DETERIORATION OF THE BLACK DRENOV GRIČ LIMESTONE ON HISTORICAL MONUMENTS (LJUBLJANA, SLOVENIA)

PROPADANJE ČRNEGA APNENCA Z DRENOVEGA GRIČA NA OBJEKTIH KULTURNE DEDIŠČINE (LJUBLJANA, SLOVENIA)

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Abstract   UDC 552.541:725.94(497.4Lj.)
Sabina Kramar, Ana Mladenović, Helmut Pristacz & Breda Mirtič: Deterioration of the black Drenov Grič limestone on historical monuments (Ljubljana, Slovenia)
The black limestone from Drenov Grič quarry (Central Slovenia) is considered one of the most beautiful Slovenian natural stones due to its typical color. The limestone was characterized from mineralogical, chemical, and petrophysical points of view. Furthermore, deterioration phenomena of the limestone from two monuments exposed to indoor and outdoor environments were studied. In situ investigation of two monuments by means of monument mapping has identified several types of deterioration phenomena, such as granular disintegration, flaking, crumbling, efflorescences, crusts, and the presence of microorganisms. Samples were characterized using Optical Microscopy (OM), Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDS), X-Ray Powder Diffraction Analysis (XRD), porosity accessible to water under vacuum, capillary absorption, Mercury porosimetry (MIP), and Ar-sorption. Although very low values of porosity of the fresh stone as well as slow capillary kinetics were determined, both monuments showed severe deterioration as a consequence of the transport and precipitation of soluble salts within the stone.
Keywords: limestone, deterioration, soluble salts, natural stone, historical monuments.

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Sabina Kramar, Ana Mladenović, Helmut Pristacz & Breda Mirtič: Propadanje črnega apnenca z Drenovega griča na objektih kulturne dediščine (Ljubljana, Slovenia)
Črni apnenec z Drenovega griča (Osrednja Slovenija) velja zaradi svoje tipične barve za enega izmed najlepših slovenskih naravnih kamnov. Apnenec smo raziskali s kemičnega, mineraloškega in petrofizikalnega vidika. Nadalje podajamo oblike propadanja preiskovanega apnenca na primeru dveh spomenikov, izmed katerih je eden izpostavljen notranjemu in drugi zunanjemu okolju. Na obeh objektih smo določili številne oblike propadanja, kot so zrnato razpadanje, luščenje, drobljenje, eflorescenca, skorje in prisotnost mikroorganizmov. Vzorce apnenca smo nato preiskali z optično mikroskopijo, vrstičnim elektronskim mikroskopom z elektronsko disperzno spektroskopijo, rentgensko praškovno difrakcijsko analizo, meritvami odprte poroznosti in kapilarnega dviga ter metodami živosrebrove porozimetrije in plinske sorpcije z uporabo argona. Kljub temu, da ima apnenec izredno nizke vrednosti poroznosti in kapilarnosti, so na obeh objektih opazne številne oblike propadanja, ki so vezane prav na transport in precipitacijo topnih soli v apnencu.
Ključne besede: apnenec, propadanje, topne soli, naravni kamen, spomeniki.

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INTRODUCTION

Limestone has been one of the most common stones used for buildings or monuments since prehistoric times. It is widely known, that all stones eventually change due to their interaction with the various environmental conditions. Thus, similarly as the weathering processes occur at the Earth's natural surfaces, they also affect man-made monuments or buildings. Limestone weathering and erosion results in a large variety of karstic forms that have been an object of interest for geologists. On the other hand, the urban atmosphere is creating special environment that affects exposed stone surfaces, usually enhancing the process of decay several times compared to that in natural rural environs (Winkler 1997). Monuments that currently exist in natural environments, or those that were removed from outdoor exposure before air pollution set in, are well-preserved after even millennia of outdoor exposure. In contrast, many of those exposed even for a few decades in industrial environments have decayed beyond recognition (Gauri & Bandyopadhyay 1999).

Many Slovenian monuments and modern buildings are built of various limestones, the consequence dependent on large access of that natural stone in the region, as around 35% of Slovenian territory consists of limestone (Gams 1974). The properties, behavior and decay of limestones as building materials have been intensively studied over the last decades, by means of different approaches (Cardell *et al.* 2003; Benavente *et al.* 2004; Cardell *et al.* 2008; Cultrone *et al.* 2008). Nevertheless, these studies have been mainly concerned with porous limestones, whereas detailed studies of the properties of compact limestones, comparable to Slovenian limestones, are still rare. Moreover, among the studies, which are focused on the characterization the limestones as building materials or estimating durability (Mladenović *et al.* 1999; Skobe & Mirtič 2005; Kramar *et al.* 2010c), there are only few studies related to the weathering phenomena of limestone on monuments from Slovenian Region and thus the behavior of the limestone in built environment (Kramar *et al.* 2010a; Kramar *et al.* 2010b; Kramar *et al.* 2011).

