4 Decay of the Monuments

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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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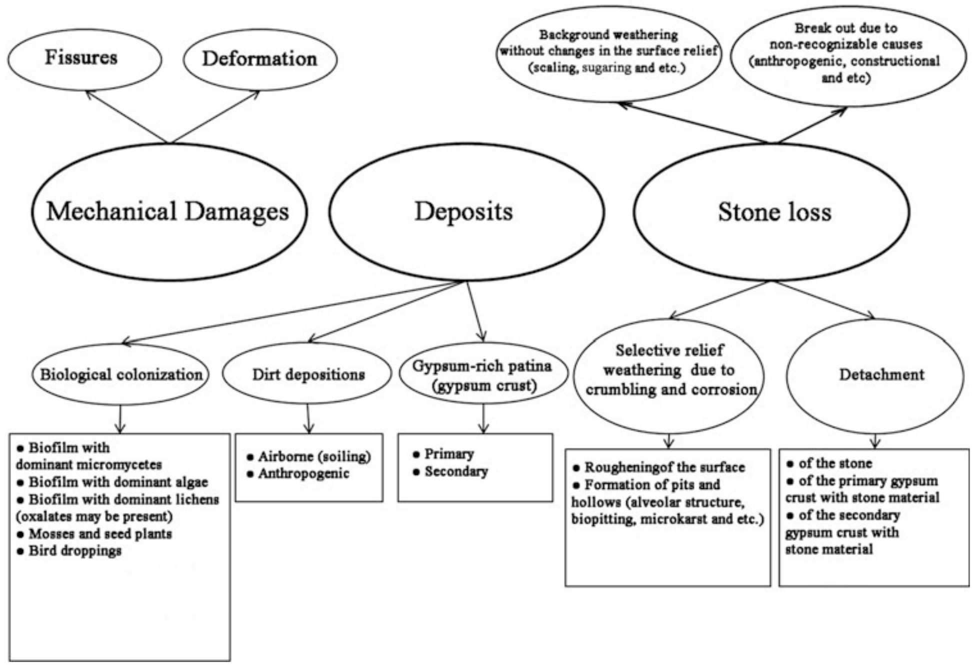

Fig. 4.1 Classification of the forms of weathering of the stone of St. Petersburg monuments

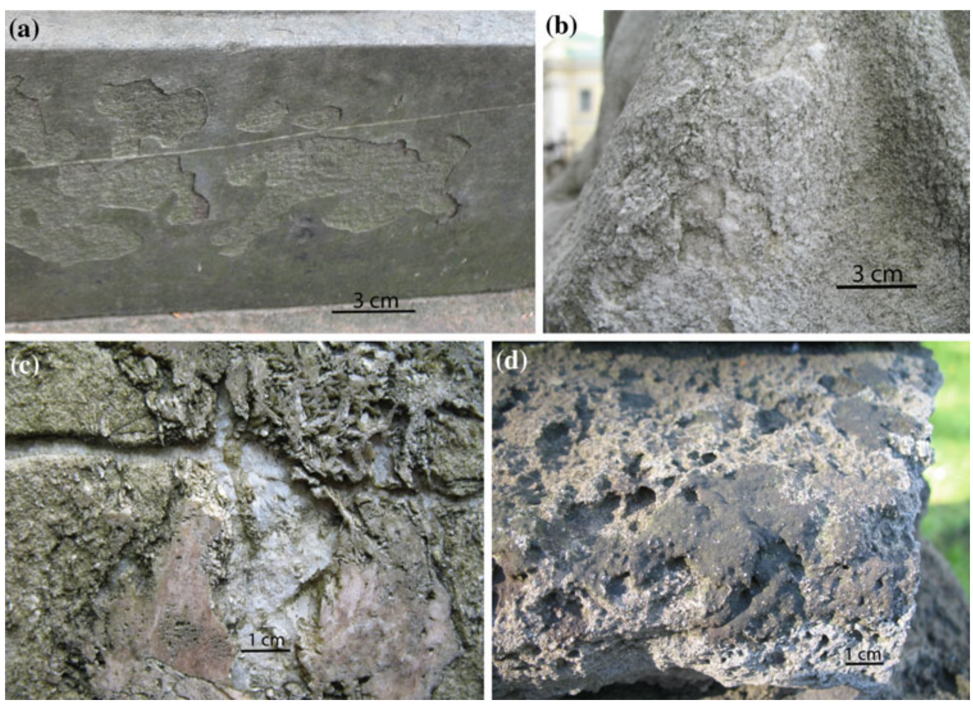

Fig. 4.2 Loss of stone on the monuments of the Necropolis of the 18th century: **a** flaking of the Serdobol granite on Monument to I.P. Bogdanovich; **b** roughening of the surface and flaking of statuary white marble due to crumbling. Monument to G.A. Demidov; **c** microkarst on the Ruskeala marble. 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

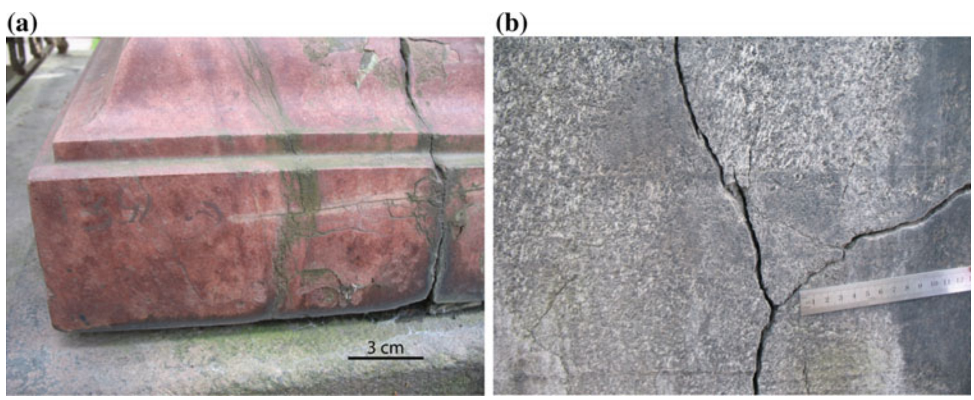

Fig. 4.4 Fissures on silicate rocks of the monuments in the Necropoleis: **a** on quartzite. Monument to A.F. Turchaninov. Necropolis of the 18th century; **b** on amphibolite. Monument to N.I. Utkin. Necropolis of Masters of Arts

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).

