Chemistry of the Russian Academy of Sciences under the guidance of Professor O.A. Shilova. In addition, titanium dioxide, which has a photocatalytic effect on microorganisms, was used in combination with other biocidal compositions.

The tests showed that application of matrices to the surface of marble monuments exhibited in the open air makes it possible to control the development of microbial community to a certain extent. The results of applying the matrices are comparable in the achieved effect with the application of the biocide primer + water repellent, and are better than in the case when only the biocide primer was used. Thus, the obtained data indicate that the tested matrices have a biocidal effect. However, this effect depends on the conditions and duration of the object exposure, characteristics of the coating and the composition of biodeterioration agents. The greatest resistance to the matrices is demonstrated by dark-colored microscopic fungi, which, as a whole, are characterized as maximally adapted for living on the stone surface in the urban environment. The obtained results of the field and laboratory work show that the chosen path is promising, opening up new opportunities for finding effective and environment-friendly ways of protecting monuments from deterioration.

Thus, the joint work of St. Petersburg scholars and the staff of the State Museum of Urban Sculpture on developing measures to protect the stone from biodeterioration allows to effectively preserve monumental and memorial artwork in the city. Comprehensive studies of the materials, research-based recommendations and use of the latest achievements in the field of combating biodeterioration agents can prolong the life of many monuments of cultural heritage.

7.2 Laser Cleaning

In recent years, the technology of laser cleaning of the monument surface (Verges-Belmin 1997; Cooper 1998; Pouli et al. 2005) has become increasingly popular for conservation and restoration work. Unlike mechanical and chemical methods, this approach allows to clean the surface of monuments from biofilms and other buildups without damaging the original surface, and preserving the color (Chapman 2000; Leavengood et al. 2000). In addition, use of laser cleaning has a number of advantages from the environmental point of view, since unlike chemical and mechanical methods it does not lead to environmental pollution.

When laser technology is used (Cooper 1998; Luk'yanchuk 2002; Parfenov et al. 2010), the pollutant particles are removed from the surface of the treated object because it absorbs high-intensity laser radiation. With a correct choice of the type and output parameters of the laser, such treatment is a selective process. This is manifested in the fact that the laser removes pollution only in the place on the surface of the monument where its beam is aimed. This compares the laser cleaning favorably with, for example, chemical treatment, where not only the treated area is exposed to the uncontrolled effect of the chemical, but also the entire adjacent part of the surface that most often does not need cleaning. Another advantage of laser cleaning is the possibility of removing contaminants from hard-to-reach areas of the monument surface, which is a serious challenge with traditional technologies.

To assess the effectiveness and safety of laser treatment when removing biofilms, mud buildups and gypsum crusts from the surface of stone monuments, a comparative analysis was made of the potential of various laser cleaning options among themselves and with the chemical biocidal treatment; The main modes of cleaning with pulsed solid-state Nd:YAG lasers have been worked out.

The experiment was carried out with the material of the monuments of the Museum Necropolis of the 18th century (St. Petersburg) and a number of other objects (Table 7.3). Samples of stone with biofouling and mud layers were taken from the surface of monuments of various types of silicate (granite, sandstone) and carbonate (marble, limestone) rocks, characterized by homogeneity and porosity (samples 1–7 of Table 7.3). The study of the potential of laser cleaning of the surface of monuments from gypsum-rich patina was made with samples of Carrara marble and Chersonesus limestone (samples 8–9 of Table 7.3).

The following species of microscopic fungi were isolated from the surface of the selected stone samples: *Alternaria*

Table 7.3 Characteristics of the research object

Sample No.	Sampling place	Bedrock
1	Foundation of the monument to I.R. Chirkin (1710–1778). Necropolis of the 18th century	Pink porphyritic coarse granite
2	Monument to I.V. Tartakov (1860–1923). Necropolis of Masters of Arts	Pink quartz sandstone
3	Cross on the monument to Alexander Stroganov (1733–1811). Necropolis of the 18th century	White homogeneous fine-medium-grained marble
4	Ledger of the monument to I.R. Chirkin. (1710–1778). Necropolis of the 18th century	White homogeneous fine- and medium-grained Carrara marble
5	Monument to E.A. Rummel (1829–1857). Necropolis of the 18th century	Gray-white, banded, inequigranular, heterogeneous, Ruskeala marble
6	Monument to A.G. Demidov (1737–1803). Necropolis of the 18th century	Porous travertine (Pudost stone)
7	The plinth of the monument to P. Neklyudov (1745–1797). Necropolis of the 18th century	Laminated limestone (Putilovo slab)
8	Sculpture on the facade of Demidov's House. 43 Bolshaya Morskaya st, St. Petersburg	White homogeneous fine- and medium-grained Carrara marble
9	Rampart in Chersonesus. Sevastopol, Crimea	Inequigranular porous Chersonesus limestone

alternata, Arthrinium phaeospermum, Aureobasidium pullulans, Cladosporium cladopsorioides, Cladosporium herbarum, *Cladosporium sphaerospermum, Coniosporium* sp. , *Epicoccum nigrum, Fusarium oxysporum, Geomyces pannorum, Hormonema dematioides, Mucor racemosus, Paecilomyces* sp., *Paecilomyces variotii, Penicillium herqueri, Penicillium oxalicum, Phaeococcomyces exophialae, Phaeosclerra* sp., *Phialophora repens, Penicillium chrysogenum, Sarcinomyces* sp., *Scytalidium lignicola*, *Ulocladium chartarum*.

For cleaning of the stone monument surface, pulsed Nd:YAG lasers operating at a wavelength of 1.06 µm are commonly used (Cooper 1998; Siano et al. 2000, 2007). For this work two different lasers of this type were used (Table 7.4). One of them—a specialized laser for restoration *Smart Clean 2*, operating in the free running generation mode, but having an atypical (shorter) pulse width for this mode (30–100 µs). Another laser was a laboratory model, developed at the All-Russian Research Center State S.I. Vavilov Optical Institute, working in the Q-switched generation mode with pulse duration of 10 ns.