The limestone known as black Drenov Grič limestone is considered one of the most beautiful Slovenian natural stones due to its typical black color interwoven with white veins. It used to be exploited in three major quarries west of Ljubljana which are all at a standstill now. The Triassic well stratified limestone occurs in 10 to 80 cm thick beds which alternate with thin sheets of marls. Some fragments of fossils of bivalvia, gastropoda, algae, foraminifera, ostracods, and chorals are also found (Ramovš 2000). Black limestones are normally micritic limestones relatively rich in carbonaceous and bituminous matter, which is supposed to be responsible for their dark color (Winkler 1997; Marinoni *et al.* 2007; Marszałek 2007). As the limestone is dense, resulting in a good polishing effect, it was popularly considered as marble. The Drenov Grič limestone was widely used particularly in baroque architecture not only in Ljubljana but also in other regions of Slovenia. Many inner and outdoor architectural elements and monuments, especially portals of houses and altars, were made of this limestone (Ramovš 2000). The extensive use of black limestones was also reported to be characteristic for the baroque period in other parts of European countries (Marinoni *et al.* 2002; Zehnder 2006; Marinoni *et al.* 2007; Marszałek 2007). However, when exposed to climatic influences, chromatic weathering and salt weathering are recognized as the main deterioration phenomena of these limestones.

As many Slovenian monuments built of the investigated black limestone are also extensively deteriorated, recognition of limestone properties and understanding of deterioration factors and processes is necessary for their successful maintenance, protection, and proper restoration/conservation interventions. Thus, the mineral composition and microstructure of the black Drenov Grič limestone has been studied in order to determine the intrinsic parameters that affect its durability and behavior when exposed to the different environmental conditions. The deterioration patterns and related weathering mechanisms of two selected baroque monuments exposed to indoor and outdoor environments have been characterized and discussed.

EXPERIMENTAL

SAMPLING

Samples of fresh limestone were collected from the main quarry in Drenov Grič near Ljubljana (Fig. 1a), which had a primary role in past centuries in supplying

building material to central parts of Slovenia (Ramovš 2000).

The samples of weathered black limestone were collected from the two monuments, which have been

exposed to environmental conditions since the baroque period. Sampling was carried out from:

• the altar in the Chapel of St. Francis Xavier in the Church of St. James, Ljubljana (Fig. 1b). The altar, made of 18 different natural stones with prevailing black limestone, was constructed during the years 1709–1722 (samples JAL).

• the portal with two Hercules at Semenišče, Ljubljana (Fig.1c), constructed during the years 1708–1772 (samples SEP).

METHODS

Detailed registration of the weathering forms was made by means of in situ monument mapping. The applied mapping method was based on a classification scheme proposed by Fitzner & Heinrichs (2002).

Polished thin sections of samples of the limestone from the quarry were studied by optical microscopy using an Olympus BX-60 equipped with a digital camera (Olympus JVC3-CCD).

Fig. 1: (a) One of the three historical quarries of the black limestone in Drenov Grič (Central Slovenia). (b) The detail of the side altar in the Church of St. James, Ljubljana (Slovenia). (c) Portal with two Hercules at Semenišče, Ljubljana (Slovenia).

The samples of both unweathered and weathered limestone were examined by a Scanning Electron Microscope (JEOL 5500 LV) using back-scattering electrons. Some particular areas of the samples were analyzed for chemical composition using Energy Dispersive Spectroscopy (EDS). The excitation voltage was 20 kV, and the pressure was between 10 and 20 Pa.

The mineral composition of both the unweathered limestone and the weathering products was determined by X-ray powder diffraction using a Philips PW3710 X-ray diffractometer equipped with Cu Kα radiation and a secondary graphite monochromator. The samples were milled in an agate mortar to a particle size of less than 50 μm. The data were collected at 40 kV and a current of 30 mA in the range from 2 to 70° 2θ. Afterwards, each sample of limestone was treated in order to extract its acid-insoluble residue. About 400 mg of each sample was crushed and dissolved in 20 ml of dilute HCl (1:10) (Marszałek 2007). The residue was then washed with distilled water in order to remove all traces of HCl. The acid-insoluble fraction was then analyzed using X-ray powder diffraction.

All the samples of the unweathered limestone were

Information regarding samples of both unweathered and weathered limestone is provided in Tab. 1.

Tab. 1: Summary of the investigated samples, related weathering forms and mineralogy as determined by X-ray powder diffraction and SEM-EDS.

Unweathered samples			
Limestone	**Location**	**Investigated Samples**	**Primary mineralogy**
	Drenov Grič quarry	DG1, DG2, DG3, DG4, DG5	calcite, dolomite, quartz, clinochlore, pyrite, muscovite/illite

Samples from monuments			
Weathering Type	**Location**	**Investigated Samples**	**Weathering products**
flaking, sublorescence	altar	JAL23, JAL24, JAL111	gypsum
eflorescence	altar	JAL12, JAL13, JAL15, JAL77	hexahydrite, pentahydrite, starkeyite, gypsum
white crust	altar	JAL88, JAL161, JAL 167	gypsum
crumbling	altar	JAL102, JAL153	gypsum
splitting	altar	JAL122, JAL 159	gypsum
bleaching	altar	JAL125	/
black crust	portal	SEP8, SEP11, SEP12	gypsum
detachment of crust	portal	SEP2, SEP4, SEP5	gypsum
flaking	portal	SEP7	gypsum
bleaching, crumbling	portal	SEP1, SEP6	/
microorganisms	portal	SEP6, SEP9, SEP10	/

analyzed for their major chemical composition in an accredited commercial Canadian laboratory (Acme Analytical Laboratories, Vancouver, BC, Canada), using different analytical methods. According to the results of the reports, SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, and P_2O_5 were measured after fusion with a mixture of lithium metaborate/tetraborate and dissolution in nitric acid by inductively coupled plasma emission spectroscopy (ICP-ES). The total carbon content was obtained by combustion in an oxygen current (LECO method) and the CO_2 and volatile contents were measured by precision scale weighing after calcination at 1100 °C (LOI). The accuracy and precision of the sample analyses were assessed using the reference material CCRMR SO-18 CSC.

