Characterization of black crusts of Robba´s fountain statues, Ljubljana (Slovenia)

Karakterizacija črnih oblog na kipih Robbovega vodnjaka, Ljubljana (Slovenia)

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Abstract: Black crusts are result of various chemical-physical reactions between stone surface and environmental factors. Detailed characterization is required to determine causes and mechanisms of black crusts formation, which enables us to chose appropriate cleaning method and prevent their further formation. Statutes of Robba fountain, made of Carrara marble, are encrustated by crusts which differ in composition, morphology and colour. Composition of black crusts and deterioration of the Carrara marble statuary has been investigated by means of optical, electron microscopy and X-ray powder diffraction. Results demonstrated that in sheltered areas of upper parts of the statues, gypsum crusts occur, while calcite crusts cover lower parts of the statues which are within range of the fountain water. In some samples, taken from the lower parts of the fountain, where moisture is constantly present, endolitic green algae and Cyanobacteria are present.

Izvleček: Črne obloge nastajajo kot posledica kemično-fizikalnih reakcij med površino naravnega kamna in različnimi okoljskimi dejavniki. Da bi jih lahko z najprimernejšo metodo odstranili in preprečili njihovo nadaljnje nastajanje, jih je treba natančno okarakterizirati ter ugotoviti mehanizem njihovega nastanka. Na treh kipih Robbovega vodnjaka, ki so izklesani iz carrarskega marmorja, so nastale obloge, ki se med seboj razlikujejo po sestavi, morfologiji in barvi. Vzorci so bili preiskani z optično in elektronsko mikroskopijo ter rtg-difrakcijo. Preiskave so pokazale, da so v zgornjih in zavetnejših delih spomenika, kjer jih deževnica ni izpirala, nastale sadrine, v spodnjem delu vodnjaka, ki je v dometu dotoka vode, pa so se odlagale kalcitne obloge. V nekaterih vzorcih, odvzetih na mestih, ki so bila v dometu vodnega curka, so bili opazni mikroorganizmi, predvsem gre za endolitske modrozelene cepljivke in zelene alge.

Review paper

Key words: black crusts, Carrara marble, Robba’s fountain, deterioration
Ključne besede: črne obloge, carrarski marmor, Robbov vodnjak, propadanje

Introduction

Stones, used in the construction of buildings and monuments, eventually change due to interaction of the stone surface with various environmental factors to which it is subjected. The form and intensity that stone deterioration takes, depends on environmental factors and duration of exposure. On stone surfaces different patinas, efflorescence, soiling of particles from the atmosphere and crusts may occur. These encrustations are the results of either inorganic or organic factors or an interaction of both. They commonly occur as a synchronous activity of different processes, for example dissolution or oxidation of minerals, soiling from the atmosphere, etc. Nevertheless, several biological factors and consequences of some previous restoration interventions could be involved in the process [1]. Encrustations on stone surfaces may differ in morphology and composition, which influences the appearance of the colour.

The formation of black crusts on stone monuments is an important process in stone deterioration. Black crusts occur due to various chemical–physical reactions between stone surfaces and different environmental factors. The most important factors in crust formation are atmospheric pollution and the presence of moisture. Apart from the aesthetical appearance, which is normally unacceptable, such crusts may house various microorganisms that can contribute to the stone degradation [2–4]. Total carbon, present in crusts, has a carbonate and non-carbonate fraction. The non-carbonate fraction includes two different components, organic carbon of biogenic and anthropogenic origin and elemental carbon that could originate from biogenic or anthropogenic sources [5, 6]. The tendency in restoration practice is to remove these crusts by the appropriate cleaning method. For that reason, a detailed characterization is required to determine the causes and mechanisms of black crust formation, to enable the choice of an appropriate cleaning method and prevent their further formation [7–13]. Precise characterization is important especially in the case of laser cleaning [6, 14–19].

Robba’s Fountain, the Fountain of the Three Carniolian Rivers, is one of the most important Baroque monuments in Ljubljana, constructed in 1751 (Figure 1). Elements of the monument consist of four different natural stones; the architectural part is made of two different Slovenian limestones and conglomerates, while the three statues are sculptured of Carrara marble. Owing to accelerated deterioration processes, affecting the monument especially in the last years, it has been decided by conservators that the fountain should be relocated into a museum.