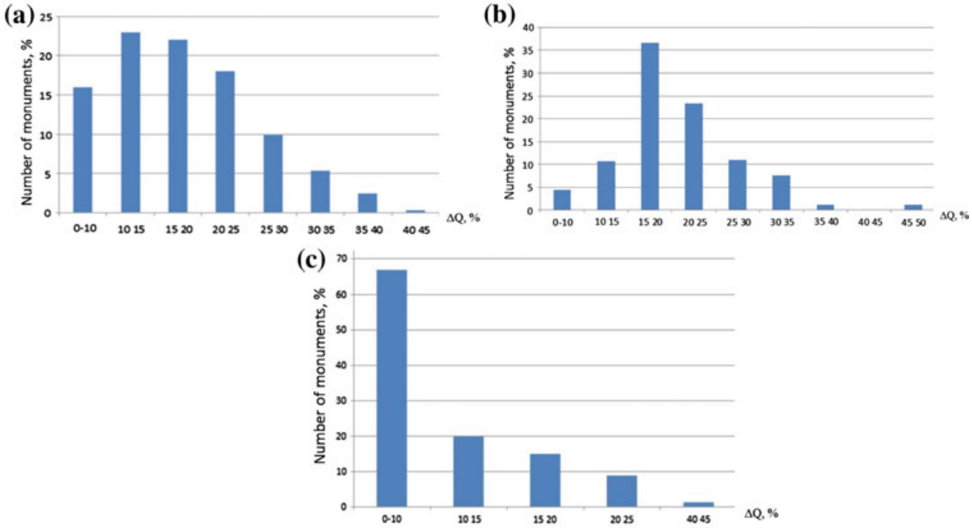

Fig. 4.5 The degree of the stone material deterioration (%) in the Necropolis of the 18th century of the surveyed monuments: **a** of marble, **b** of limestone, **c** of granite and other hard rocks

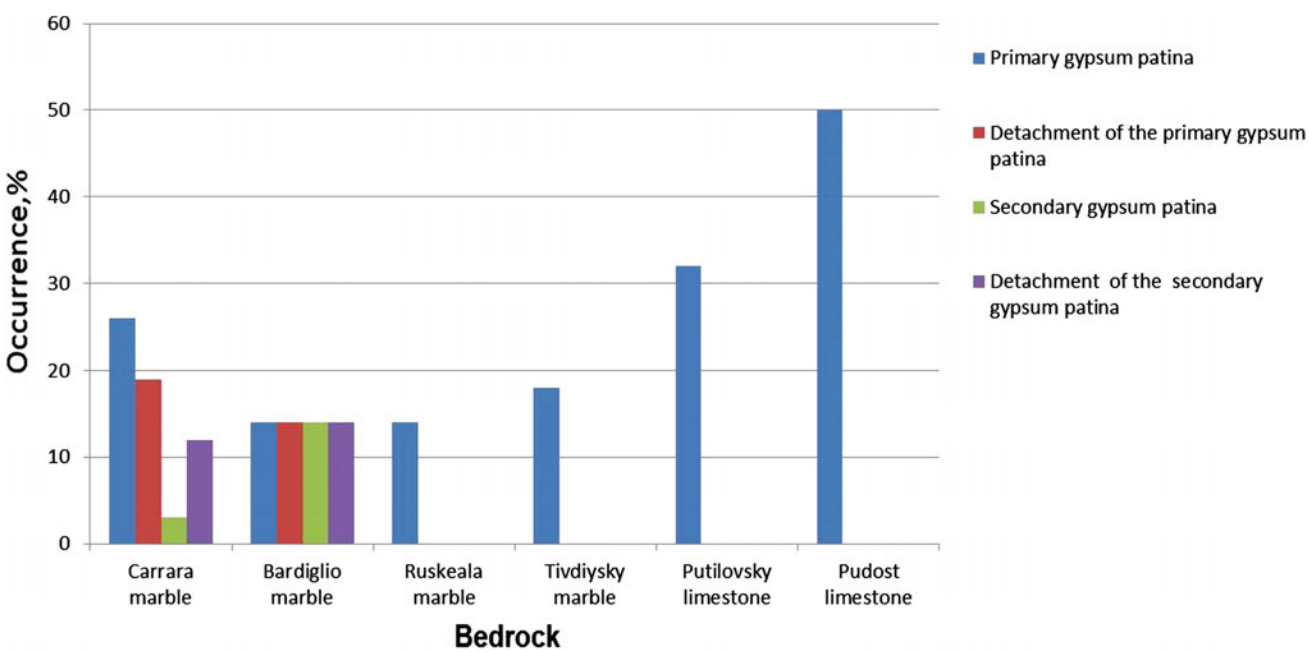

Fig. 4.6 The occurrence (%) of gypsum-rich patina on the surface of the examined monuments of carbonate rocks in the Necropolis of the 18th century

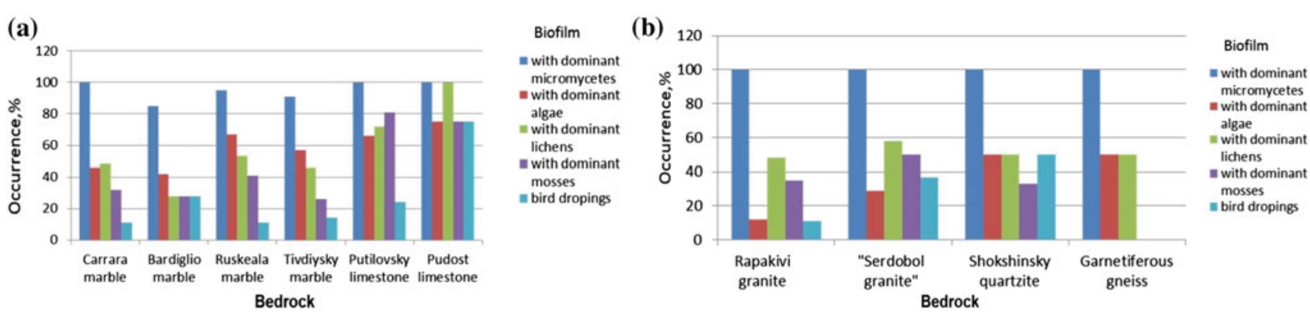

Fig. 4.7 The occurrence (%) of various forms of biofouling in the Necropolis of the 18th century on the surface of the surveyed monuments of: **a** marbles, **b** limestones, **c** granite and other hard rocks