The total porosity (N_t) of the samples of unweathered limestone ($50 \times 50 \times 50$ mm) was measured by water uptake under a vacuum, according to the RILEM recommendations: RILEM I.1 Norm (RILEM 1980). The water absorption coefficient (A), expressed in g m^{-2} s$^{-1/2}$, was measured according to the RILEM II.6 Norm (RILEM 1980).

The pore systems of the samples of unweathered limestone were further characterized by means of mercury intrusion porosimetry and gas sorption. Small blocks, approximately 2 cm^3 in size, were dried in an oven for 24 hours at 60 °C and analyzed on a Micromeritics Autopore IV model 9500 porosimeter. Adsorption and desorption isotherms of argon were obtained at –196 °C on a Micromeritics ASAP 2020 Analyzer. Ar adsorption measurements of samples with a surface area of less than 5 m^2·g^{-1} are more accurate than using N_2, which usually yields excessively high values (Sing *et al.* 1985). Prior to measurement, samples were heated at 250 °C for 8 h, and outgassed to 10^{-3} Torr. Gas adsorption analysis in the relative pressure range of 0.05 to 0.3 was used to determine the total specific area, the BET surface area of the samples (Brunauer *et al.* 1938, Gregg & Sing 1982, Adamson & Gast 1997). The pore size distribution curves, the pore volume, and the mean pore size of the rock samples were determined from argon desorption data by the BJH method (Barret *et al.* 1951).

In order to determine the microorganisms, the samples were carefully scratched from the limestone surface and put in sterile flasks containing liquid media BG11. Samples were incubated under fluorescent light at 25 °C and relative humidity of 88% for three months in a climatic chamber (Binder, KBWF 240). After the incubation, a drop of the culture medium was put on a thin section and observed under an optical microscope using a Carl Zeiss model Jenavert.

RESULTS AND DISCUSSION

LIMESTONE PROPERTIES
Petrographical characterization

The limestone is determined as micritic and biomicritic according to Folk (1962) and mudstone and packstone according to Dunham's classification of carbonate rocks (1962). Fragments of fossils are also present (ostracods, bivalvia, foraminifera), and recrystalized bivalvia bioclasts are especially abundant. Observation with a polarizing light microscope evidences veins, macroscopically exhibited as white color, as well as the presence of stylolithes and laminas occurring due to patching of limestone during the diagenesis (Fig. 2a). Samples are interwoven by veins of different generations, which could be up to 150 μm thick. The veins are composed mainly of sparitic calcite; some of them are partially substituted with dolomite, as seen in Fig. 2b. Some veins are filled with organic mater. Non-carbonate components include pyrite, clay minerals, quartz, and organic matter. Pyrite is represented as authigenic mineral or more frequently as framboidal pyrite. It is concentrated in clay veins and around fragments of fossils, where it could be concentrated in areas 100 μm in length and 50 μm in width. Some samples contain spots of authigenic quartz ranging in size from 5 to 200 μm. Clay minerals could occur either as stylolithes together with organic matter or as veins. SEM-EDS analysis of clay minerals evidences the presence of K, Al, Si, Na, and Mg and is assumed to be sericite.

The mineral composition was determined with X-ray diffraction and besides the main component, calcite, the presence of dolomite, quartz, pyrite, and illite/muscovite, indicating sericite, was also confirmed. Additionally, the insoluble fraction revealed quartz, pyrite, and illite/muscovite as well as the presence of graphite and clinochlore.

The chemical composition of limestone samples by ICP-ES is given in Tab. 2. The results are in accordance with X-ray powder analysis. The values of SiO_2, Al_2O_3, Fe_2O_3, Na_2O, and K_2O could be attributed to quartz (Si) and clay minerals (Si, Al, K, Fe, Mg). Thus, the value of SiO_2 is relatively high in samples where the presence of illite/muscovite and clinochlore were determined. Addi-

Tab. 2: Bulk chemical composition of the limestone samples (percentages by mass).

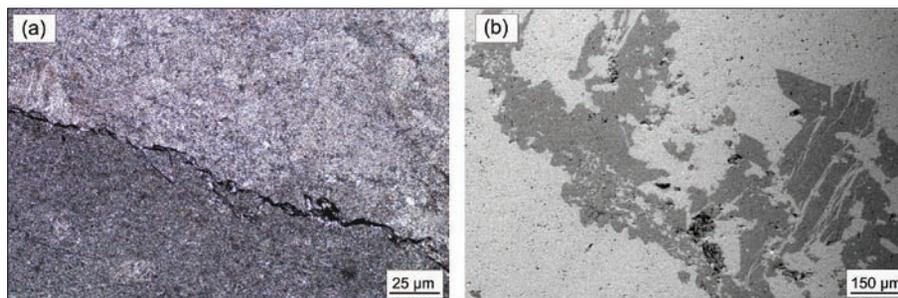| ELEMENT	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	LOI	TOT/C	TOT/S
SAMPLE	%	%	%	%	%	%	%	%	%	%
DG1	1.83	0.72	0.36	0.82	54.19	0.04	0.13	41.17	12.20	0.08
DG2	1.17	0.75	0.23	0.72	53.96	0.03	0.16	42.80	12.90	0.07
DG3	0.61	0.19	0.25	0.94	56.36	0.02	0.04	41.50	13.91	0.11
DG4	1.52	0.33	0.14	1.14	53.5	0.03	0.08	43.2	12.6	<0.01
DG5	3.78	1.62	0.52	0.67	51.63	0.13	0.28	41.1	11.66	0.2