The previous removal of black crusts was carried out in restoration interventions in 1983 [20]. Since then new crusts have formed, differing in composition, morphology and colour. As part of a broader conservation–restoration project, representative samples from Carrara marble statues were taken in

Figure 1. Marble statuary of Robba's Fountain with marked locations of taken samples; Photo: Valentin Benedik, fotodocumentation of Restoration Centre
Slika 1. Kipi Robbovega vodnjaka iz carrarskega marmorja z označenimi lokacijami odvzetih vzorcev; Foto: Valentin Benedik, fotodokumentacija Restavratorskega centra

2006 to characterize and study the marble deterioration.

Experimental

With permission from the current authorities, representative samples of black crusts from each of the three marble statues shown in Figure 1 were collected. Eleven samples were taken from different locations of the marble surfaces. Crusts were carefully detached from the stone surface. On some areas it was possible to take crusts with stone substrate.

Samples were studied with optical microscopy, using a standard petrographic microscope NIKON eclipse E600 pol and scanning electron microscopy (SEM JEOL 5600 LV with X-ray energy microanalysis).

Mineral composition of an average powdered sample was determined by X-ray powder diffraction, using X-ray diffractometer Philips PW3710 with Cu Kα radiation and graphite secondary monochromator. Data were collected at a voltage of 40 kV and current of 30 mA in the range of 2–70° (2θ), with a speed of 3 °/min. Mineral phases were determined using the computer program Philips X'Pert software.

Results and discussion

Macroscopical description

It is possible to distinguish four types of crust, by morphology and colour, on the sculptures: In the upper rough parts of the sculptures poorly adhesive deposits due to soiling by particles from the atmosphere (type 1: sample RO75) are present. Compact black crust, tracing (type 2: RO66, RO67, RO69, RO70 and RO71, RO73) and changing (type 3: sample RO65) the surface and white crusts (type 4: RO63), changing the surface, occur within reach of the fountain water, mostly on lower parts of the sculptures. Black crusts (type 2: samples RO68, RO76), tracing the surface, are also present on sheltered areas of upper parts of the sculptures.

Mineral composition

On the monument it is possible to distinguish two types of crusts by mineral composition. In general, one type of crust consists of gypsum, while the other consists of calcite (Table1). Both types are described in detail in the following text.

Table 1. Mineral composition of samples, determined by optical, electron microscopy and X-ray powder diffraction

Tabela 1. Mineralna sestava vzorcev, določena z optično in elektronsko mikroskopijo v presevni in odsevni svetlobi, s SEM in z rentgensko difrakcijo

Sample	Prevailing mineral
RO63	micritic calcite
RO65	micritic calcite
RO66	laminated calcite
RO67	laminated calcite
RO68	gypsum
RO69	laminated calcite
RO70	laminated calcite
RO71	micritic calcite
RO73	laminated calcite
RO75	gypsum and calcite crystals
RO76	gypsum

Calcite crust

On the lower parts of the monument, which are within range of the fountain water, crusts are predominately composed of calcite (samples RO63, RO65, RO66, RO67, RO69, RO70, RO71, RO73). These crusts occur as well-known calc-sinters [21] with parallel-banded layers. The majority of crusts are laminated (type 2: samples RO66, RO67, RO69, RO70, RO71, RO73) probably due to seasonal precipitation of calcite from water during the summer period, when water circulates in the fountain. They are also known as microstromatholitic carbonate crusts [22]. Crusts consist of white laminas of calcite crystals, elongated perpendicular to the stone surface, which alternate with black laminas rich in silica (Figure 2). Silica-rich laminas equate to winter time, when water circulation in the fountain is absent and soiling of combustion particles occurs. Silica is probably derived from ash released by industrial sources, which is for the most part composed of silicates. Thus, laminas of crust alternate in colour and composition according to the season of the year. Under the laminated calcite layers a micritic zone is present, which represents the deteriorated stone surface (Figure 2a and 2b). Grains of marble are micritized and deeper decohesion of marble grains is present. An unreacted zone of marble is beneath this zone.

In some areas, lamination of calcite crusts is absent; crusts are less dense and respectively more porous (type 3 and type 4: samples RO65, RO63). They consist of fine-grained calcite – micrite. Several calcite and dolomite grains are entrapped and form in areas with inconstant water motion.