Compresses of hydrogen peroxide with kaolin were used for chemical biocidal treatment of the samples. This method of biofilm removal is commonly used in St. Petersburg in the conservation of outdoor monuments (Lazarev 2006).

The efficiency of laser and biocidal treatment was assessed both visually and with light and electron microscopy. Examinations was performed both before and after treatment. Microscopic fungi on the surface of stone samples were identified by isolating micromycetes on the agarized nutrient media. The obtained isolates were identified using conventional mycological techniques (Vlasov et al. 2001).

When assessing the effect of cleaning, account was taken of the completeness of the buildup removal, changes in the development of the microbial community (by the example of micromycetes), and changes in the structure of the stone surface.

Visual observations showed that all methods of cleaning led to destruction or significant weakening of dark buildups from the surface of the samples under study, i.e. proved to be quite effective (Fig. 7.5).

The results of light microscopy confirmed the elimination of most mud deposits as a result of all methods of treatment (Table 7.5). According to biological studies, the microscopic fungi have lost their viability as a result of cleaning by all methods.

A combined interpretation of the results of the light and electron microscopy indicates that the complete removal of non-viable microorganisms from the surface of the monument depends, first of all, on the method of cleaning, and also on the species composition of the biological fouling and the homogeneity and porosity of the underlying bedrock (Table 7.5; Figs. 7.6, 7.7, 7.8, 7.9, 7.10, 7.11 and 7.12).

The most complete removal of mud buildups and biofouling occurs when a SC laser is used. Microcolonies of dark-colored fungi after this treatment in most cases completely disappeared (samples 1, 4, 5, 7, Figs. 7.6, 7.8, 7.10) or remain in trace amounts (<2% of the treated surface) in the pits on the surface (sample 2, Fig. 7.7). When a QS laser is used, in most cases (except for sample 6) microcolonies of dark-colored fungi remain on 5–15% of the treated surface.

Table 7.4 Technical characteristics of the lasers used in the experiment

Laser	Manufacturer	Wavelength, 1.064 μm	Pulse duration	Pulse repetition rate, Hz	Beam size on the stone surface, mm	Fluence, J/cm^2
SC-laser (commercially available) Nd: YAG laser with lamp pumping, Smart Clean 2 model	El. En. Spa., Italy		30–100 μs	10–20	1,5–2,5	10–20
QS-laser (Q-switched Nd:YAG laser with diode laser pumping)	Laboratory model, developed by S.I. Vavilov Optical Institute		10 ns	16	0,1	2

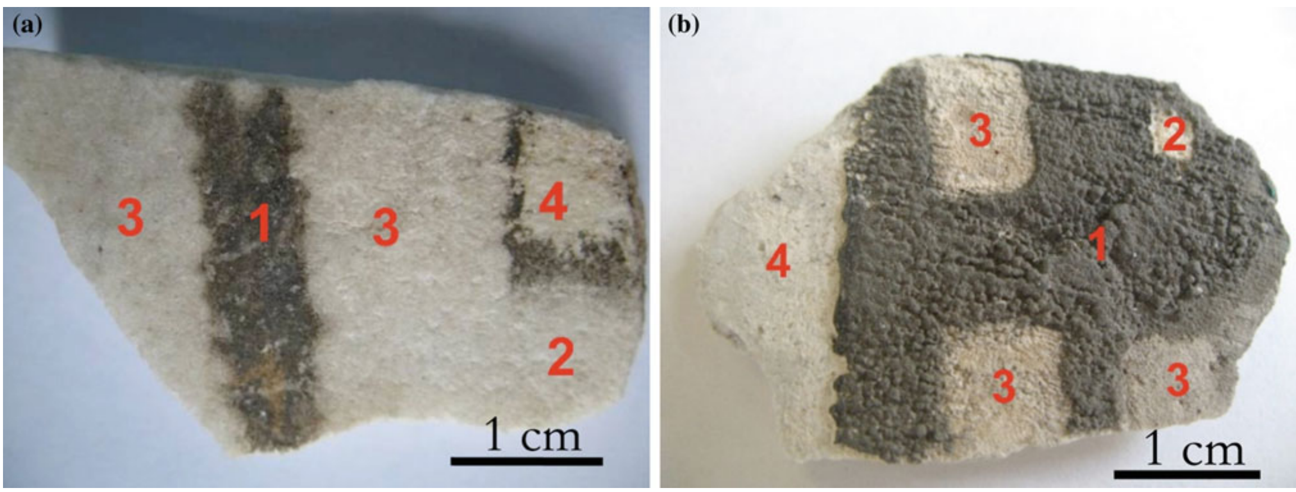

Fig. 7.5 Surface of white Carrara marble: **a** with a biofilm (Sample 3, Table 7.3); **b** with gypsum crust (sample 8, Table 7.3) before (1—initial surface) and after cleaning (2—QS laser, 3—SC laser, 4—hydrogen peroxide)

In addition, when this laser is used to remove buildups from the surface of heterogeneous Ruskeala marble and Putilovo layered limestone (samples 5 and 7), the surface of the stone is cleaned unevenly (dark and light stripes are observed).

The efficiency of mud and biofouling removal by hydrogen peroxide is in most cases comparable with laser cleaning (samples 1–3). In the case of dense fouling containing moss turf (specimen 4, Fig. 7.8a) and lichen thalli (sample 7, Fig. 7.10a), the efficiency of peroxide treatment is much lower (Figs. 7.8d, 7.10d) than that by lasers (especially SC-laser) (Figs. 7.8b, c, 7.10b, c).