Fig. 2: (a) Micritic limestone with stylolithe in sample DG1. Transmission light, parallel polars. (b) Dolomitized areas in calcitic veins of the limestone in sample DG1. SEM-BSE.

tionally, the presence of Al_2O_3 is also enhanced in these two samples. A high fraction of Fe_2O_3 and total sulfur (TOT/S) indicates the presence of pyrite. Mg is attributed mainly to dolomite and the concentration is enhanced in samples where dolomite was also evidenced by X-ray powder diffraction.

Petrophysical characterization

As water plays a fundamental role in stone deterioration, the properties of the stone structure and water transfer were measured. Porosity and pore size distribution influence rock susceptibility to weathering, as nearly all weathering processes rely on the presence and transport of moisture to transport salts or other contaminants into stone and to enable chemical reactions to occur (Nicholson 2001; Warke *et al.* 2006). The results revealed that porosity of the limestone is very low, as the value of total porosity accessible to water under vacuum is 0.77 ± 0.46%. On the other hand, mercury porosimetry, influenced by free porosity and therefore by the pore network connectivity, yielded values of 3.34 ± 1.40%. The capillary curves of limestone illustrate a weak water absorption affinity. The coefficient of capillarity is rather low as well, being –0.38 ± 0.31 $gm^{-2}s^{-0,5}$. The obtained values are of the same order of magnitude as data published for comparable limestones, where low values were also reported (Sahlin *et al.* 2000; Marinoni 2002; Kramar *et al.* 2010b; Miller *et al.* 2006). Samples that exhibited the highest values of porosity also showed high water absorption capillarity coefficients.

To investigate the microporosity (<0.1 μm), the BET method is used to detect nanoscale pores. When considering the damage due to salt crystallization, the critical pore radius where the crystallization pressure is effective ranges below 0.05 μm (Steiger *et al.* 2005). The gas-physisorption method is thus suitable for investigation of this range of pore radii. Scherer *et al.* (1999) established that the maximum pressure that salt crystallization can achieve is highly dependent on the size of the pores, predicting that most of the damage occurs when salt-rich fluids migrate from pores of larger size to pores of smaller size in the range between 4 nm and 50 nm. All samples share a similar pore size distribution with relative maxima located around 2 nm. Values of specific surfaces area vary from 0.4323 to 3.3318 m^2/g and are higher in samples with higher porosity. The samples of micritic limestone show a type II isotherm (Sing *et al.* 1985) indicating the non-microporous or macroporous nature of its pore system network; this is further supported by their very low surface area. In contrast, samples with abundant bioclasts exhibit hysteresis loops (i.e. contrasting shapes of the initial adsorption and final desorption curves) and much higher surface areas. These hysteresis loops can be further classified as H3 or H4 and are commonly interpreted as being due to aggregates of plate-like particles giving rise to slit-shaped pores (e.g. Sing *et al.* 1985; Lowell *et al.* 2004). The presence of these kinds of particles in the biomicritic limestone results in a significant increase in the micropore volume relative to the non-microporous micritic limestone.

DETERIORATION PHENOMENA ON THE MONUMENTS
Weathering forms

As a part of broader conservation/restoration projects, in situ investigation of the side altar of St. James' Church and the portal at Semenišče by means of monu-

Tab. 3: Weathering forms of limestone exposed to the indoor environment.

Groups of weathering forms	Main weathering forms		Individual weathering form
	Terminology	Definition	
Group 1- Loss of stone material	Back weathering	Uniform loss of stone material parallel to the original stone surface	Back weathering due to loss of scales
			Back weathering due to loss of pieces
			Back weathering due to loss of crumbs
	Relief	Morfological change of the stone surface due to partial or selective weathering	Rounding/notching
			Weathering out of stone components
			Alveolar weathering
	Break out	Loss of compact stone fragment	Break out due to natural cause
Group 2- Discoloration/ Deposits	Discoloration	Alteration of the original stone colour	Bleaching
	Loose salt deposits	Poorly adhesive deposits of salt aggregates	Efflorescences
			Sublorescences
	Crust	Strongly adhesive depostis on the stone surface	Light-coloured crust tracing the surface
Group 3- Detachment	Crumbly disintegration	Detachment of larger compact stone pieces of irregular shape	Crumbling
	Flaking	Detachment of small, stone pieces (flakes) paralel to the stone surface	Single flakes
	Detachment of stone layers depending on stone structures	Detachment of larger stone sheets or plates following the stone structure	Splitting up
Group 4- Fissures/ Deformation	Fissures	Individual fissures or systems of fissures due to natural or constructional couses	Fissures independent on stone structure

ment mapping has shown several types of deterioration phenomena (Kramar *et al.* 2010b). Weathering forms of the Drenov Grič limestone, documented according to the Fitzner classification (Fitzner & Heinrichs 2002), are given in Tabs. 3 & 4 for the altar and the portal, respectively. Examples of weathering forms are shown in Fig. 3.