During calcite precipitation, soiling from the atmosphere occurs as well, i.e. soiling of anthropogenic particles, which are entrapped in crusts and also result in the black colour of the crust. Calcite crusts contain spherical aerosols, which are rich in iron and chromium (Figure 3). Lefevre and Ausset [23] reported that atmospheric particles could originate from anthropogenic sources (ash, dust rich in Fe and Si-Al, glass particles), sea (halite), terigene sources (calcite, gypsum, alumosilicates) and biogenic sources (spore, pollen). The black colour is the result of mainly ash particles and dust [24–26]. These particles often contain metal oxides, which catalyze the oxidation of SO_2 and consequently crust formation [24]. In fuel combustion various black carbonaceous particles such as ash and organic matter are emitted. Diesel engines especially are an enormous source of ash. The main component of ash, produced as waste material in burning coal is silica, while liquid fuels emit porous carbonaceous particles, i.e. ash [27]. As all combustion sources produce black carbon particles, this is the reason why the stone surfaces blacken.

Gypsum crust

Crust on the upper parts of the statues, above the range of the fountain water, consists of gypsum (samples RO68, RO75 and RO76). Gypsum crusts occur in sheltered areas of the statues that are not exposed to rain water. Crusts are present as compact black crusts, tracing the surface (type 2: samples RO75 and RO 76) or poorly adhesive deposits (type 1: sample RO75). Gypsum crystals fall in the range of 50 μm to 100 μm (Figure 4). Between crystals several aerosols are present. Since soiling of atmospheric particles rich in iron, nickel or chromium could catalyze SO_2 oxidation, which is present on stone surfaces, these aerosols contribute to enhanced stone deterioration when the process is followed by soluble salt crystallization, for example

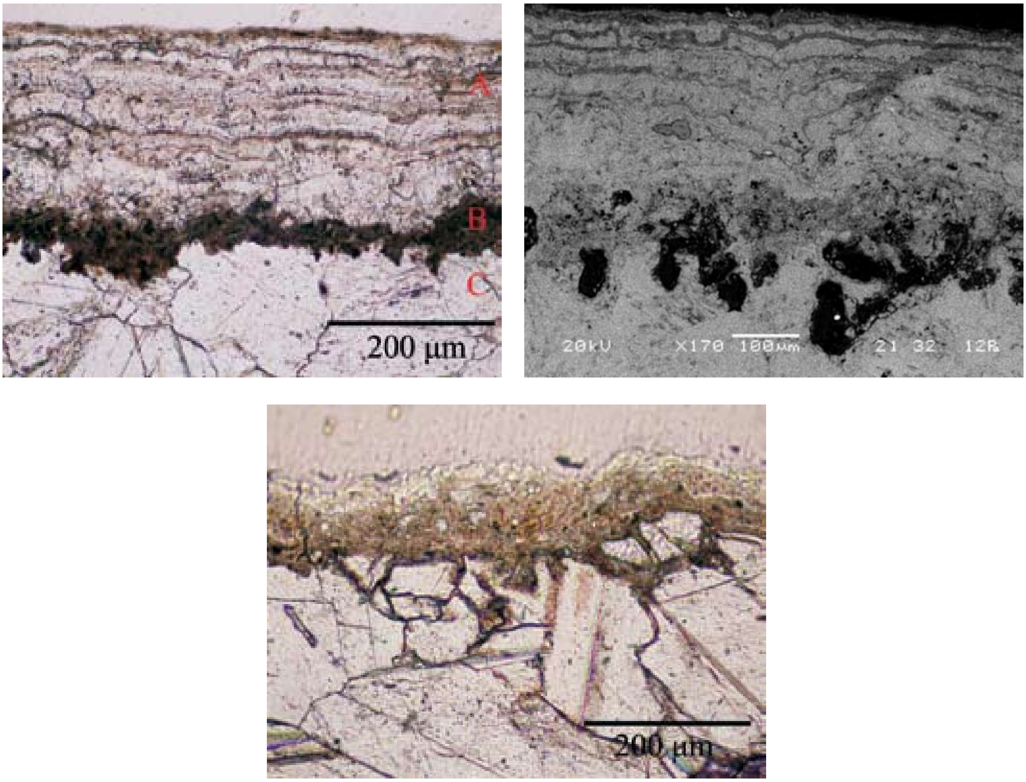

Figure 2. A transverse profile of weathered marble (sample RO 70), the laminated calcite crust, where white laminae of calcite crystals alternate with black siliceous laminae (zone A), as seen under transmitted light (a) and electron microscope (b). Crust is followed by micritized zone (zone B), underneath unaltered marble is present (zone C). Under the micritized zone etched calcite grains of marble are noticed. (c) Decohesion between calcite grains and etched calcite crystals. Transmitted light, crossed polars.