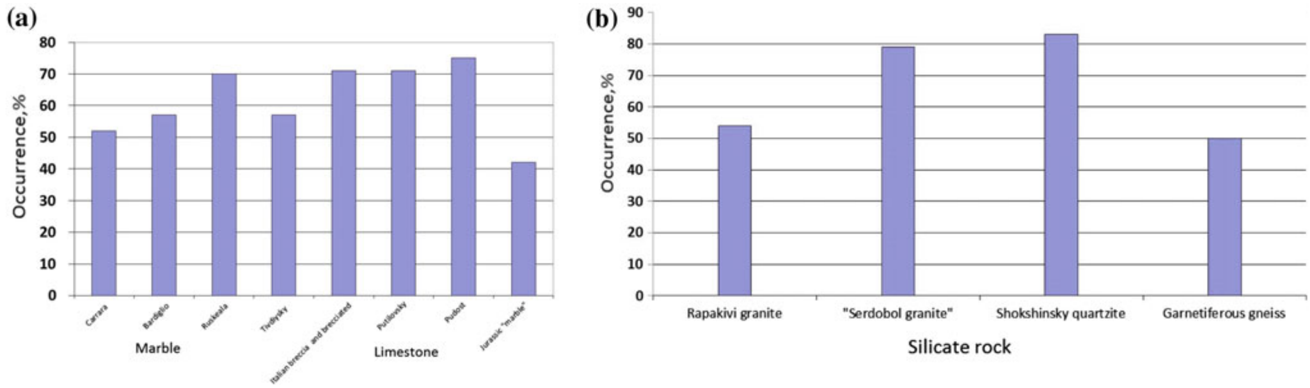

Fig. 4.8 The occurrence (%) of cracks on the surface of the surveyed monuments in the Necropolis of the 18th century: **a** of carbonate rocks, **b** of silicate rocks

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

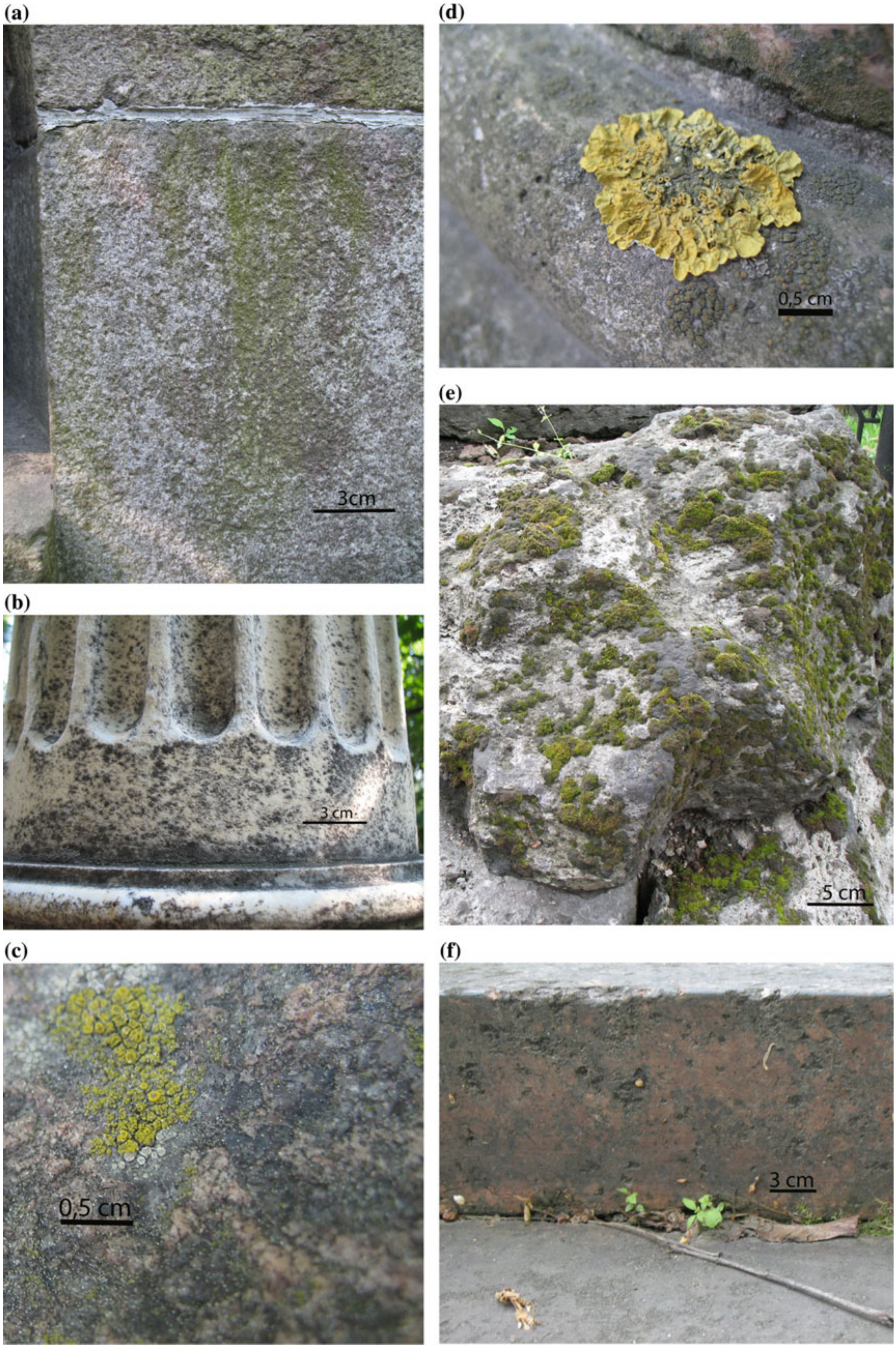

Fig. 4.9 Biofouling on the surface of stone monuments of the museum Necropoleis: **a** algae (Chlorophyta division). Monument to S.S. Botkin; **b** colonies of dark-colored micromycetes. Monument to E.I. Zagryazhskaya; **c** crustose lichens. Monument to I.I. Labensky; **d** foliose lichens. Monument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

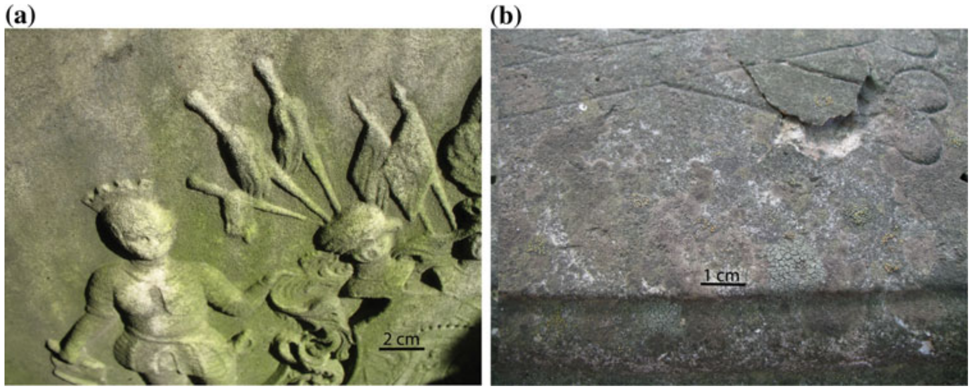

Fig. 4.10 Extensive biofilms on the surface of stone monuments: **a** continuous biofilm with the dominance of green algae. Development of biological damage leads to the erosion of the surface of white statuary marble. Monument to S. Kh. Münnich; **b** continuous biofilm with domination of crustose lichens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