Indoor monument

Back weathering and break out represent very frequent weathering forms characterizing loss of stone material in the case of limestone exposed to the indoor environment. Especially in the lower part of the altar, back weathering is strikingly high in a range of capillary rise. Loss of stone material is also represented by relief in lower parts. Loose salt deposits, crusts, and color change are the main weathering forms characterizing deposits and discoloration Efflorescence (salt crystallization on the surface) and subflorescence (salt crystallization under the surface) are frequent in the lower part of the altar in a range of capillary moisture levels and in areas with joint mortar and walls (Figs. 3a & 3b) as also observed in the case of Lesno Brdo limestone (Kramar *et al.* 2010b). A color change to grey occurs in the upper part of the monument. White crusts are present about 1 m from the ground. Crumbling, flaking, and splitting are

most abundant in a group characterizing stone detachment. Depending on the orientation, the detachment of the limestone is expressed as splitting (not parallel) or flaking (parallel to the surface). Flaking of the limestone represents one step before loss of material (Fig. 3b). The most intense detachment of the material occurs at about 0.5 m from the floor, although it is distributed to a smaller extent over the whole monument. In some areas fissures are notable, indicating salt crystallization under the surface. Lower parts of the altar in particular are extensively damaged by salt crystallization, while in the upper parts the original color has been bleached. Flaking is leading to back weathering.

Outdoor monument

Black limestone exposed to the outdoor environment is affected by a wide range of weathering forms as well. On the exposed areas of the portal (fingers, figures of angels, and decorative balls) there is an intensive loss of stone material, expressed as back weathering and relief. Color change (discoloration), crusts, and biological colonization are the main weathering forms characterizing deposits and color change. The monument shows changes in the original black color, which turns to grey over the whole area. On sheltered areas of the monu-
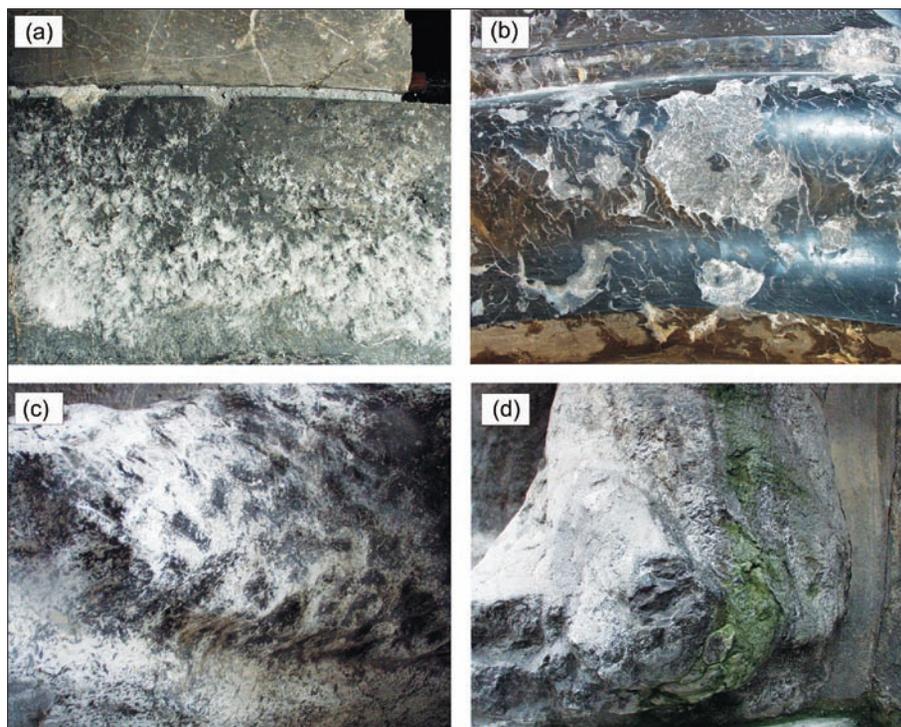
Fig. 3: Examples of weathering forms of the black micritic limestone. (a) Crystallization of salts on the surface (efflorescence), stone element on altar. The image is about 20 cm in width. (b) Sublforescence resulting in flaking of the limestone. The presence of surface fissures of limestone indicates salt crystallization under the limestone surface. The image is about 10 cm in width. (c) Black crust, detail of the portal. The image is about 10 cm in width. (d) Presence of microroganisms, foot of the Hercules statue of the portal. The image is about 30 cm in width.

ment, compact black crusts are presented (Fig. 3c). The presence of microorganisms is documented in areas of the monument which are exposed to humidity without direct light (Fig. 3d). Crumbling, flaking, and crust detachment are the most abundant types in a group of stone detachment. Crumbling is also seen on volutes on the upper parts of the monuments. Detachment of black crust is present in some areas.

WEATHERING PRODUCTS AND MECHANISMS
Indoor monument
X-ray diffraction analysis confirmed the presence of gypsum and soluble salts of the $MgSO_4.nH_2O$ series, such as starkeyite ($MgSO_4.4H_2O$), pentahydrite ($MgSO_4.5H_2O$), and hexahydrite ($MgSO_4.6H_2O$) (Tab. 1).