Slika 2. Profil preperele kamnine (vzorec RO70), cona A: laminirana kalcitna obloga. Izmenjujejo se svetle lamine kalcitnih kristalov ter temne lamine, bogate s silicijem. Cona B: mikritizirana površina marmorja, cona C: nespremenjen marmor; a) presevna svetloba, prekrižani nikoli, b) SEM, BSE. c) Dekohezija med kaclitnimi zrni in najedkani kalcitnimi kristali. Presevna svetloba, prekrižani nikoli.

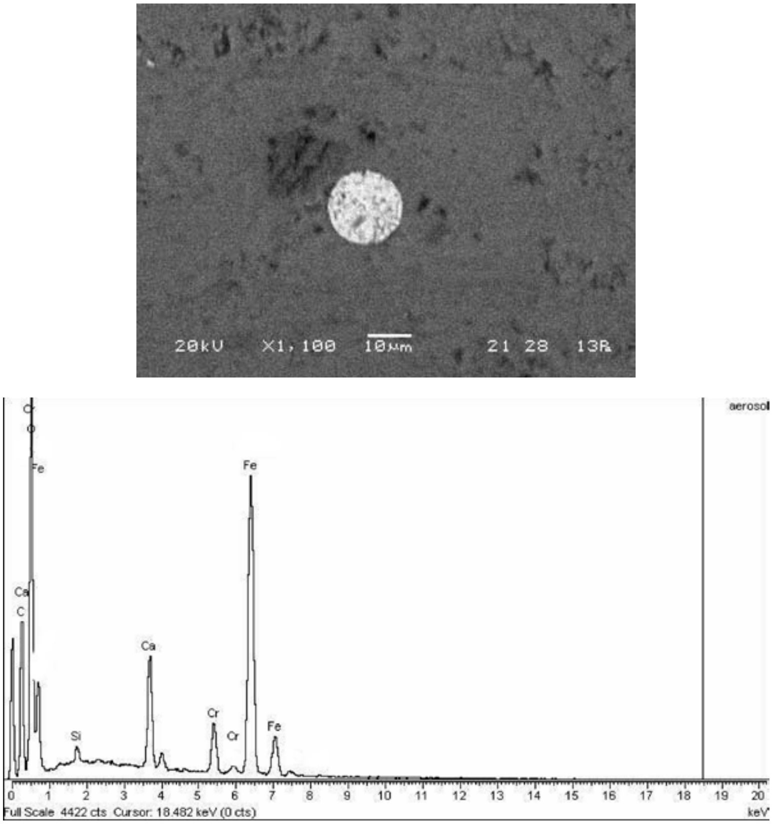

Figure 3. a) Aerosol, rich in Fe and Cr, SEM, BSE; b) chemical composition of aerosol, EDX

Slika 3. a) Aerosol, bogat z železom in kromom, SEM, SE; b) kemična sestava aerosola, EDS

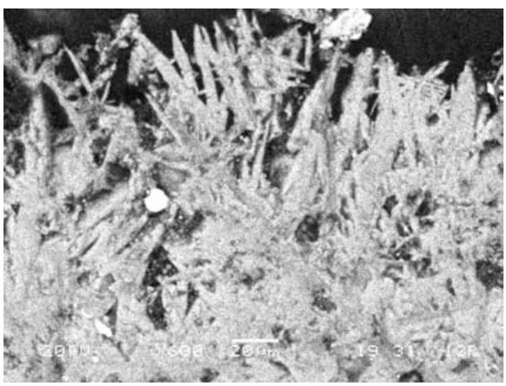

Figure 4. Crystals of gypsum in sample RO68; SEM, BSE.

Slika 4. Kristali sadre. Vzorec RO 68; SEM, BSE.

gypsum formation [9–10, 26].