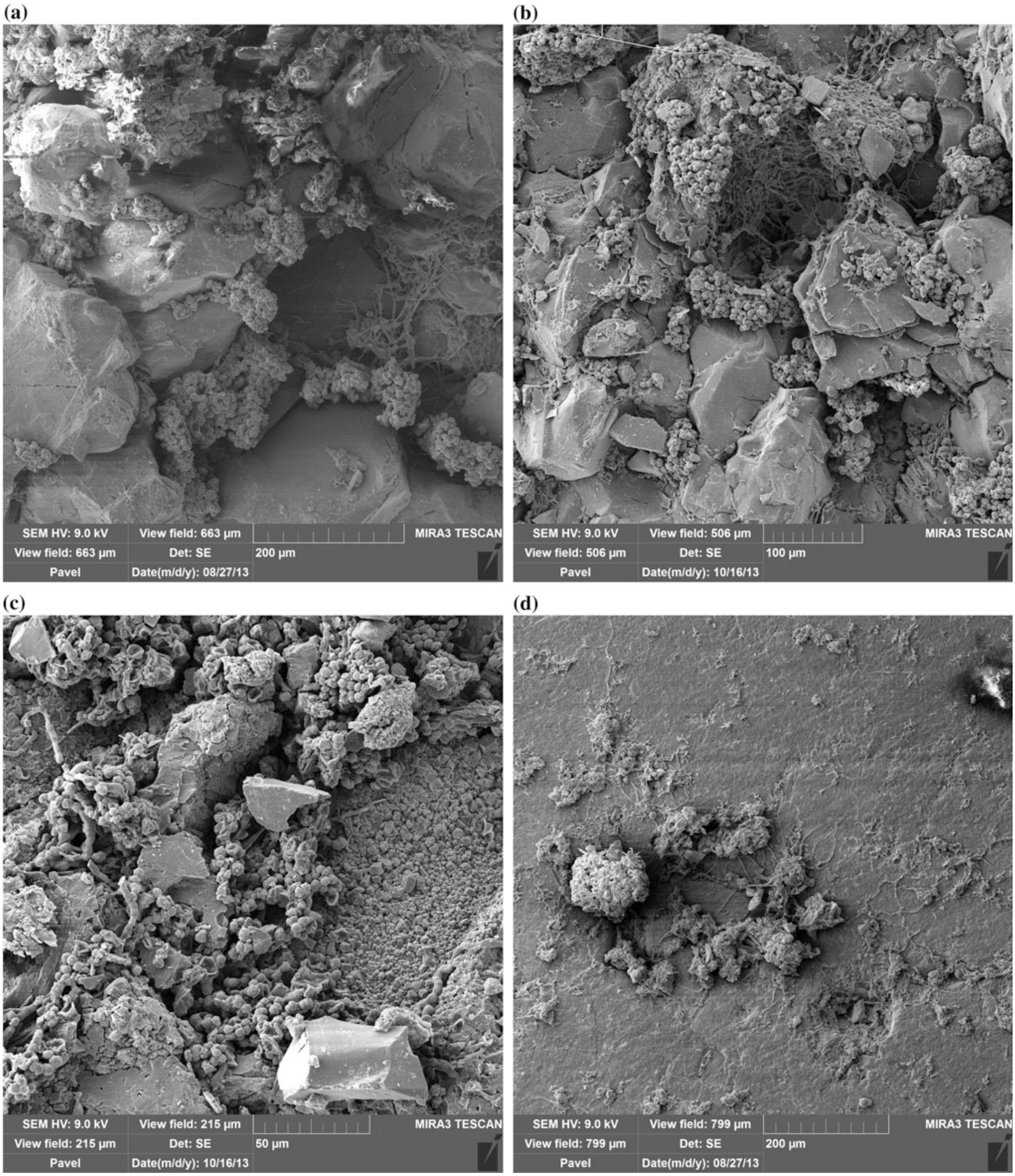

Fig. 4.11 SEM images of weathered stone surface, colonized by microorganisms: **a** homogeneous statuary marble; **b** heterogeneous Ruskeala marble; **c** flaglike Putilovo limestone; **d** Serdobol granite. Microcolonies and hyphae of fungi are visible, as well as bioclusters in microfissures and microcavities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