The visual observations demonstrate the efficiency of removal of the gypsum-rich patina using laser technologies (sample 8–9, Fig. 7.5b). The surface becomes lighter in color, being not uniformly cleaned with a QS laser. When an SC laser is used with fluence level of 16 J/cm^2, the surface remains grayish. According to the data of scanning electron microscopy, small crystals are removed, while medium and large crystals of gypsum remain in the pits (Figs. 7.11b, c, 7.12b, c). As the fluence increases, their number goes down (Table 7.5). The use of biocidal treatment to remove the gypsum patina is effective only if it leads to the removal of the crust together with the marble, which results in effacement of the surface relief (sample 8, Fig. 7.5b, 7.11d). Otherwise, the gypsum patina remains practically unchanged (sample 9, Fig. 7.12d).

In some cases, laser cleaning may have a destructive effect on the surface of stone monuments, leading to roughening of the surface and melting of the individual grains of minerals. For example, in the case of laser cleaning of homogeneous marble from mud and biofouling, roughening of the surface occurred with the QS laser (Fig. 7.8b, c). Cleaning of the granite surface from mud and biofouling with QS and SC lasers resulted in melting of mica grains (sample 1, Fig. 7.6c, d). Cleaning of the surface of Putilovo limestone with an SC laser - to melting of glauconite grains, increasing with an increase in fluence from 16 to 25 J/cm^2 (sample 7, Fig. 7.10c).

Table 7.5 Description of the buildups on the surface of the samples before and after cleaning by the results of light and electron microscopy

Sample no. (Table 7.3)	Stone surface before treatment	Stone surface after treatment		
		QS-laser[a]	SC-laser	Peroxide
1	Thin black uniform coating consisting of contaminants, microcolonies and short hyphae of dark-colored fungi (Fig. 7.6a, b)	In places (∼5% of the treated surface) a less intense dark buildup is retained. Fused fragments corresponding to the particles of mica are visible (Fig. 7.6c)	With fluence of 15 J/cm^2 there are no contaminants and dark-colored fungi. Fused fragments corresponding to the particles of mica are visible (Fig. 7.6d)	No contaminants or dark-colored fungi[b]
2	Mud buildup and microcolonies of dark-colored fungi in the depressions between the grains (Fig. 7.7a)	No contaminants. Microcolonies of dark-colored fungi are there in a small amount (∼10% of the treated surface) (Fig. 7.7b)	With fluence of 14 J/cm^2 there is no contamination. Microcolonies of dark-colored fungi are preserved in trace amounts (<2% of the treated surface) (Fig. 7.7c)	No contaminants. Microcolonies of dark-colored fungi are preserved in trace amounts (<2% of the treated surface) (Fig. 7.7d)
3	Intensive homogeneous black buildup, consisting of contaminants, microcolonies and short hyphae of dark-colored fungi	No contaminants. Microcolonies of dark-colored fungi are there in a small amount (∼10% of the treated surface)	With fluence of 15 J/cm^2 there is no contamination. Microcolonies of dark-colored fungi are preserved in trace amounts (<2% of the treated surface)	No contaminants. Microcolonies, short hyphae of dark-colored fungi and moss turfs are discolored but remain on the surface in large amounts (∼40% of the treated surface)
4	Intensive homogeneous black buildup, consisting of contaminants, microcolonies and short hyphae of dark-colored fungi. Moss turfs (Fig. 7.8a)	No contaminants. Microcolonies of dark-colored fungi are there in a small amount in the depressions (∼10% of the treated surface) (Fig. 7.8b)	With fluence of 15 J/cm^2 there is no contamination or microcolonies of dark-colored fungi (Fig. 7.8c)	No contaminants. Microcolonies, short hyphae of dark-colored fungi and moss turfs are discolored but remain on the surface in large amounts (∼40% of the treated surface) (Fig. 7.8d)
5	Intensive homogeneous black buildup, consisting of contaminants, microcolonies and short hyphae of dark-colored fungi	The surface of the stone is cleaned unevenly—light and dark bands are observed. Microcolonies of dark-colored fungi remain in small amounts in the depressions on the surface of the stone (∼15% of the treated surface)	With fluence of 16 J/cm^2 there is no contamination or microcolonies of dark-colored fungi	No contaminants. Colonies of dark-colored fungi remain in the pits in small amounts (∼40% of the treated surface)
6	Intensive mud stratification and thalli of crustose lichens, colonies of dark-colored fungi (Fig. 7.9a, b)	There are no contaminants and colonies of microorganisms (Fig. 7.9c, d)	It was not carried out	It was not carried out
7	Intense mud buildup. The surface of the stone is covered with thalli of crustose lichens and colonies of dark-colored fungi (Fig. 7.10a)	The surface of the stone is cleaned unevenly—light and dark bands are observed. There are no contaminants or lichen thalli on the light bands. On the dark bands, the remaining fragments of the thalli of crustose lichens are visible (Fig. 7.10b)	With fluence of 16 J/cm^2, the structures of thalli of scale lichens are preserved. Melted fragments corresponding to glauconite inclusions are visible. When using pulse fluence of 25 J/cm^2, rare fragments of the lichen thalli are preserved on the surface, mainly in the depressions of the stone. Numerous fused glauconite fragments are visible (Fig. 7.10c)	In some areas of the surface fragments of lichen thalli and colonies of dark-colored fungi remain (Fig. 7.10d)

(continued)

Table 7.5 (continued)