The process of sulphation is one of the most important reactions and contributes to calcium carbonate deterioration [13] and is already a well-known phenomenon [7, 28–30]. A crust of gypsum is formed as a result of the reaction between water, calcite and sulphuric acid. As gypsum crust is more soluble compared to calcium carbonate substratum [31], it remains on sheltered zones of the monument, while on zones exposed to rain it is washed out. The process of sulphation continues under the crust. A higher solubility of gypsum compared to calcite enables water infiltration and processes of recrystallisation, but favours water retention under the crust as well [13, 32].

Presence of microorganisms

Investigation of samples with an optical microscope showed the presence of cyanobacteria, green algae and lichen (Table 2). Endolitic, unicellular or filamentous cyanobacteria, green algae and lichens colonize lower parts of the fountain, which are within range of the circulating water. Unicellular green algae are, in some places, already subjected to the process of fossilization. On some samples of calcite crusts, microorganisms and the consequences of their activity are observable. These microorganisms are present on the surface of calcite crusts, in calcite crusts or they penetrate into the marble substrate. Filamentous cyanobacteria and green algae in sample RO69 form crust coating under the laminated calcitic crust (Figure 5a). Filaments are perpendicular to the stone surface, penetrating into the marble. By penetrating between the marble grains and by etching crystals in the form of biopitting they contribute to the physical and chemical deterioration of marble (Figure 5b).

Sarro et al. [33] reported that filamentous green algae are frequently present in fountains. It was reported [34] that cyanobacteria and chlorophycea comprise the two of most common groups of algae found on building stones, as endolithic habitats provide good growth conditions in otherwise harsh environments. Cyanobacteria and algae are normally pioneers in colonizing stone surfaces because they are autothrophic organisms [22, 35]. Thus, organic matter, necessary for the growth of heterotrophic organism is ensured by dead cells of autotrophic organisms.

The presence of algae on stone surfaces favours carbonatization as a result of the process of respiration and fixation of CO_2. Although all taxonomic groups of algae and cyanobacteria are capable of contributing to carbonate precipitation, this is especially seen in the case of green algae and cyanobacteria [33, 36]. On the other hand, organic acids, which are produced in their metabolic processes, could dissolute minerals.

Table 2. Groups of microorganisms, present in crusts

Tabela 2. Skupine mikroorganizmov v oblogah

Sample	Microorganisms
RO63	lichen on calcite crust surface
RO65	-
RO66	cyanobacteria
RO67	cyanobacteria and green algae
RO68	-
RO69	cyanobacteria and green algae
RO70	-
RO71	cyanobacteria and green algae
RO73	cyanobacteria and green algae
RO75	-
RO76	-

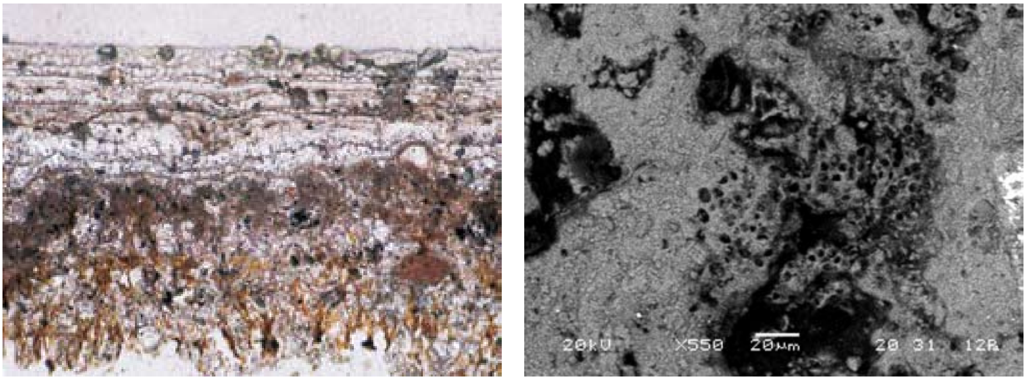

Figure 5. a) Filamentous algae and cyanobacteria under laminated calcite crust. Sample RO69, transmitted light, parallel polars; b) Effect of microbial activity in the form of biopitting, sample RO70, SEM, SE
Slika 5. a) V spodnjem delu slike pod laminirano kalcitno oblogo so vidne filamentne alge. Vzorec RO 69, presevna svetloba, vzporedni nikoli; b) posledice delovanja mikroorganizmov v obliki luknjičastega raztapljanja zrn kalcita – biopiting; vzorec RO 70, SEM, BSE