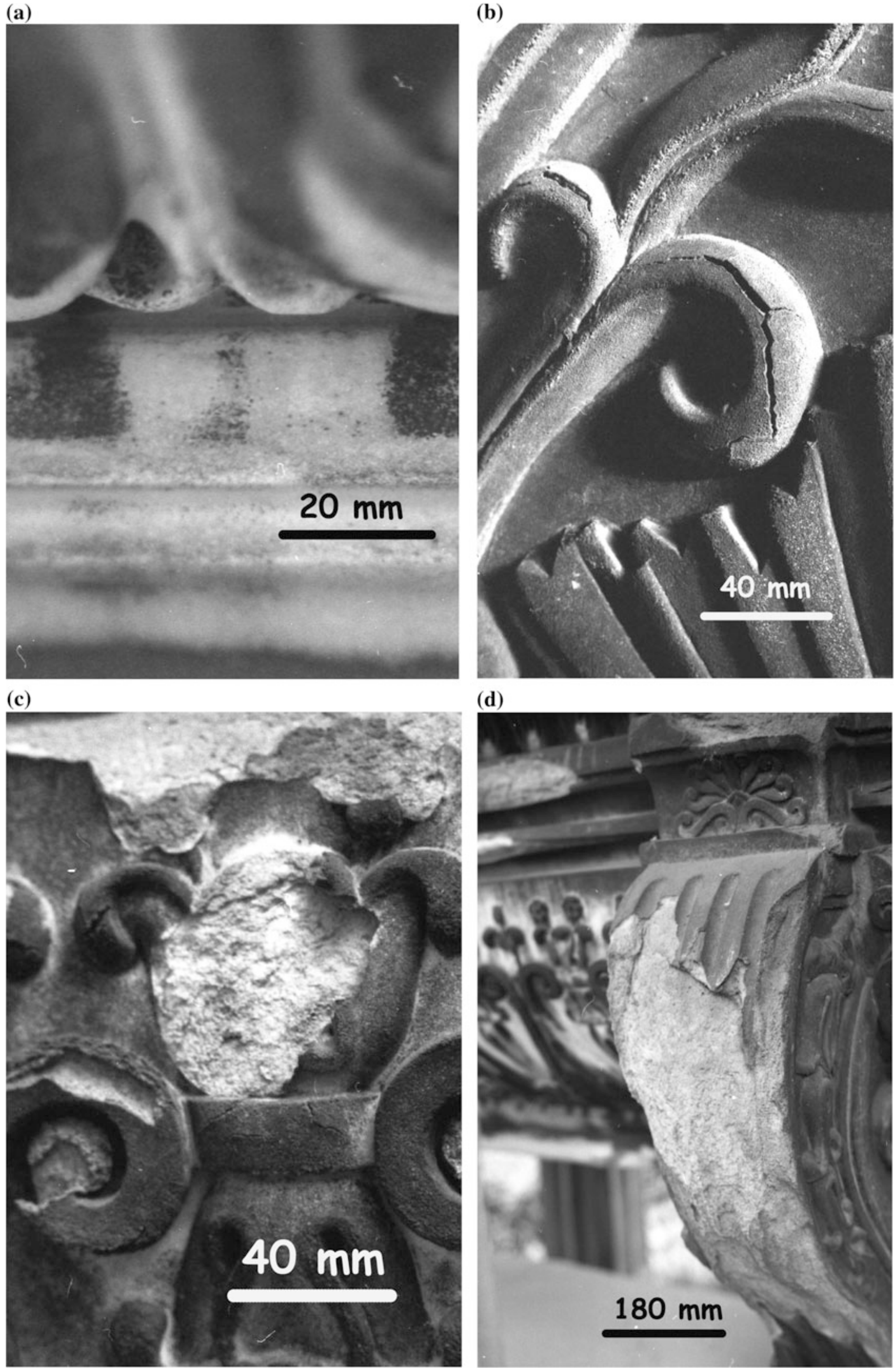

Fig. 4.12 Gypsum-rich patina on the surface of Carrara marble (monument to A.I. Kosikovsky, Necropolis of Masters of Arts): **a** primary thin patina; **b** primary formed thick patina with cracks; **c** sugaring marble surface after detachment of the primary patina; **d** young secondary patina

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

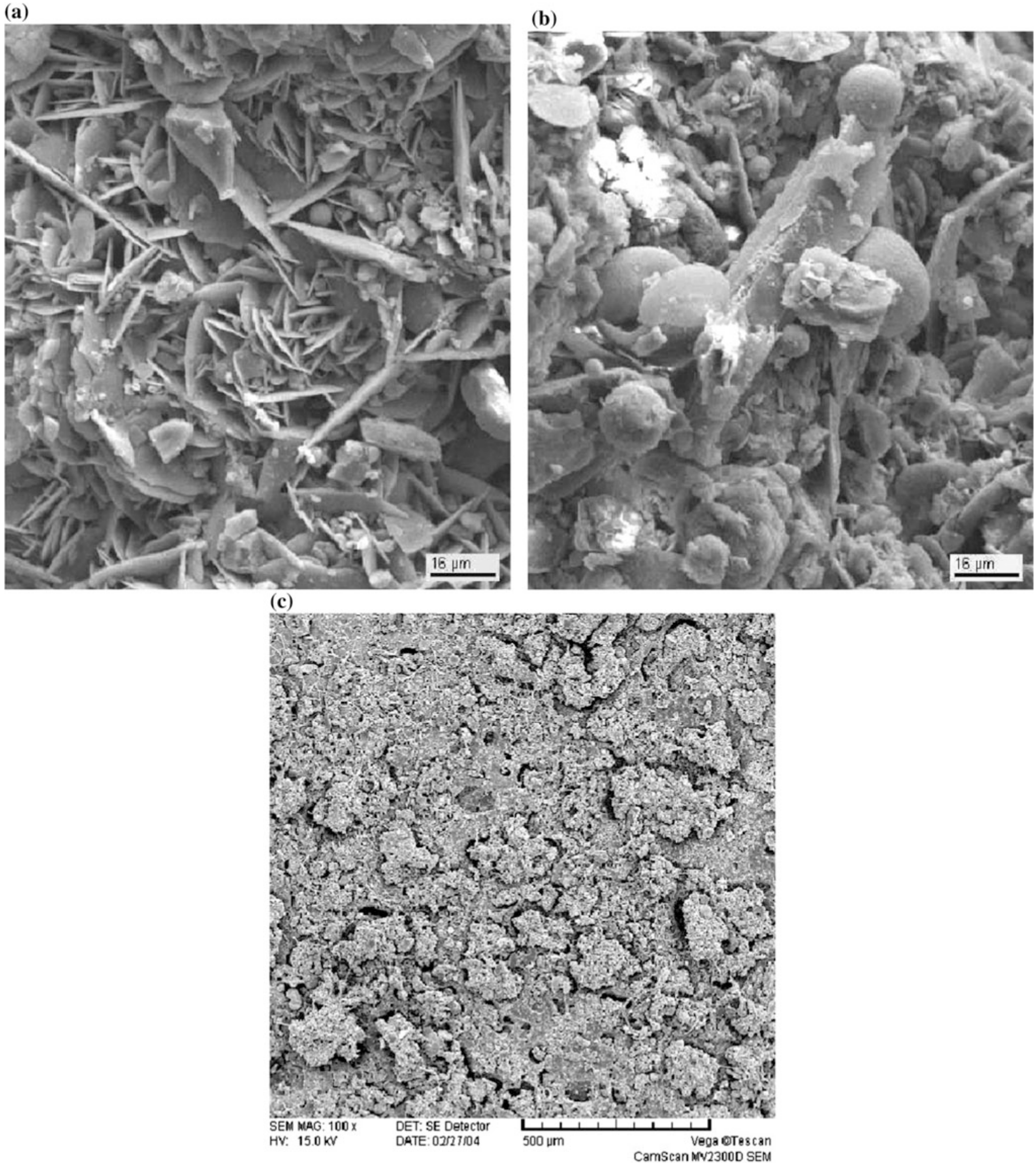

Fig. 4.13 SEM images of the surface of Carrara marble with different degrees of sulphation: **a** rosettes of tabular crystals, monument to A.I. Kosikovsky; **b** elongated crystal of prismatic habitus and algal cells, monument to A.I. Kosikovsky; **c** biofilm, monument to V.B. Golitsyna