Gypsum occurs in both subflorescence and efflorescence, whereas the absence of magnesium sulfates hydrates is obvious in subflorescence and they are not present on the outdoor monument. It is important to note that niter, forming the efflorescence on another limestone (Lesno Brdo Limestone) of the same monument, is absent here (Kramar *et al.* 2010a, Kramar *et al.* 2010b). White crust also consists of gypsum, and occurs in out-

door and indoor monuments. Black crust is composed of gypsum crystals which are orientated perpendicular to the limestone surface. Platy crystals are 50 μm in size. Crusts exhibit denser crystal aggregation with respect to the crystals of the efflorescence. The origin and growth of the sulfated crusts have been widely studied in past years (Camuffo *et al.* 1983). White crust is composed of gypsum (Fig. 4a). For crust formation the amount of supplied solution must be high: the substrate is very humid or wet when substrate forms (Arnold & Zehnder 1985), suggesting a sufficient water supply in that area of the altar, whereas outdoors it occurs in sheltered areas. A network of fissures occurs about 100–800 μm below the limestone surface. The fissures are about 5 to 50 μm thick. Fissures under the surface of the limestone are filled with gypsum. Crystals of gypsum in fissures are oriented parallel to the fissure wall and are not in contact with limestone, while on the surface they are orientated perpendicular to the surface.

Efflorescence consists of acicular and hair-like crystals, indicating so-called whisker growth (Arnold & Kueng 1985). The successive penetration of solutions occurs through migration from the ground by capillarity, and they are then evaporated, with soluble salts precipitation. Whisker growth indicates either a very low water content of the porous substrate, a very low water supply, or a very slow evaporation rate. In contrast to the whisker growth, crust formation requires a comparatively high solution supply. Fluffy efflorescence preferentially develops on dense looking substrate (Arnold & Kueng 1985). Polymineral efflorescence consists of magnesium sulfate hydrates and gypsum. Hexahydrite and epsomite are common hydrates on the Earth's surface that occur at ambient temperature and moderate and elevated relative humidity (RH) (Chipera & Vaniman 2007). With the exception of hexahydrite-epsomite, transformations between the various species involve more than simple removal of water, requiring significant crystal structure rearrangement and overcoming of activation energy bar-

Tab. 4: Weathering forms of limestone exposed to the outdoor environment.

Groups of	Main weathering forms		Individual weathering form
weathering forms	Terminology	Definition	
Group 1- Loss of stone material	Back weathering	Uniform loss of stone material parallel to the original stone surface	Back weathering due to loss of scales Back weathering due to loss of pieces Back weathering due to loss of crumbs
	Relief	Morfological change of the stone surface due to partial or selective weathering	Rounding/notching Weathering out of stone components
Group 2- Discoloration/ Deposits	Discoloration	Alteration of the original stone colour	Bleaching
	Crust	Strongly adhesive depostis on the stone surface	Dark-coloured crust tracing the surface
	Biological colonization	Microbiological colonization	
Group 3- Detachment	Crumbly disintegration	Detachment of larger compact stone pieces of irregular shape	Crumbling
	Flaking	Detachment of small, stone pieces (flakes) paralel to the stone surface	Single flakes
	Detachment of crust with stone material	Detachment of crusts with stone material sticking to the crust	Detachment of a dark coloured crust tracing the stone surface
Group 4- Fissures/Deformation	Fissures	Individual fissures or systems of fissures due to natural or constructional couses	Fissures independent on stone structure

riers. Close to room temperature, epsomite is the stable form in the presence of liquid water. Under dry conditions, epsomite can dehydrate to form hexahydrite and finally the monohydrate kieserite (Juling *et al.* 2000). While the occurrence of magnesium sulfate hydrates is limited to the bottom parts of the altar, gypsum appears to occur on higher parts of the altar as well. It is present in fissures, and leads to the scaling and crumbling. The presence of gypsum also in the areas of the capillary range suggests that the solution migrates and water also penetrates through other mechanisms such as condensation. SEM micrographs of black limestone in transverse section show a highly fractured limestone surface, while the inner part of the limestone shows a low porosity and a compact structure. Humidity and temperature fluctuations cause cycles of salt precipitation and dissolution. During the one-year monitoring period, the RH ranged from a maximum of 100 % to a minimum of 40%, whereas the ambient temperature ranged from -0.6 °C to 28.1 °C (Kolenc 2006). As gypsum is less soluble it crystallizes first, whereas magnesium sulfate hydrates stay longer in a solution. In our context, supersaturation probably results from evaporation. Salt weathering is primarily a mechanical process that disrupts the physical integrity of stone, whereas chemical weathering processes degrade specific chemical elements within the crystal lattice of constituent minerals (Warke *et al.* 2006). Crystallization of salts below the stone surface (subflorescence) is leading to flaking. The damage is

