Black “marble”: the characteristic material in Baroque architecture of Cracow (Poland)

Chapter · January 2010

DOI: 10.1007/978-90-481-26842-2_6

Mariola Marszałek
AGH University of Science and Technology in Kraków

Chapter 6
Black "Marble": The Characteristic Material in the Baroque Architecture of Cracow (Poland)

Mariola Marszałek and Andrzej Skowroński

6.1 Introduction

The oldest examples of architectural use of Polish black limestone date back to the late 16th century. The rock was commonly applied starting from the beginning of the 17th century, both as a structural and decorative stone used above all in tombstones and epitaph tablets, but also in fragments of altars, inner and outer portals, railings, floor slabs, baptisteries, even whole chapel interiors, etc. The rock became so popular because it is very suitable for being polished, resulting in glassy, mirror-like surfaces. The black, solemn colour was thus a perfect choice in the Counter Reformation period. The sculptors working in Dębnik, where the quarries were situated, and in Cracow, the then capital of Poland located nearby, produced countless works of small-scale architecture that spread all over the Commonwealth of Two Nations, as Poland was called. In terms of its territorial range, Poland was then the largest country in Europe, reaching the Dnieper and the Dvina to the east; and it consisted of two united parts, i.e., the Crown lands of proper Poland and the Grand Duchy of Lithuania. As a result, examples of the use of the Dębnik limestone are so numerous that in the Polish history of art the 17th and 18th centuries have been given the name "the period of the black marble". It should be added that artifacts made of the Dębnik limestone were widely exported to the neighbouring countries. Today they can be found, e.g., in Germany (Frankfurt am Main) and Austria (Vienna, Graz, Salzburg) (Rajchel 2004; Niemcewicz 2005).

Black marble-like limestones and marbles were also commonly used in Baroque architecture all over Europe. Some occurrences of these rocks are well known on a regional scale, among others in Belgium (Namur province: *Belge Noir*—Upper Devonian, eastern Belgium near Sankt Vith: *Rechter Blaustein*—Lower Devonian),

M. Marszałek (✉)
Department of Mineralogy, Petrography and Geochemistry
AGH-University of Science and Technology
Krakow, Poland
Tel.: +48-12-6172376
Fax: +48-12-6334330
e-mail: mmarszal@agh.edu.pl

M. Bostenaru Dan et al. (eds.), *Materials, Technologies and Practice in Historic Heritage Structures,* DOI 10.1007/978-90-481-2684-2_6, © Springer Science+Business Media B.V. 2010

Germany (Aachen: *Aachener Blaustein*—Lower Carboniferous; Zehnder 2006, Schupbach near Limburg: *Schupbach Marmor*—Middle Devonian), northern Italy (the Southern Alps, the region between Lake Como and Lake Garda: *Calcare di Varena, Grigi Carnico, Nero di Rovere*—Triassic; Marinoni et al. 2002, 2007), Spain (Vizcaya province near Marquiña: *Negro Marquiña*—Cretaceous, Alicante province, the Betic External Zone: *Jabalina Stone*—Triassic; Benavente et al. 2006) and Switzerland (the Northern Alps: *Alpenkalk*—Triassic and Jurassic; Zehnder 2006). The stones mentioned here without reference have been found on respective web pages, where they are identified as black in colour, although in the web photographs the colour of not all of them seems to be really black. The Dębnik limestones being Middle Devonian are one of the oldest rocks among those specified above.

6.2 Materials and Methods

6.2.1 Characteristic of the Stone

The deposits of black, compact limestone discussed in this chapter occur in the southern part of Poland, about 20 km west of Cracow, in the vicinity of the Dębnik village. The rock is of the Middle Devonian age and represents Givetian (Fig. 6.1; Narkiewicz and Racki 1984; Baliński 1989; Bednarczyk and Hoffmann 1989). Another deposit of black limestone, but with stones of inferior quality, is situated in Kajetanów (the Holy Cross Mts, central Poland). They were used on a very limited, regional scale.