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

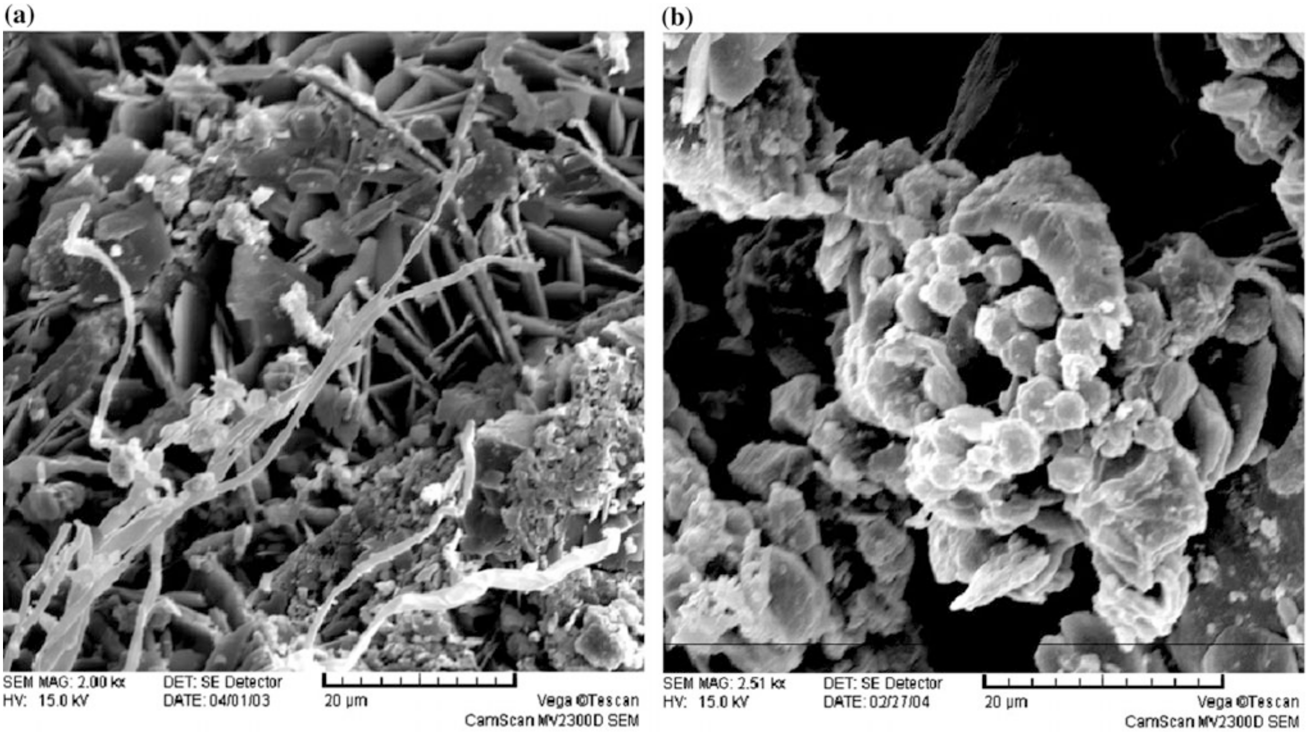

Fig. 4.14 SEM-images of the surface of Ruskeala marble, monument to E.A. Rummel: **a** lamellar gypsum crystals in the fissure, hyphae of fungi; **b** a biocluster

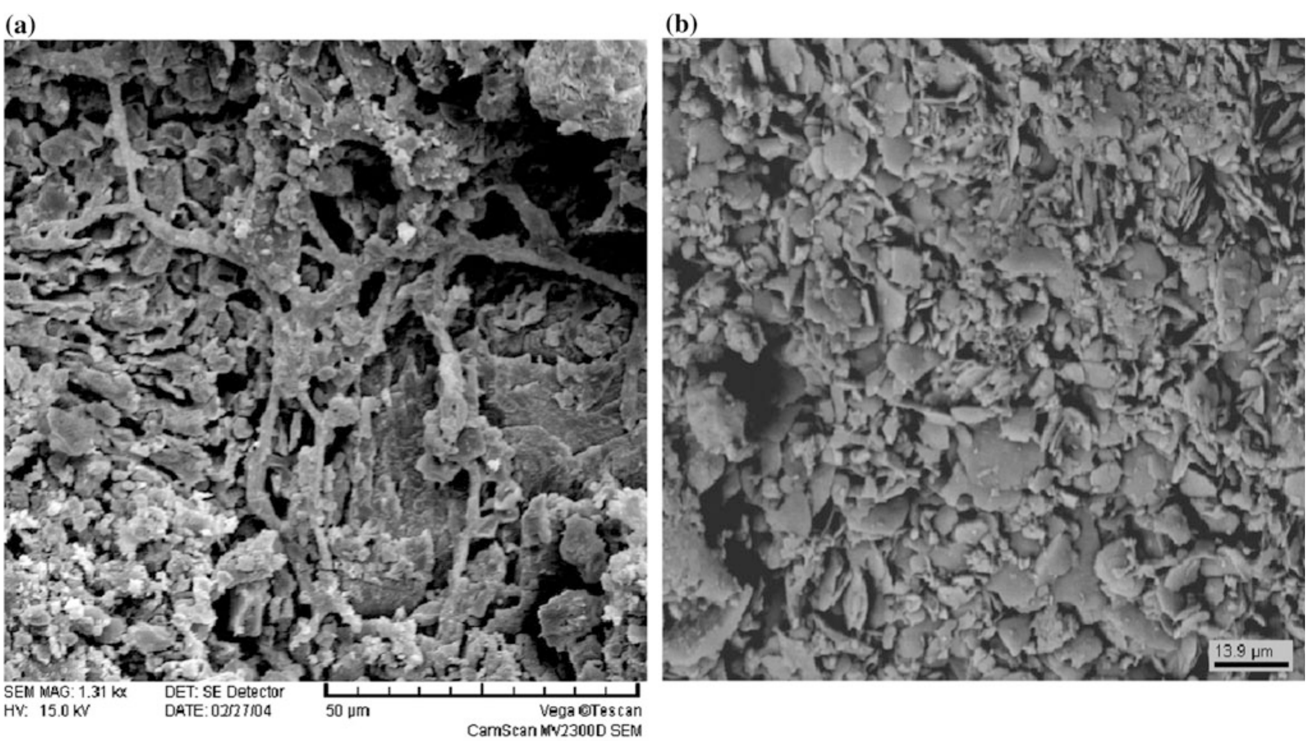

Fig. 4.15 SEM images of the surface of Putilovo limestone, monument to S.I. Lavrov: **a** rare small crystals of gypsum under the biofilm; **b** a layer of gypsum crystals