Sample no. (Table 7.3)	Stone surface before treatment	Stone surface after treatment		
		QS-laser[a]	SC-laser	Peroxide
8	The surface of the stone is evenly covered with gypsum crust of a dark color (Fig. 7.11a). Numerous tabular gypsum crystals are seen	The surface of the stone is cleaned unevenly (light and darker bands are visible). Crystals of gypsum are present (Fig. 7.11b)	With fluence of 16 J/cm^2, the surface remains grayish. Crystals of gypsum are present in the depressions. When the pulse fluence is 22 J/cm^2, the surface becomes lighter, but gypsum crystals remain in the depressions in small amounts (Fig. 7.11c)	The surface is lighter. The crust and the marble were removed to a depth of 0.5–1 mm (Fig. 7.5b, Sect. 4), which led to effacing of the surface relief. No gypsum crystals were noticed (Fig. 7.11d)
9	The surface of the stone is evenly covered with a crust of dark color. Numerous platy crystals of gypsum are seen (Fig. 7.12a)	The surface is unevenly cleaned from dirt: light and dark bands are visible. Crystals of gypsum remain (Fig. 7.12b)	With fluence of 13 J/cm^2, the stone surface is evenly cleaned of dirt (lightened). Numerous areas with large crystals of gypsum have remained. With pulse fluence of 29 J/cm^2, the surface of the stone is evenly cleaned of dirt, but severely damaged (pits and multiple caverns). Crystals of gypsum are in a small amount in the depressions (Fig. 7.12c)	The surface was made partially lighter, but the gypsum crystals remained practically unchanged (Fig. 7.12d)

Notes [a]for a QS laser in all cases, the fluence is about 1 J/cm^2
[b]treated additionally with an SC laser

The results of the experiments showed that the laser cleaning technology for removal of biofilms from the surface of the stone is comparable, and in some cases even superior to chemical treatment with hydrogen peroxide and kaolin. In the case of intensive development of biofouling, containing mosses and lichens, the efficiency of laser cleaning is significantly higher than the efficiency of chemical biocidal treatment. The use of laser cleaning to remove gypsum-rich patina is also effective, but does not always lead to the complete removal of gypsum crystals. In some cases, both laser and chemical cleaning cause changes in the structure of the surface of stone monuments. For example, an Nd:YAG laser with a nanosecond pulse duration and hydrogen peroxide can damage the marble surface, and an Nd:YAG laser with pulse duration of dozens of microseconds also can damage the surface of some stone monuments, leading to intense fusion of layered minerals (mica, glauconite and others). This indicates the need of careful selection of the laser type and adjustment of its output parameters when working with a specific monument. For the practical conservation work to remove buildups from the marble surface, it is advisable to use a pulsed Nd:YAG laser with a pulse duration of 50–100 microseconds, for example, a specialized device for restoration *Smart Clean 2* manufactured in Italy. The advantage of this laser as compared with Nd:YAG lasers with a nanosecond pulse duration is that it removes biological buildups more efficiently and, with a correct choice of fluence, practically does not damage the surface structure of the marble.

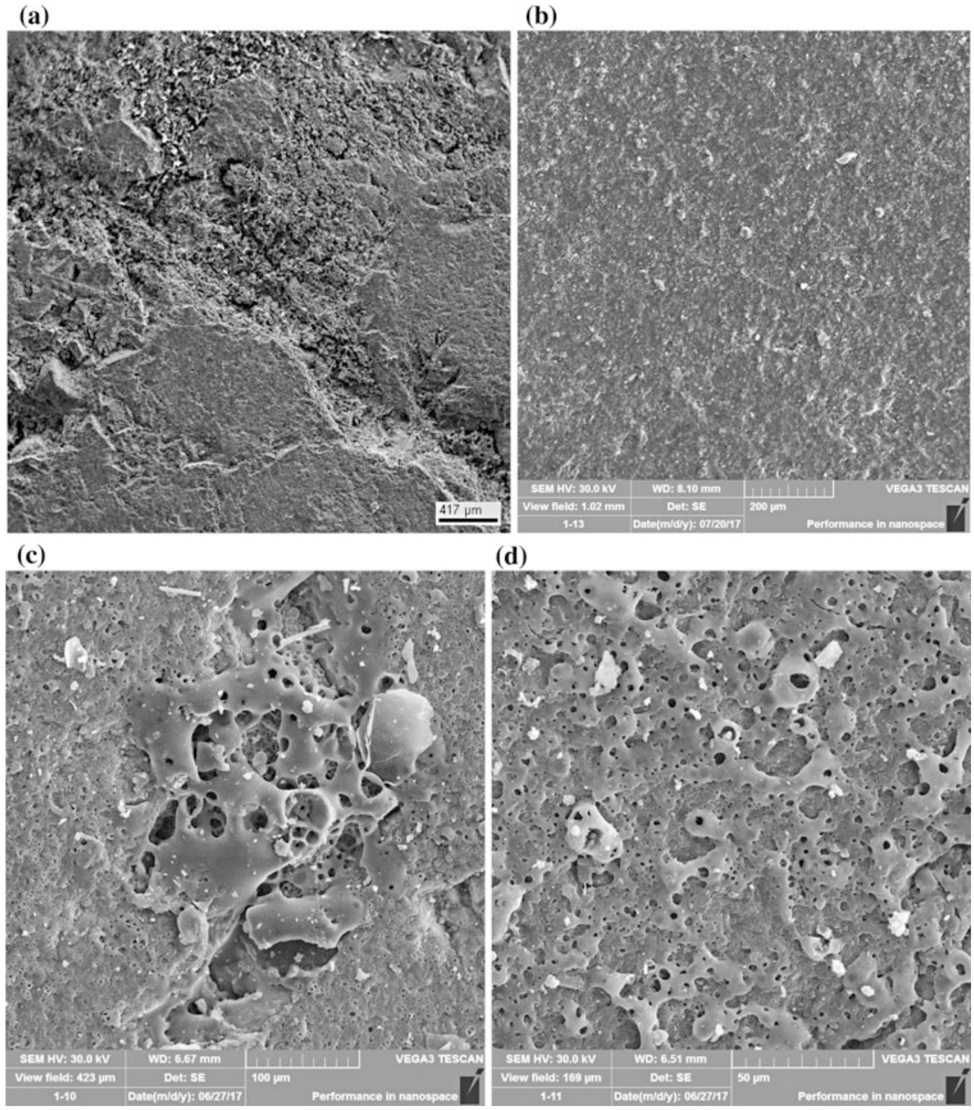

Fig. 7.6 SEM images of the granite surface (sample 1): up to (**a**, **b**) and after purification by QS-laser (**c**) and SC-laser (**d**)