mainly restricted to the upper 400 µm of the limestone surface. The mechanisms of salt decay are based on the pressure exerted on the walls of the stone pores when the salt crystallizes with repeating cycles. The solutions can migrate inwards in the stone by capillarity. On the stones contaminated by salts, at relative humidities >75% the presence of water vapor until the salts dissolve ensures a weak superficial penetration by capillary suction, evaporation of the solution, and participation of the gypsum inside the pores and cracks underneath the superficial crystals (Chabas & Jeanette 2001). Crystallization of these salts and hydration–dehydration transformations, depending mainly on relative humidity and temperature, lead to flaking and alveolar weathering of the limestone. As joint mortars between the stone elements of the altar contain high quantities of soluble calcium and magnesium (Kramar *et al.* 2007), they are thus considered as a potential source of these damaging salts. The deterioration occurs as a consequence of crystallization close to the surface of the stone. Any subsequent decrease in the ambient RH at the exposed surface will cause the dissolved salts to migrate towards the surface, as surface water evaporates to compensate for the change in RH (Colston *et al.* 2001). Slow evaporation promotes salt crystallization inside the stone with a greater disruptive effect. The factors determining the occurrence of efflorescence over cryptoflorescence are kinetically driven (Colston *et al.* 2001). When the petrophysical properties allow fast and long-distance transfer
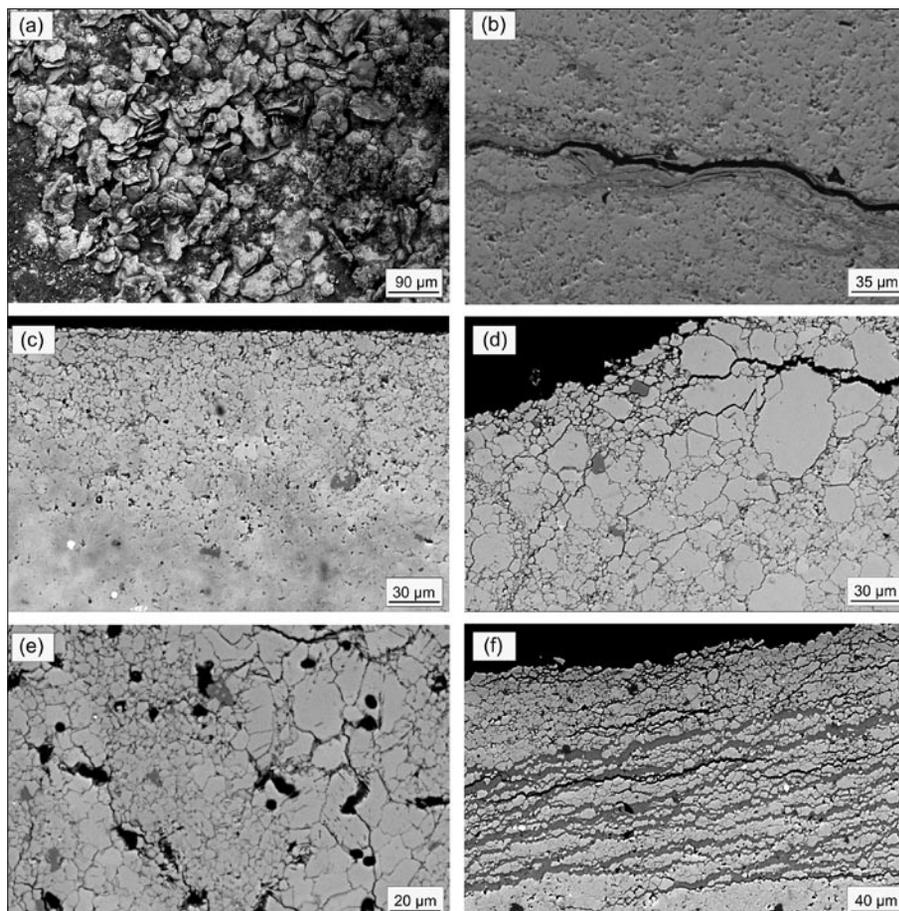
Fig. 4: SEM microphotographs of deteriorated limestone. (a) Crystallization of gypsum at the surface of limestone. Sample JAL176. (b) Irreversible fissures occur in veins of clay minerals; the presence of K, Al, and Si evidence the sericite. Na and Fe are present in minor amounts. Sample JAL122. (c) Granular disintegration in She area about 100 μm under the surface of the limestone, indoors. Sample JAL125. (d) Highly fractured black limestone surface outdoors. Granular disintegration caused due to the anisotropic thermal expansion. Sample SEP1. (e) Biopitting. Sample SEP7. f) Alternation of layers of gypsum with limestone. Sample SEP3.

erals. Fig. 4c shows an area of about 100 μm of granular disintegration that is responsible for the color change of the limestone.

Outdoor monument

On limestone exposed to the outdoor environment, decohesion between the grains is observed (Fig. 4d). A change of the original black color into grey is observed on both monuments. In the majority of cases the situation is seen due to the granular disintegration, whereas in a small number of cases in the indoor environment it is due to the surface cover of a thin crust of salts. The surface is rough, with discontinuities characterized by a system of intra- and inter-crystalline microfractures in the first 200 μm. Marinoni (2007) reported that decohesion and higher porosity are present on the outer layer of the samples, suggesting that thermal weathering may play a key role in black limestone discoloration. This was also suggested by Zehnder (2003), whereas other researchers ascribed this phenomenon as

and the porosity allows a flow that compensates evaporation, salts crystallize on the surface without causing significant weathering. In contrast, when the capillary supply does not compensate evaporation, salts precipitate inside the stone, under the surface, where looseness of superficial crystals results (Lewin 1982; Chabas & Jeanette 2001). The lowering of the RH significantly affects the decay, and a combination of a lower RH and a longer drying time produces the greatest rate of decay (Colston *et al.* 2001).