The Dębnik limestone also known as the Dębnik marble (although the name "marble" should properly be limited to metamorphic rocks) was recorded as early as the Middle Ages. The first reference about quarrying the Dębnik stones comes from 1415 (see Rajchel 2004). In the 17th and 18th centuries there were 15 or so quarries close to the Dębnik village. The oldest of them, with stones of the best quality and owned by the monks from a nearby monastery of the Discalced Carmelites, has been duly named the Carmelite quarry (Fig. 6.2). The rocks quarried include pelitic limestone with fossils as well as detrital and laminated limestone (Bromowicz 2001), making up approximately 36 and 41% of the profile, respectively. The third type, i.e., homogeneous, pelitic limestone, makes up the remaining 23%. The average thickness of the limestone beds usually ranges between 40 and 60 cm. Fossils identified in the limestone include corals, brachiopods, pelecypods, gastropods, and hydrozoans (*Amphipora* sp. and *Stromatopora* sp.).

The decorative properties of the Dębnik limestone include its deep black colour and taking excellent polish, as well as the presence of veins, fossils, and sparite calcite nests within the micritic background. These elements combined with structural and textural features provide a diversified appearance to polished stone surfaces. Considering the Dębnik limestone as an ornamental material, three varieties have been distinguished:

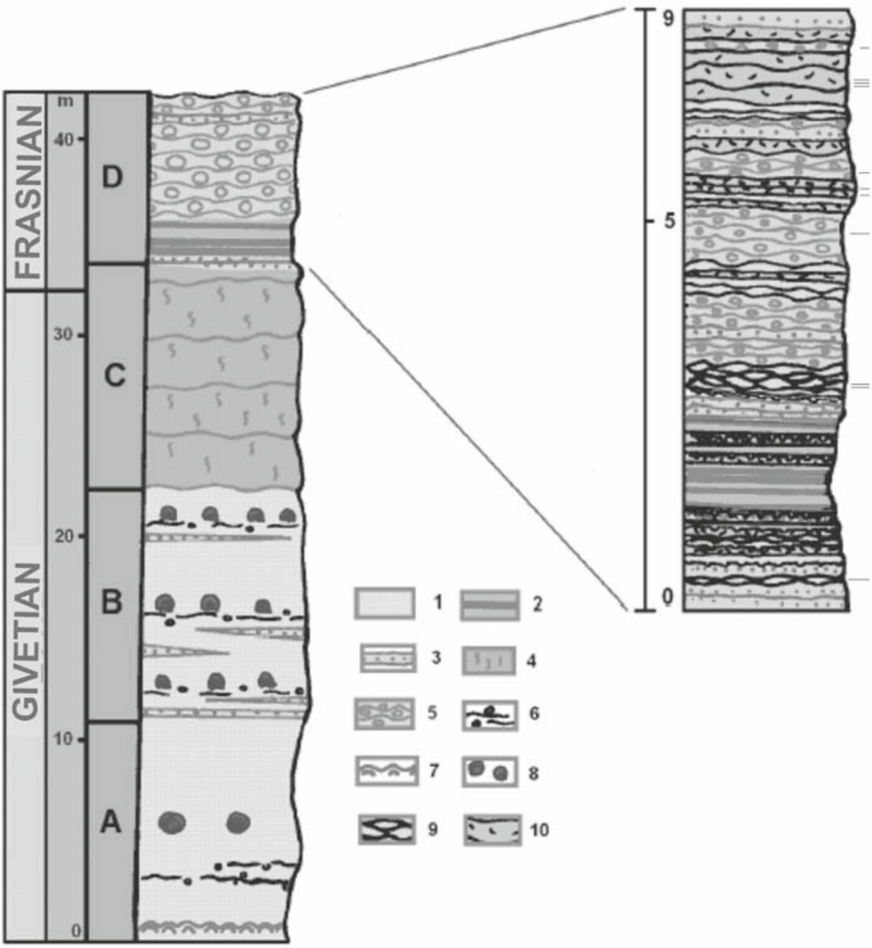

Fig. 6.1 Simplified profile of the Dębnik limestones (after Bednarczyk and Hofmann 1989). **1** pelitic limestones, **2** marls, **3** detrital limestones, **4** bioturbated pelitic limestones, **5** nodular limestones, **6** erosional surfaces, **7** stromatolites, **8** stromatoporoids, **9** streaky-nodular limestones, **10** concentrations of fossil shells (Reproduced by permission of Uczelniane Wydawnictwa Naukowo-Dydaktyczne AGH-UST)

- homogeneous, black pelitic limestone;
- homogeneous, black pelitic limestone with fossils;
- heterogeneous, black and dark grey detrital limestone, laminated in places and intercalating with the pelitic variety.

Work has now been initiated to restart quarrying in Dębnik. The uppermost parts of the profile, about 15–20 m thick, do not meet requirements, due to the undulated structure and thin bedding of the stone, and a lower level needs to be developed.