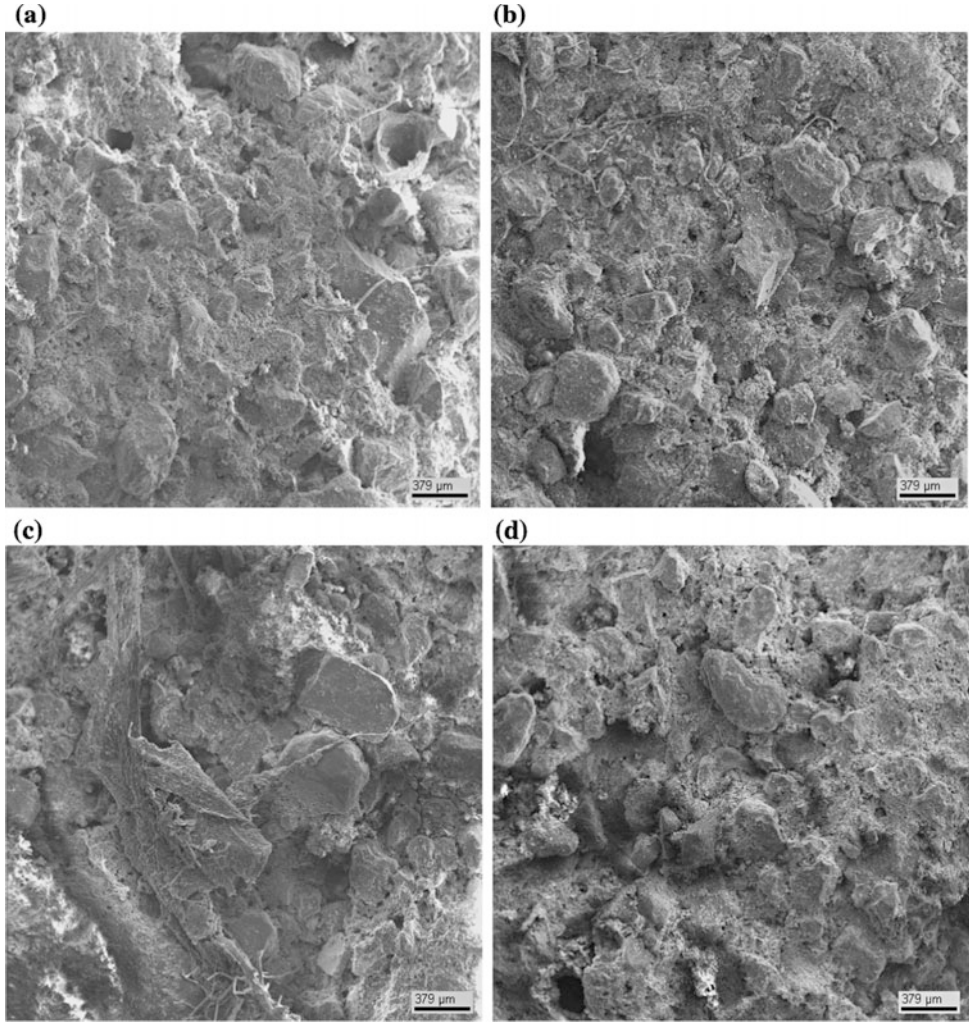

Fig. 7.7 SEM images of the surface of quartz sandstone (sample 2): before cleaning (**a**); after cleaning with QS-laser (**b**); after cleaning with an SC laser (**c**) and after biocidal treatment with hydrogen peroxide (**d**)