As proved by SEM examination (Fig. 4b), in areas of veins with clay-mica group minerals (presence of K, Al, Si) disrupture of the limestone occurs. Due to water absorption/desorption clays are swelling resulting in irreversible crumbling of the limestone. The phenomena are observable outdoors as well as indoors. Sometimes gypsum is evidenced in the area enriched with clay min-

the oxidation of organic matter, with hydrocarbons being the least stable carbon pigments (Winkler 1997). The reasons for granular decohesion could be ascribed to mechanical weathering, in particular thermal cracking of the calcite crystals. Limestone can have good properties in pure water but deteriorates rapidly when freezing in a salt solution (Lindquist *et al.* 2007). Damage caused by freezing in salt solutions will be dependent on the nanopores, while the damage caused by freezing in pure water is more dependent on the micron-sized porosity (Lindquist *et al.* 2007). In the outdoor samples, the alternation of gypsum and limestone occurs in bands of 10 to 20 μm, suggesting that gypsum filled the areas between the laminas of the limestone (Fig. 4f). Dissolution of calcite crystals under the gypsum crust, which is about 300 μm thick, is evident. Delamination and disrupture in areas with clay minerals occur both outdoors and indoors,

similar as in the case of Lesno Brdo limestone (Kramar *et al.* 2010b).

The results indicate that microorganisms which form green patina on the limestone surface are represented by unicellular cyanobacteria (Chroococcale) and unicellular (Bracteacoccus) and filamentous (Ulotrichales) Chlorophyceae. It was reported (Ortega-Calvo *et al.* 1995) that cyanobacteria and Chlorophyceae comprise two of the 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 autotrophic organisms (Peraza-Zurita *et al.* 2005). On the other hand, organic acids, which are produced in their metabolic processes, could contribute to the limestone dissolution. Indeed, biopitting is evidenced from samples taken from the outdoors, as proved by SEM analysis (Fig. 4e).

Although limestone consist mainly of calcite, it can show significant variations in compositions, texture and structure, resulting in complex and contrasting weathering behavior, as suggested by the results of the present study and supported with the observations of previously studied Lesno Brdo limestone (Kramar *et al.* 2010b). Wide range of identified weathering forms indicates that the primary cause of extensive weathering is mechanical rather than chemical weathering. Processes of mechanical weathering are fully operative in polluted environments, but this is also believed for a natural environment (Gauri & Bandyopadhay 1999).

Study indicates that weathering and deterioration of the limestone in urban environment is controlled in great extent by the environmental factors, one of the most important weathering factors being water and soluble salt crystallization. Still, intrinsic properties of the limestone influence the type of the weathering form; for instance veins filled with phyllosilicates will cause a disruption of the stone. As the latter was observed at monuments made of Drenov Grič limestone and Lesno Brdo limestone (Kramar *et al.* 2010b), exposed to indoor and outdoor environment, the same behavior it can be expected in natural environments as well. Also, karst and related phenomena are sensitive to environmental conditions (Faniran & Jeje 1983), where dissolution (relief, erosion) and secondary deposits (crust formation) are known. One characteristic of the natural environment pertinent to rock weathering is that lacks the industrial affluent sulfur dioxide and nitrogen dioxide, which influence the weathering significant in the urban environment.

CONCLUSIONS

Besides calcite as the main mineral of the limestone, dolomite and non-carbonate components including pyrite, clay minerals, quartz, and organic substances were determined. The micritic grains of the limestone and its very dense structure are consistent with small pore radii, low porosity, and small capillary kinetics. The small porosity and weak water transfer kinetics mean that solution transport is low, increasing the possibility that high oversaturation ratios are reached below the stone surface, precipitating as subflorescence.

A great variety of weathering forms characterized by loss of stone material, discoloration/deposits, and detachment were identified on the monument. Besides color change, soluble salts formation was found to be the most important degradation of the investigated monuments, outdoors as well as indoors.

Salt causes different types of degradation under different environmental conditions. Gypsum crystallization leads to scaling and crumbling of the limestone as well as crust and efflorescence formation, whereas magnesium sulfate hydrates occur only as efflorescence indoors. Disrupture of the limestone in areas with clay minerals occurs both outdoors and indoors. The change of the original black color into grey is attributed to the granular integration and occasionally to the thin surface covering with gypsum (indoors). Granular decohesion is more obvious outside, where the changes in temperature are higher. There is no evidence of microorganisms inside, whereas the presence of microorganisms (Cyanobacteria and Chlorophyceae) outdoors resulted in biopitting.

Although the limestone yielded good physical characteristics, the deterioration is relatively high in both indoor and outdoor environments. Deterioration is mainly controlled by the environmental factors, such as water and crystallization of soluble salts, but is also influenced by the intrinsic parameters, such as veins of phyllosilicates (mineral composition).

Urban environment represent a specific environment where karstic processes are enhanced due to the presence of anthropogenic pollutants. However, the properties of the limestone, such as presence of specific mineral or porosity will influence the behavior of the weathering in the similar manner also in the natural rural environs.

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