Selected physical and mechanical properties of the limestone have been given after Bromowicz (2001) for lower parts of the Dębnik and Dębnik I quarries. This is

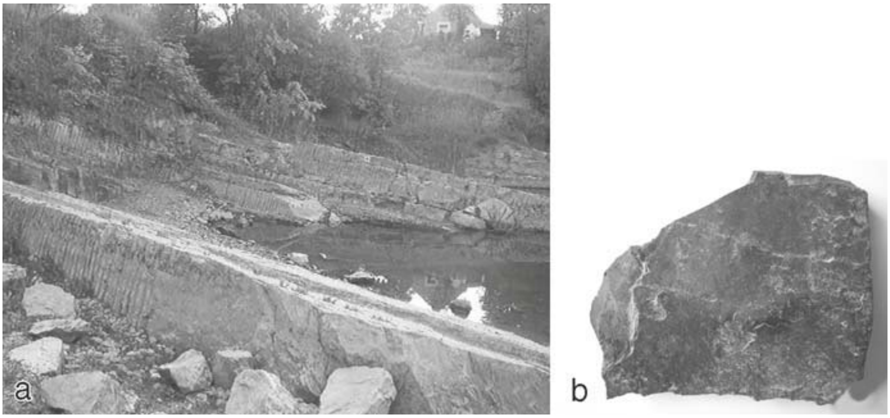

Fig. 6.2 **a** Old Carmelite quarry—marks after wedging of stone blocks can be seen (photo by courtesy of M. Wójtowicz), **b** black limestone displaying a deep black colour in its inner part

limestone corresponding to the Dębnik limestone that was extracted centuries ago in the historic quarries mentioned above. The properties determining the durability of the rock when exposed to the atmosphere are apparent density, water absorption, frost resistance, abrasion resistance, and strength resistance. They were measured according to Polish standards (see Bromowicz 2001 for details).

The apparent density of the Dębnik limestone (2.68 tm^{-3}) classifies the rock as very heavy. Its water absorption is very low (<0.5%) to low (0.5–5%), with an average value of 0.29%. Consequently, the low water uptake results in the high frost resistance of the rock.

The compressive strength in the air-dry state (58–194 MPa, average 119 MPa) characterizes the Dębnik limestone as of medium and high resistance. The abrasiveness of the Dębnik limestone using the Boehme method (0.16–1.18 cm, average 0.34 cm) classifies it as having medium and low abrasiveness. Two systems of joints promote the working out of blocks with sizes up to 2 m.

These technical properties of the Dębnik limestone are very advantageous and they ensure good preservation of the stone elements when worked out. The influence of atmospheric factors results however in uniform or spotty whitening of the stone and considerably lowers its aesthetic value. Even a short walk along Cracow streets reveals changes in its appearance. Exposition to atmospheric factors, especially of the stones situated outdoors, changes their original black colour, fading to grey or even white; and the stone, if polished, loses its shiny appearance. These effects can be widely seen in architectonic elements but can also be observed in outcrops. Superficial whitening, or as some call it, greying or bleaching, of the Dębnik limestone when exposed to a polluted, urban atmosphere is combined with deposition of anthropogenic particulates on the stone surfaces, which makes a plausible explanation of the phenomenon additionally difficult.

6.2.2 Sampling

The material analysed was collected from the Carmelite quarry in Dębnik and it represents homogeneous limestone, including both fresh and weathered varieties. The latter shows changes from its original black colour into grey or even white.

The natural, fresh samples were used for identification of stone components, especially of the non-carbonate fraction. These samples were mortar-crushed and dissolved in diluted HCl (1:10), providing the first part of the acid-insoluble grain fraction. The other part was obtained from the acid-insoluble fraction calcined at 700°C to remove organic matter. This procedure was applied to identify and quantify the non-carbonate components. These results were reported in part by Marszałek and Muszyński (2001) and Marszałek (2007). More detailed analyses of organic substances were made of the extracts, obtained from the solid residue treated with C_2Cl_4. The weathered parts of the Dębnik limestone were used for identification of changes in composition of the outer stone layers.

6.2.3 Analytical Techniques

6.2.3.1 Inorganic Fraction

The mineralogical, chemical, and microstructural characteristics of the stone were obtained by optical microscopy and scanning electron microscopy, X-ray powder diffraction (XRD) and X-ray fluorescence (XRF) analysis.