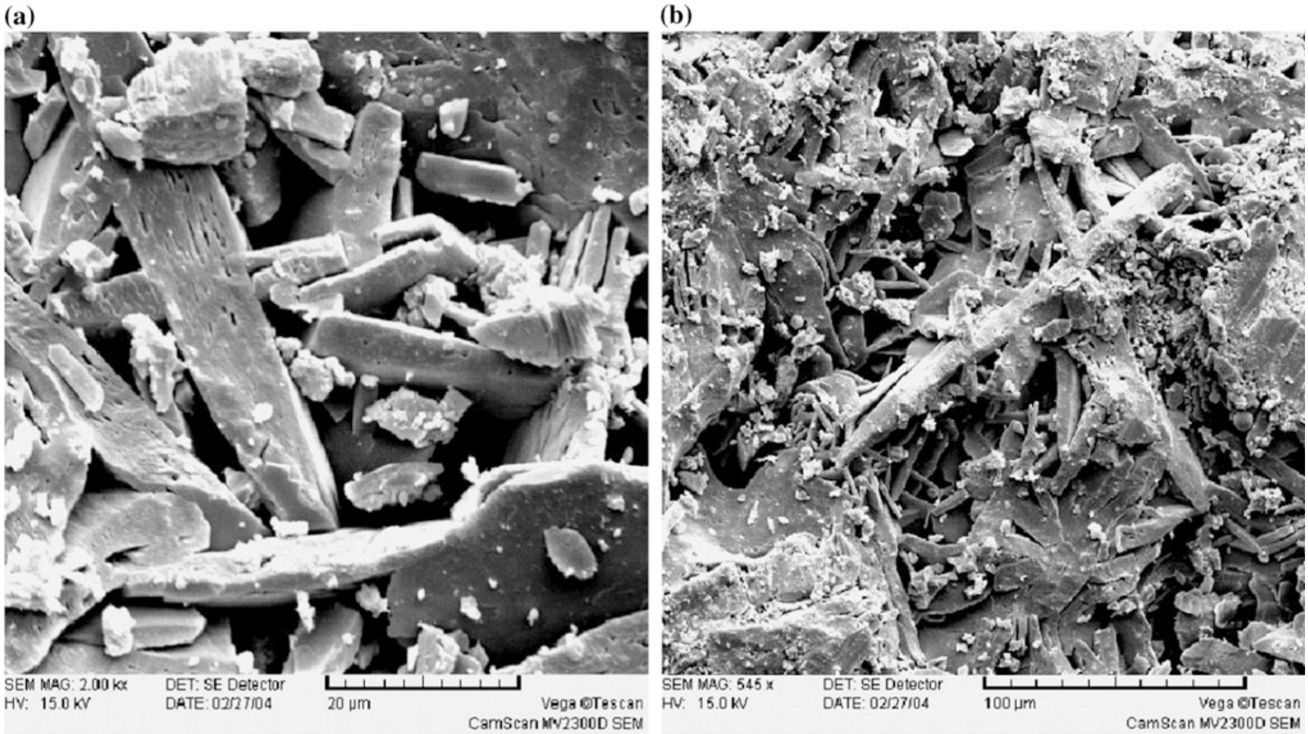

Fig. 4.16 SEM images of the surface of porous travertine: **a** layer of large prismatic gypsum crystals with hatching; **b** needle-like and lamellar gypsum crystals

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).

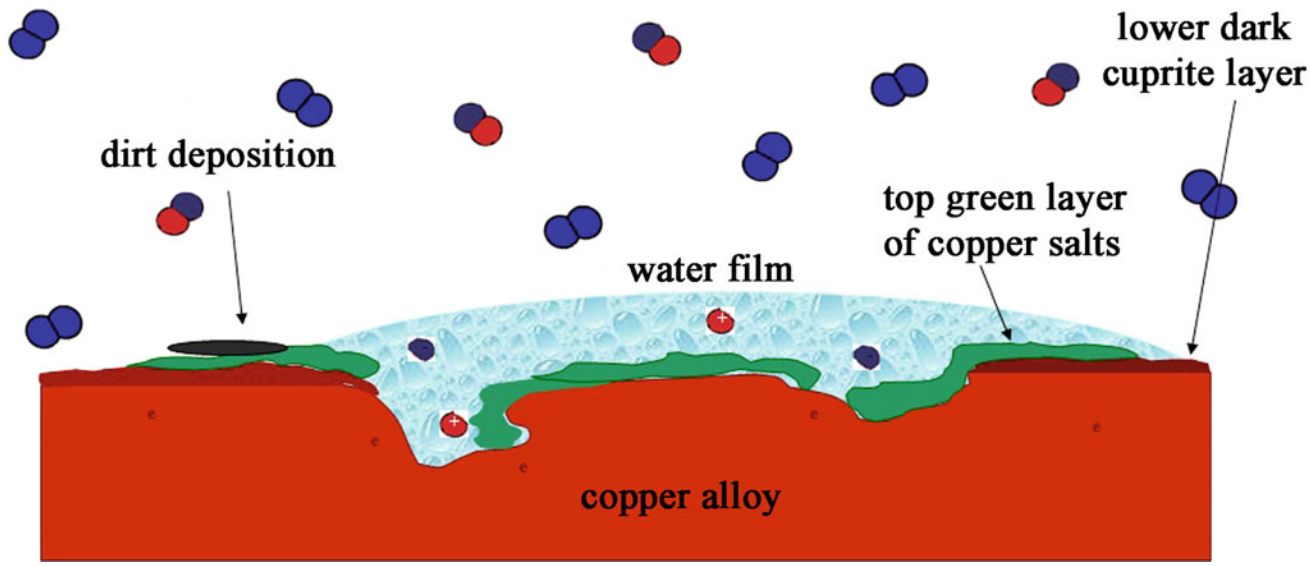

Fig. 4.17 Water film and different deposits on the surface of copper alloys in urban environment (http://www.icom-cc.org/54/document/meeting-at-dac-s1-p-letardi/?id=467#.W4fPlMJ9iUk)