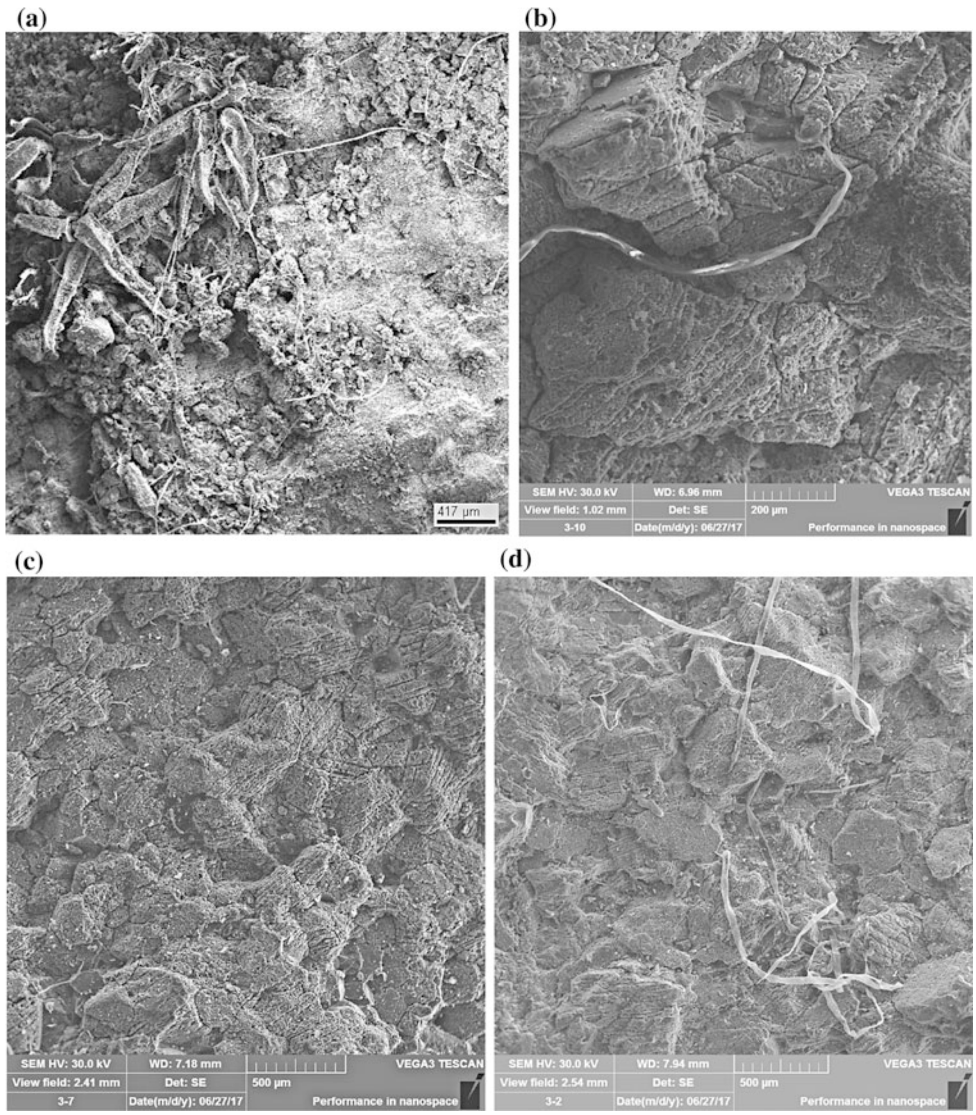

Fig. 7.8 SEM images of the surface of a white homogeneous marble (sample 4): before (**a**) and after cleaning with a QS laser (**b**), SC laser (**c**) and hydrogen peroxide (**d**)

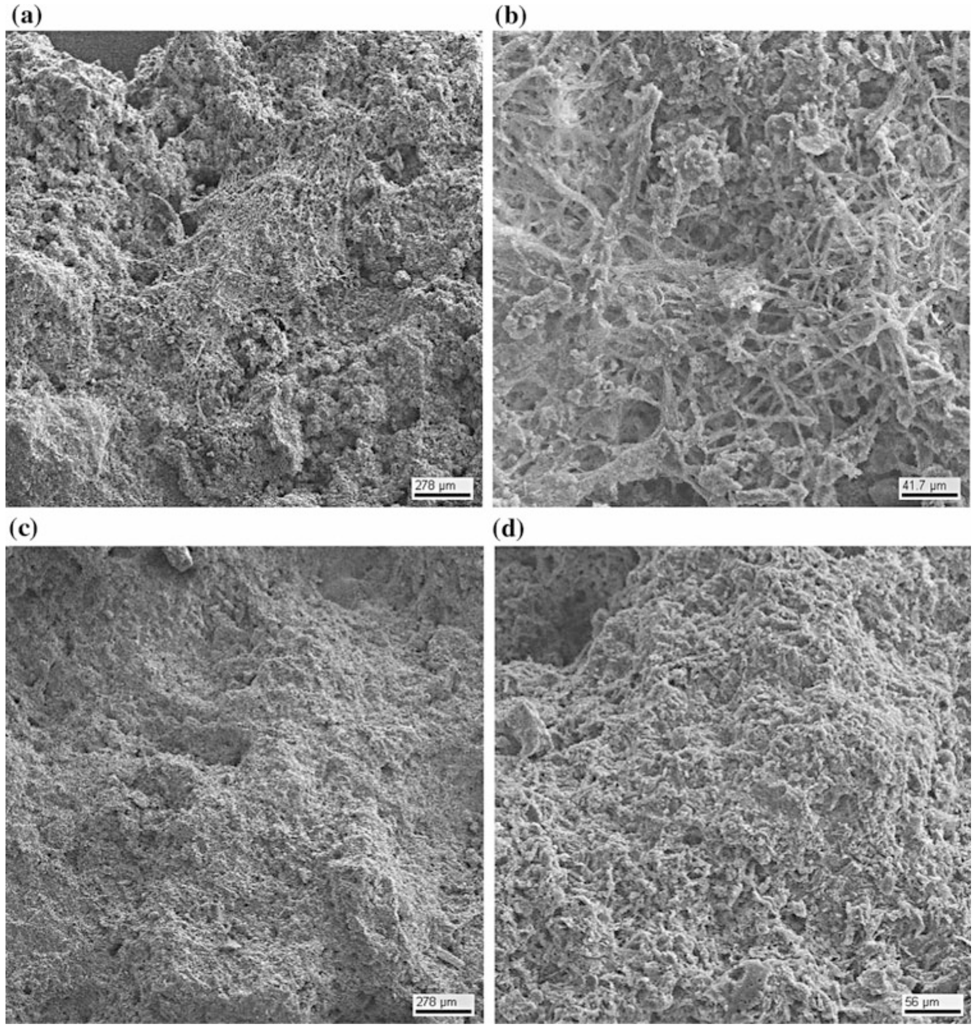

Fig. 7.9 SEM images of the surface of the Pudost travertine (sample 6): before (**a**, **b**) and after cleaning with QS-laser (**c**, **d**)