Optical and scanning electron observations were made of the universal polished thin sections cut perpendicular to the stone surface. Additionally, broken surfaces of inner (non-weathered) and outer (weathered) parts of the samples were observed using the SEM/EDS method. XRD analyses were performed on bulk samples, insoluble residues, and weathered layers of the stone. Chemical analyses were carried out using the XRF technique.

Typical mineralogical equipment included: an optical microscope Olympus BX 51, a field emission scanning electron microscope FEI Quanta 200 FEG with energy dispersive spectrometer EDAX, an X-ray diffractometer Philips X’Pert APD and an XRF analyser Philips PW 2400, all of them working in standard conditions, and are therefore not specified here.

Another method was applied in order to characterize the chromatic properties of the fresh limestone and its weathered layers. They were measured using a Konica Minolta CM-2500d colorimeter, equipped with Xenon lamps as a source of light in the spectral range of 360–740 nm, applying a viewing angle of 8°and an illumination area with a diameter of 8 mm.

6.2.3.2 Organic Fraction

The characteristics of the organic compounds were obtained using FTIR spectroscopy, Rock-Eval pyrolysis and gas chromatography combined with mass spectroscopy GC-MS.

The FTIR analyses were made for both the acid insoluble fraction of bulk samples and the solid fractions left after treating a sample with HCl and then separating out C_2Cl_4-soluble organic extracts and letting them evaporate. Rock-Eval pyrolysis was made on the bulk and weathered parts of the stone and provided information on the nature of the organic substances and respective differences between these two layers. These differences are expressed by hydrogen HI (mg HC/g TOC) and oxygen OI (mg CO_2/TOC) indices. Total organic carbon TOC was estimated by LECO analyses as well. The components of the organic matter (identified in the form of methyl esters because of an analytical procedure; Hermosin et al. 2004) were investigated using GC-MS analyses.

The research equipment included a FTIR Bio-RAD model 165 spectrometer, a GC8000/MD/800 gas chromatograph in combination with a mass spectrometer, a Rock-Eval II pyrolyser, and a LECO apparatus.

6.3 Results and Discussion

6.3.1 Mineralogical and Petrographical Study

The Dębnik limestone from the Carmelite quarry is biomicritic with generally nodular fabric and undulatory bedding, revealing few microveins and stylolites. In some sections of the profile the limestone is compact, with fewer fossils.

Carbonate components are represented by micritic calcite with traces of dolomite. Non-carbonate components include K-feldspar, smectite, illite, occasionally pyrite and organic substances, as well as traces of detrital quartz and hydromuscovite. The organic matter concentrates are parallel to the bedding (Fig. 6.3).

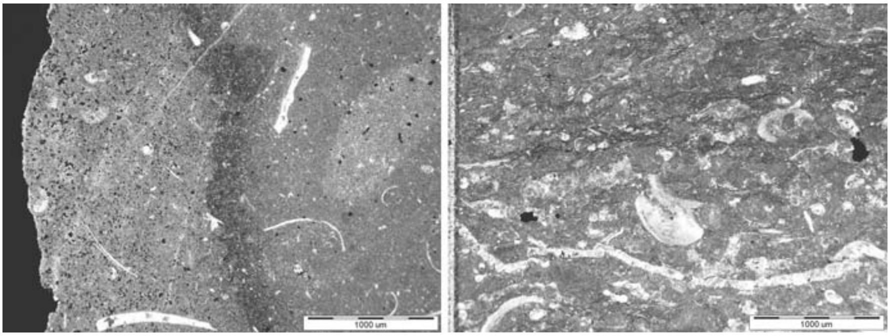

Fig. 6.3 A lamina of the organic matter. Optical microscope, one polaroid

The Dębnik limestone is composed (XRF analyses) mainly of CaO – 53.92 wt.%, accompanied by minor amounts of SiO_2—1.2 wt.%, Al_2O_3—0.53 wt.%, K_2O—0.45 wt.% and MgO—0.85 wt.%. Recalculation of the total CaO gives 96.3 wt.% of calcite; silica alumina, and potassium are contained mainly in feldspars and clays; whereas magnesium probably in dolomite. Other elements occur in traces and do not exceed 0.0X wt.%. The rock can therefore be considered a relatively pure limestone.