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

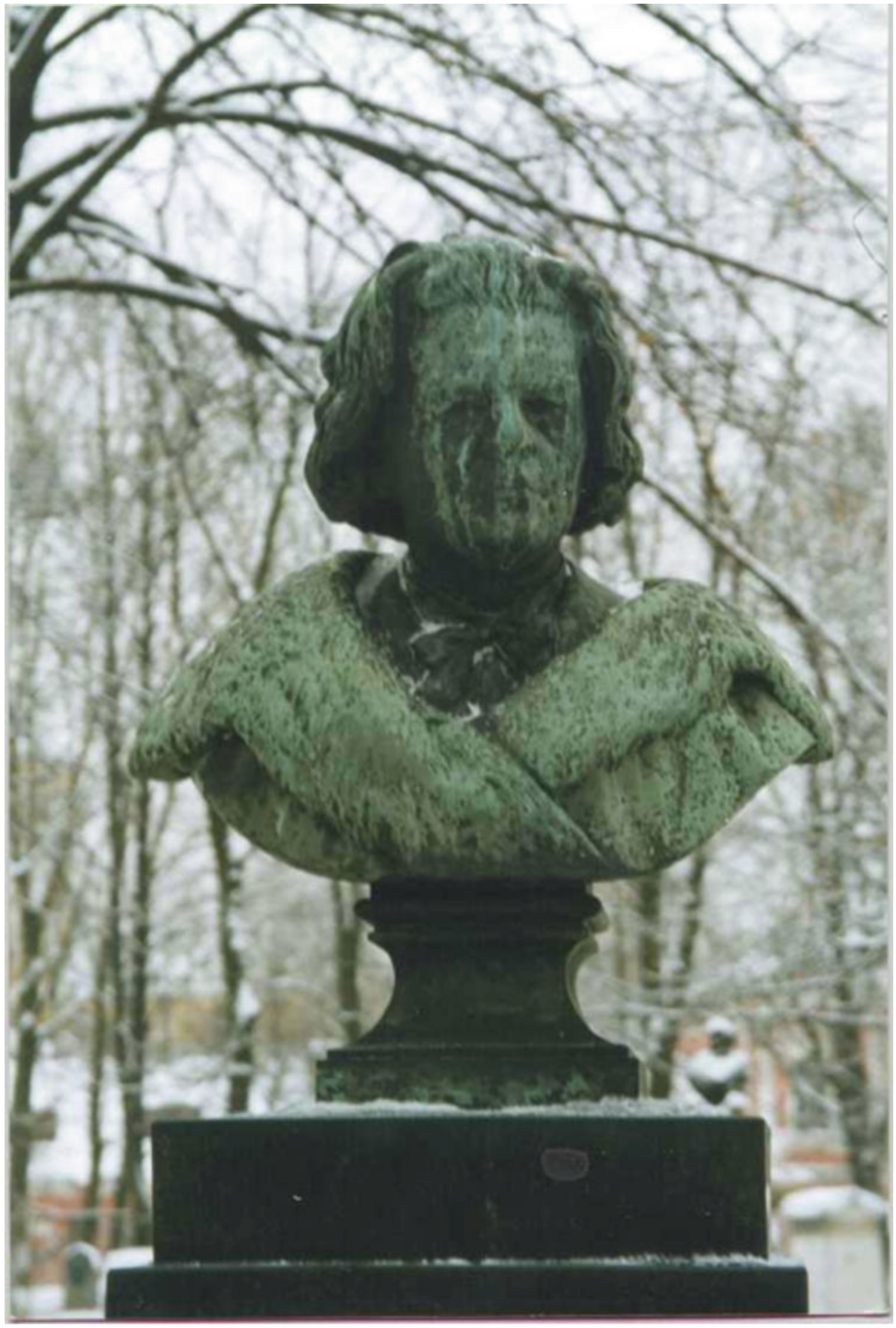

Fig. 4.18 Loose heterogeneous patina on the surface of the monument to A.G. Rubinshtein. Necropolis of Masters of Arts (1999)

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,

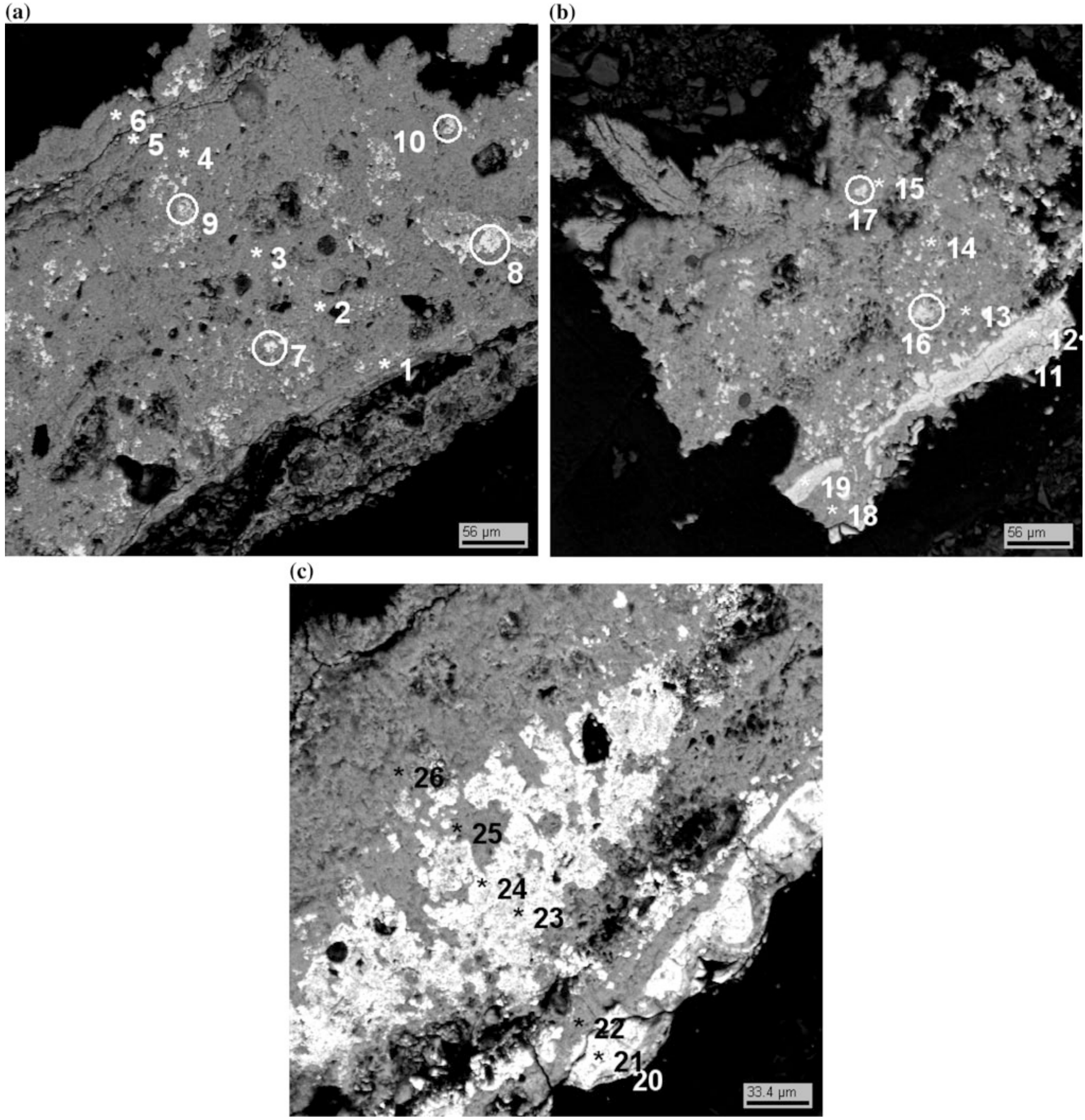

Fig. 4.20 SEM images of patina on the surface of the monument to V. F. Komissarzhevskaya in the Necropolis of Masters of Arts: **a** copper salts (light spots) interspersing the oxide layer (type 1), **b** two-layer patina (type 2), **c** multi-layer patina (type 3). The figures indicate the points where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