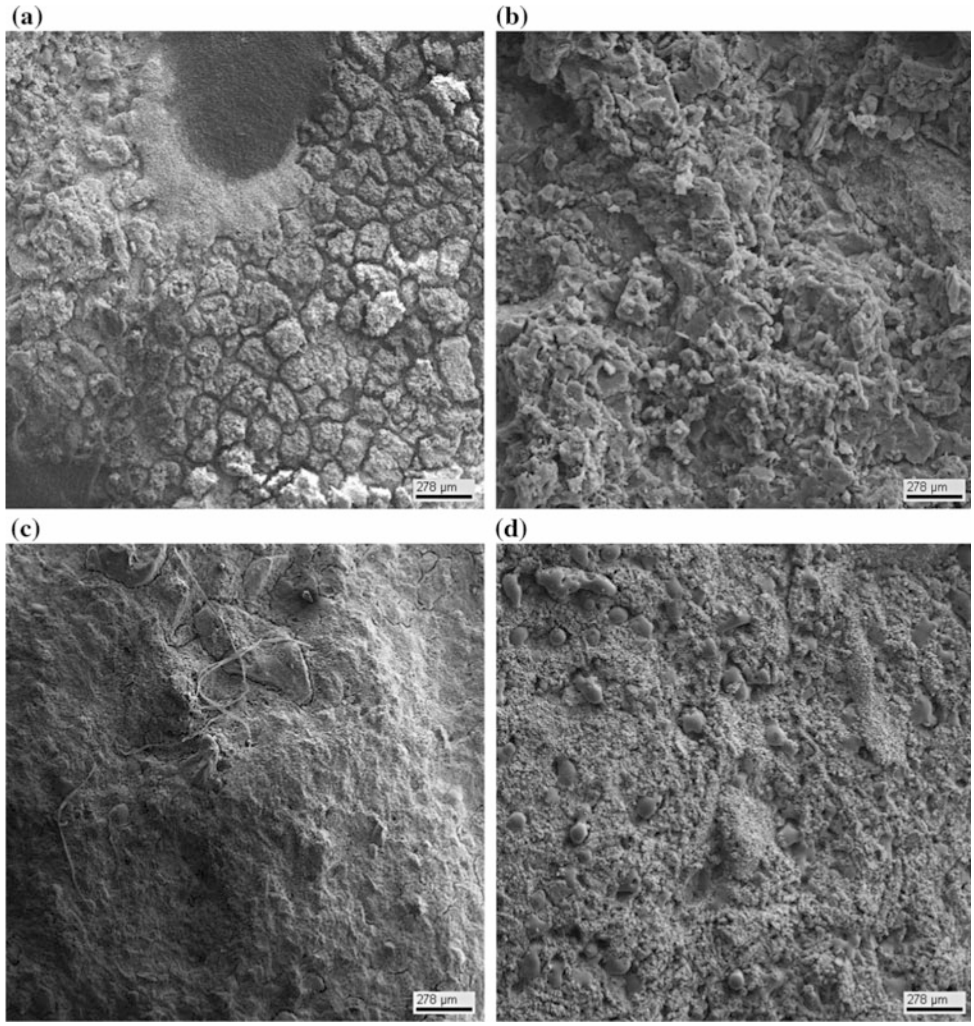

Fig. 7.10 SEM images of the surface of the Putilov plate (sample 7): before cleaning (**a**); after cleaning with QS-laser (**b**); after cleaning with a SC laser (**c**) and after biocidal treatment with hydrogen peroxide (**d**)

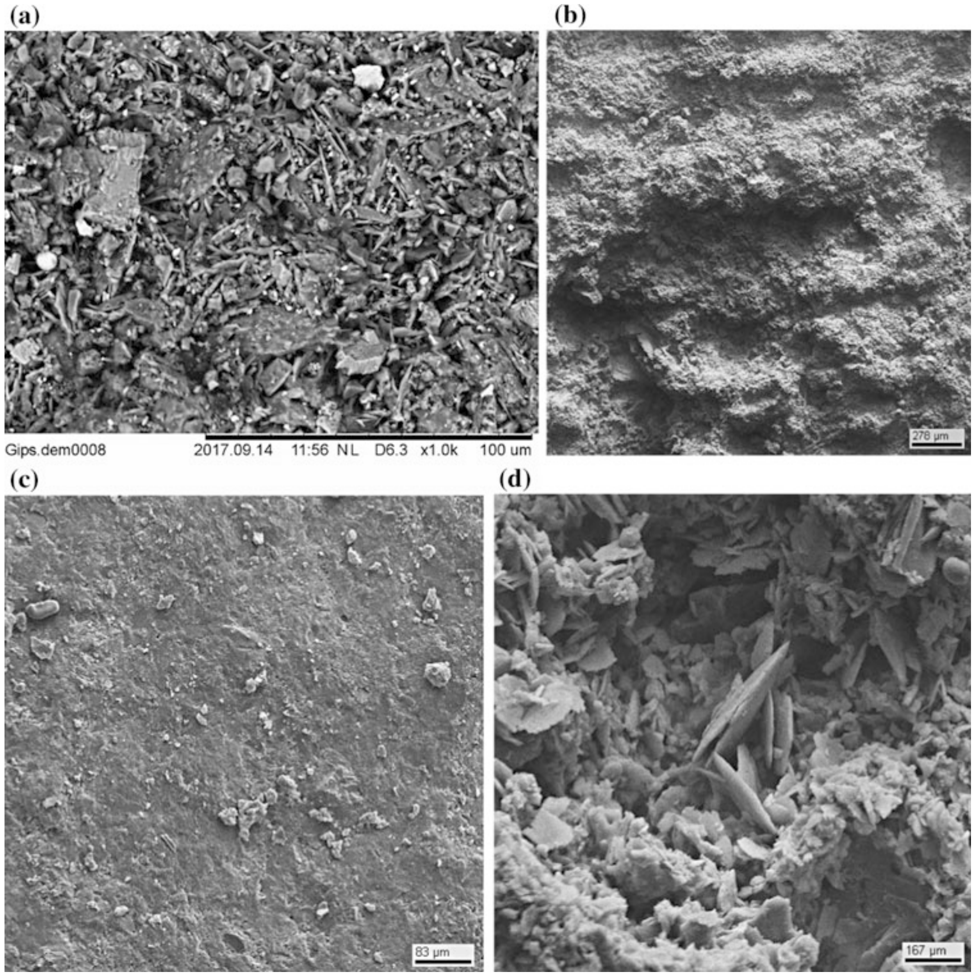

Fig. 7.11 SEM-images of the surface of a white homogeneous fine- and medium-grained marble (sample 8): before cleaning (**a**); after cleaning with QS-laser (**b**); after cleaning with an SC laser (**c**) and after biocidal treatment with hydrogen peroxide (**d**)