The total amount of pyrite in the Dębnik limestone is about 2 wt.% but this mineral is distributed rather erratically. Pyrite is represented by two populations of grains:

1. Crystals that are various combinations of cube, dodecahedron and octahedron, with sizes 0.002–0.025 mm. They are a dominant pyrite type; and
2. Euhedral, cuboidal crystals with sizes reaching 2 mm (Fig. 6.4).

The organic content in the whole of the rock samples was estimated at 0.30 wt.% TOC (TOC—total organic carbon) which represents 4.4 wt.% of the HCl–insoluble fraction (Marszałek and Muszyński 2001). The correlation between hydrogen (HI) and oxygen (OI) indices in Rock-Eval pyrolysis points to the type III of kerogen, i.e., the kerogen derived from humic organic matter of probably algal and bacterial origin (Marszałek 2007).

The FTIR results (Fig. 6.5) indicate that the organic matter is composed mainly of aliphatic long-chain hydrocarbons (characteristic bands around 2930 and 2960 cm^{-1}, due to oscillation within the CH_2 and CH_3 groups, respectively). The remaining part of the spectra in the range 2000–500 cm^{-1} is inherently complex and difficult to interpret. Only the band around 1740 cm^{-1} can be ascribed to the presence of carboxyl groups. There are no aromatic condensed hydrocarbons in the samples as can be inferred from the lack of bands around 3040 cm^{-1}. The organic compounds yield complex mass chromatograms (GC-MS), in which fatty acids, saturated (e.g., nonanoic, decanoic, undecanoic, dodecanoic, tridecanoic, tetradeca-

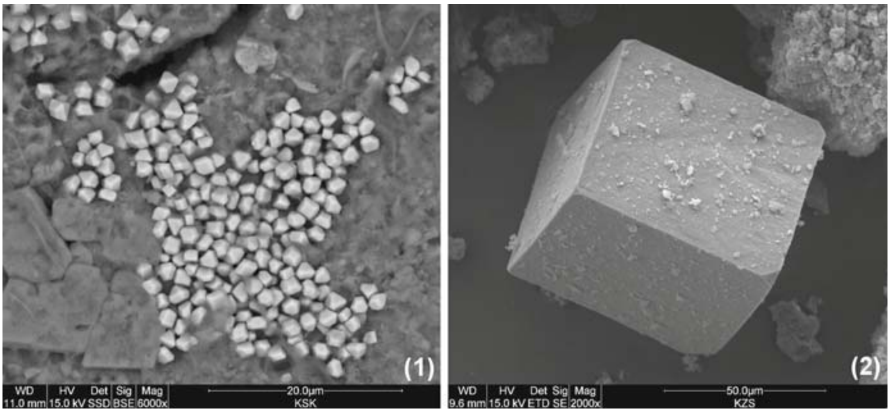

Fig. 6.4 SEM micrograph of euhedral pyrite crystals (type 1/type 2)

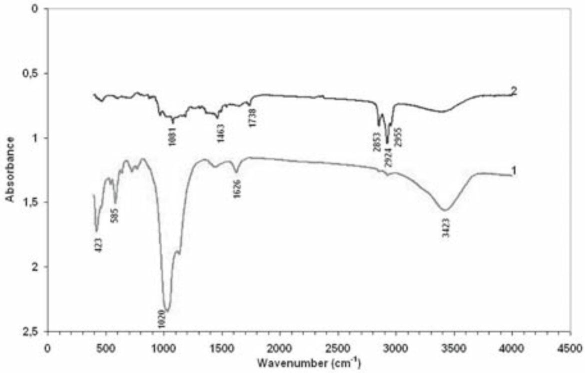

Fig. 6.5 FTIR spectra of the **1** acid insoluble fraction of the bulk sample and **2** evaporated C_2Cl_4 extract of the HCl-insoluble fraction

noic, pentadecanoic, hexadecanoic, octadecanoic, heneicosanoic), and unsaturated (hexadecenoic and octadecenoic), n-alkanes C_{16}–C_{20}, (hexadecane, heptadecane, octadecane, eicosane), aromatic hydrocarbons and policyclic hydrocarbons predominate (anthracene, pyrene).

The black colour of the Dębnik limestone is thought to be caused by an admixture of bitumens (Gradziński 1972; Kozłowski and Magiera 1989; Lewandowska 1998) or pyrite (Bednarczyk and Hoffmann 1989). The stone spontaneously releases a smell of petroleum if hit with a hammer.