Deterioration of marble

The deterioration can be expressed in a simplified form as a function of the principal parameters only. Distinction can thus be made between parameters whose effect is decidedly predominant and those whose incidence is practically negligible. The surface of Carrara marble is subjected to various processes of deterioration. In some areas a micritized zone (Figure 2a) is present, which is a result of several factors, probably also due to activity of microorganisms. The role of microorganisms in micritizing processes is reported by Kabanov [37]. Mineral dissolution and decohesion between calcite crystals is easily observable (Figure 2c), while on the surfaces different crusts occur. Formation of different crusts and biofilms is caused by various mechanisms of marble deterioration [38]. Crusts have a different thermal expansion compared to marble substrate. In repeated heating–cooling cycles, tension between the stone and crust occurs, which leads to mechanical breakdown and disintegration of the stone. As can be seen, crusts can represent a habitat for various microorganisms, which with their metabolic products and growth affect and cause the structure of marble to deteriorate. Chemical weathering is induced due to excreted metabolic products, such as organic acids, proteins, pigments and sugars [39]. Fissures in the marble are enhanced due to swelling caused by water absorption and growth of the microorganisms present. It has been reported [22], that biodeterioration of fountains is mainly caused by the activity of microalgae, which are generally pioneers in the processes of biodeterioration. Their action is direct and also indirect, since they promote other mechanisms of deterioration and the growth of other communities.

Erosion of marble surfaces in areas where crusts are not present is enormous due to acid rain.

Conclusions

The statues of Robba's Fountain, made of Carrara marble, are covered by crusts which differ in composition, morphology and colour. Results have demonstrated that two different crusts can be distinguished by mineral composition. In sheltered areas of upper parts of the statues, gypsum crusts occur, while calcite crusts are present within the range of water in lower parts of the statues. The marble surface is subjected to process of micritization of crystals, which increases the specific surface of the grains and consequently the reactive surface. Above that zone, various crusts are formed.

The lower parts of the fountain, which is within water range, colonize endolitic, unicellular or filamentous green, cyanobacteria and lichens. These microorganisms are present in calcite crusts or they penetrate into the marble substrate. Continuous exposure to moisture enables the existence and growth of microorganisms on the marble, which contribute to its chemical and physical deterioration by micritization of the marble surface and calcite dissolution. On the other hand, they could contribute to the calcium carbonate precipitation from the fountain water and thus calcite crust formation.

Crust formation is cyclic with regard to season and as a consequence to a period of the marble being constantly wet from the fountain's water and to the quantity of atmospheric particle soiling (dust, ash), which blackens the marble surface. The main factors resulting in crust formation are atmospheric pollution and circulation of the fountain's water. Calcite crust could also function as a protection of the marble surface, since calcite precipitation prevents dissolution of marble and thus erosion of the statues.

Detailed characterization enables an appropriate cleaning method to be chosen for crust removal and to prevent further formation.

Acknowledgements

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Povzetek

Površina kamnine, uporabljene pri gradnji spomenikov in stavb, se z leti spreminja zaradi interakcije kamnine z okolico, s katero je v neposrednem stiku. Vrsta in jakost spremembe sta odvisni od časa trajanja stika in od medija, s katerim je kamnina v stiku. Na površini kamnine nastajajo različne patine, oprhi in celo kompaktne skorje. S skupnim imenom jih označujemo kot obloge. Lahko so anorganskega ali organskega izvora ali kombinacija obeh. Obloge pogosto nastanejo zaradi hkratnega delovanja različnih procesov, kot npr. raztapljanja ali oksidacije kamnite podlage, usedanja delcev iz atmosfere itd. Po navadi so posledica kemično-fizikalnih procesov med površino kamnine in okoljskimi dejavniki. Nastanejo tudi zaradi številnih bioloških dejavnikov ter kot posledica preteklih restavratorskih posegov (VAZQUES-CALVO et al., 2007). Med seboj se lahko ločijo tako po morfologiji kot po sestavi, ki vpliva tudi na njihovo barvo.