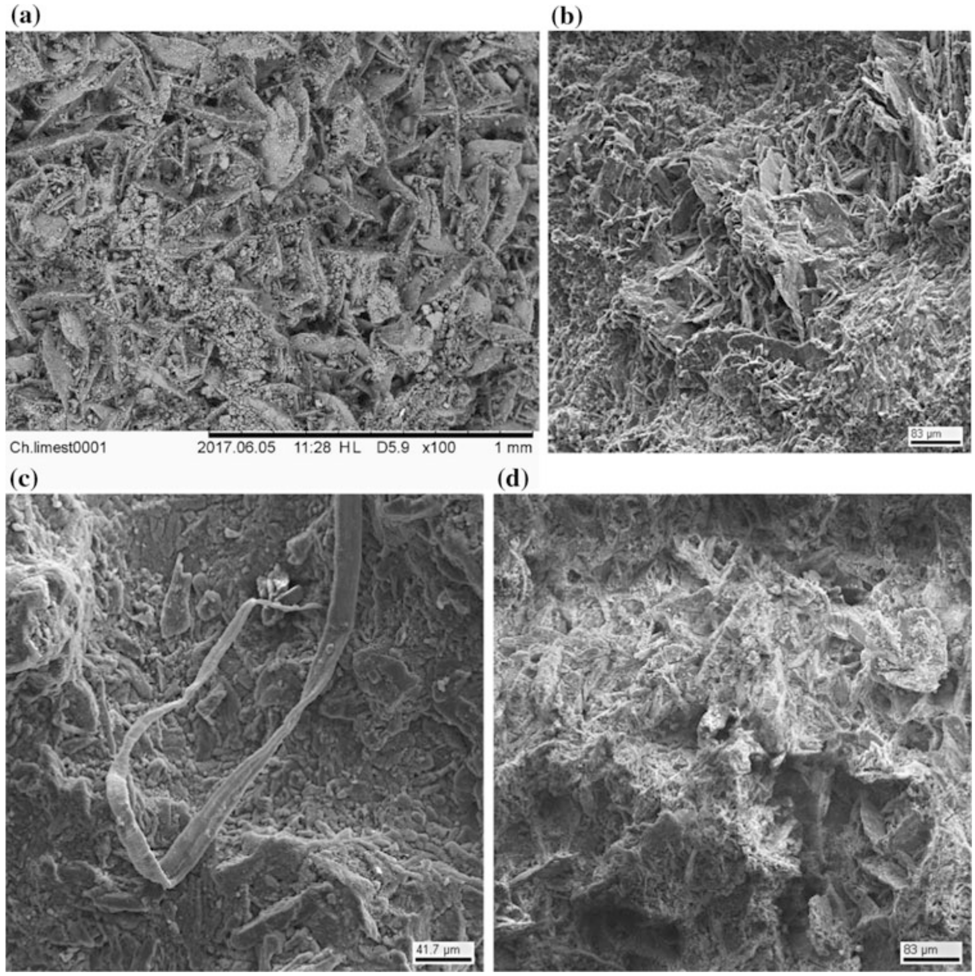

Fig. 7.12 SEM images of the limestone surface (sample 9): before cleaning (**a**); after cleaning with QS-laser (**b**); after cleaning with a SC laser (**c**) and after biocidal treatment with hydrogen peroxide (**d**)

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8 Results and perspective

Nadezhda N. Efremova

The long large-scale work on monitoring the state of monuments in St. Petersburg, the results whereof are presented in this collective monograph, and which pooled the efforts of the museum staff and St. Petersburg scientists, has the ultimate goal of putting into action a scientific strategy for the preservation of the monuments of cultural heritage.

Integrated monitoring provides an objective picture of the state of the materials of monuments in the urban environment, makes it possible to take timely interventions for the restoration and conservation of works of art, to plan the necessary work.

Proceeding from the conducted scientific research, a description of the rare in its variety and beauty collection of natural stone in the museum Necropoleis, of the types and processes of deterioration of the materials of St. Petersburg monuments under the influence of physicochemical and biogenic factors was made. The unique material obtained on the processes of destruction of monuments in St. Petersburg allows to develop scientific strategies for preservation of monuments in other cities with similar climatic and ecological conditions.

Many years of fruitful experience in monitoring and preserving the unique collection of monumental art makes it possible to implement a major international project. It is there that a global perspective is seen in the cooperation of museum professionals and scientists.

Of course, further streamlining of the monitoring methods will be necessary, taking into account the continuous development of computer technologies, the new achievements in various fields of natural science, enabling us to study in detail the specifics of the interaction of the material of the monumental sculpture with the environment.

Studies should be continued, aimed at searching for effective protection of monuments made from various materials (stone, bronze, cast iron, etc.). A comprehensive study of the properties and causes of deterioration of various types of stone and metal alloys is the key to the successful selection of restoration methods and tools from the wide range of materials offered by the modern science. Therefore, preliminary examinations, scientific research of monument materials and the products of their deterioration should be mandatory when developing the restoration techniques. It is the monitoring system that allows you to objectively determine the need, timing and scope of the next complex restoration.

A particular attention should be paid to monitoring the condition of monuments after restoration and conservation work, to be largely determined by the properties of the materials and methods used. It is essential that the specific aspects of the monument's structure were taken into account, including all internal supporting elements. To this end, it is necessary to use more actively modern research tools that allow quantification of the occurring changes (ultrasonic sounding, laser scanning, etc.).

For any museum, restoration is a special kind of custodial work, for which the research component is fundamental. That is why it is hard to overestimate the need for further scientific research aimed at performance-enhancing methods of restoration and conservation.

The study of the impact of the environment on the state of the monument materials, the search for effective ways to protect them, make it possible to preserve and adequately exhibit the works of monumental sculpture and memorial art, which are an impressive, imaginative part of the world history and culture.

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Index

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