Črne obloge, ki jih najdemo na spomenikih iz naravnega kamna, so s stališča konservatorsko-restavratorske stroke estetsko moteče, škodljive za samo kamnino in jih je treba z najustreznejšo metodo odstraniti. V ta namen jih je treba natančno okarakterizirati ter ugotoviti mehanizem njihovega nastanka, da bi jih lahko primerno odstranili in preprečili njihovo nadaljnje nastajanje (VERGES-BELMIN, 1993, MORPOULOU et al., 1998, AUSSET&LEFEVRE, 2000, BUGINI et al., 2000, MARAVELAKI-KALAITZAKI, 2001, MARAVELAKI-KALAITZAKI, 2005, GIAVERINI et al., internet). Natančna karakterizacija je pomembna predvsem v primeru odstranjevanja oblog z laserskim čiščenjem (PINI et al., internet, CATALANO et al., internet, MARAVELAKI-KALAITZAKI et al., 1999, MARAKIS et al., 2000, BROBLET et al., 2003, MARAKIS et al., 2003, POTGIETER-VERMAAK et al., 2005).

Trije kipi Robbovega vodnjaka »Vodnjak treh kranjskih rek« so izklesani iz carrarskega marmorja. Črne obloge na njih so bile nazadnje odstranjene pri restavratorskih posegih leta 1983 z mikropeskanjem. V tem času so nastale nove obloge, ki se med seboj razlikujejo po sestavi, morfologiji in barvi. Kot del konservatorsko-restavratorskega projekta »Robbov vodnjak – Vodnjak treh kranjskih rek« smo v letu 2006 odvzeli značilne vzorce oblog na kipih iz carrarskega marmorja za njihovo karakterizacijo ter študij propadanja te kamnine v mestnem okolju.

Na kipih iz carrarskega marmorja po morfologiji lahko ločimo štiri tipe oblog. Gre za črne usedline atmosferskih delcev, ki so slabo vezane na kamnito površino in se pojavljajo v zgornjih delih kipa na hrapavih površinah. V spodnjem delu kipov, ki so bili v dosegu tekoče vode vodnjaka, so bile kompaktne temne obloge, ki sledijo reliefu kamnine, in temne ter svetle obloge, ki spreminjajo relief kamnine. Kompaktne temne obloge, ki sledijo reliefu kamnine, so bile tudi v zgornjih delih kipov v zavetnejših predelih.

Na spomeniku po sestavi ločimo dva tipa črnih oblog, po morfologiji pa vsaj štiri različne vrste oblog. Površina kamnine preperева. Pojav označujemo kot mikritizacija kamnine. Pri tem se specifična površina zrn poveča in s tem reaktivna površina. Nad to mikritizirano cono pa nastajajo različne vrste oblog. V zgornjih predelih spomenika, kjer je marmor v stiku z atmosfero, nastajajo sadrine obloge, v spodnjem delu vodnjaka, ki je v dometu dotoka vode, pa se odlagajo kalcitne obloge. V nekaterih vzorcih, odvzetih z mest na vodnjaku, ki so bili v dometu vodnega curka, so bili opazni mikroorganizmi, predvsem gre za endolitske modrozelene cepljivke in zelene alge. Stalna izpostavljenost kamnine vlagi omogoča obstoj in rast organizmov v kamnini, ki povzročajo in pospešujejo propadanje – mikritizacijo in kasnejše raztapljanje kamnine. Rast oblog je ciklična glede na letni čas in/oz. glede na obdobja stalne omočenosti kamnine z vodo iz vodnjaka ter glede na količino atmosferskih delcev (prah, pepel), ki se vgrajujejo v obloge in jih pri tem obarvajo. Glavni dejavniki nastajanja oblog so onesnaženost ozračja ter voda. Kalcitne obloge lahko delujejo tudi kot zaščita površine, saj nalaganje kalcita iz vode preprečuje raztapljanje kamnine in s tem erozijo kipov.

Natančna analiza sestave oblog in vzrokov za njihovo nastajanje omogoča primeren izbor učinkovite metode čiščenja in odpravljanje vzrokov propadanja. Pri izbiri najučinkovitejše metode moramo upoštevati določena merila, ki bi pripomogla k izboljšanju stanja objekta. Metoda, ki jo izberemo, ne sme povzročiti neposredne ali posredne škode na kamniti površini.

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