The grey to black colour of the sedimentary rock can have been induced by organic substances as well as by iron pigment. Organic matter is a very common component of carbonate rocks averaging 0.33 wt.% TOC (Lewandowska 1998). The colour change of the rock expected during weathering may be attributed to stability of the pigmenting carbon compounds, of which in sedimentary rocks hydrocarbons, asphalt and kerogen are possible. The hydrocarbons, being the least stable carbon pigment, particularly the aromatic hydrocarbons, determine the dark colour of the sediments. Dark grey and black limestones bleach quite easily to light grey after a few years exposure to weathering (oxidation environment). Reactions with aggressive solutions present in the ambient air enhance colour changes towards a very light shade (Winkler 1997).

On the other hand, iron is the most common and strongest pigment in sedimentary rocks. It can give the stone the colours from deep red to orange, yellow, brown, or tan to green, blue and black, depending on the ferric/ferrous (Fe^{3+}/Fe^{2+}) ratio in the given rock. The deep grey to black colour of the stone is connected with the predominance of ferrous iron. In this case Fe^{2+} may occur as finely distributed pigment that is bluish green to black and results from the presence of pyrite and/or marcasite (FeS_2). The powder (i.e., streak) of these minerals is actually black, although when recrystallized to larger grains the minerals become yellowish-brass. These ferrous sulphides are formed in a reducing environment. The presence of organic matter in the limestone is proof of such a reducing environment in a sedimentary basin, in which sulphates are reduced to hydrogen sulphide with further formation of iron dioxides (Lewandowska 1998). Iron pigments in sedimentary rocks are generally unstable if exposed to weathering and light, but the degree of colour stability is hard to predict.

6.3.2 Weathered Surfaces of the Limestone—The Quarry

The change of the original colour of the outer stone parts in the case of the homogeneous Dębnik limestone is the main sign of stone weathering. In another variety—the nodular limestone that occurs in the form of horizontal layers separated by discontinuities filled with clay minerals—exfoliating is also visible.

The changes of colour measured between bulk limestone and weathered layers reveal that the total colour change ΔE* is mainly due to the lightness variation ΔL*. The differences of the chromatic coordinates, Δa* and Δb*, are much lower (Table 6.1). The results cannot be univocally interpreted, as the measurements had to be made using broken, uneven surfaces that bear signs of alterations. Anyway, a marked shift of the b* values towards positive values in the case of the weathered samples means that these rocks have become yellowed. It is a far going assumption whether such a change may be associated with the presence of pyrite.

No secondary mineral phases have been found (XRD); and observations using scanning electron microscopy revealed that the outer surface often shows karst-like alterations and signs of leaching, but is covered only by fine calcite grains (Fig. 6.6). Similar descriptions were given by Kozłowski and Magiera (1989) and Wilczyńska-Michalik (2004). Additional microstructural changes measured between the bulk and the weathered part of the stone were noticed. The outer, i.e., weathered part of the stone (ca. 20–30 μm), is characterized by discontinuities and intra- and inter-crystalline microfractures, which are parallel to the surface and grade into an unaltered, massive rock. The inner part of the black limestone, reveals a compact structure and low porosity (Fig. 6.7). Some authors explain this phenomenon as thermal cracking of the calcite crystals. The cracking is caused by the anisotropy of thermal expansion of calcite grains due to differences between the thermal expansion coefficients along the *a* and *c* lattice directions (Marinoni et al. 2007). Other authors suggest that the stress resulting from changes of air temperature (this process starts at about 40–60°C) can impart microfractures among mineral grains (Winkler 1997; Marinoni et al. 2007).

Similar effects were observed when studying the fractal recurrence of karst phenomena. One of them was represented by the constant presence of an optically whitened layer on the surface of rock undergoing weathering (karstification). In hand specimen inspection, particularly using a binocular, this layer strongly resembles

Table 6.1 The values of chromatic parameters (L*, a*, b*) and total colour differences (ΔL*, Δa*, Δb*, ΔE*) in the samples from the Carmelite quarry

Sample	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE*
KB1	34.64	0.01	−0.09	15.64	0.37	4.16	21.50
KW1	50.31	0.38	4.07				
KB2	36.14	−0.06	−0.3	23.51	0.61	4.95	24.03
KW2	59.65	0.55	4.65				
KB3	32.12	−0.05	0.29	25.7	0.07	6.04	26.40
KW3	57.82	−0.12	6.33				

KB – bulk black limestone, KW – weathered layer

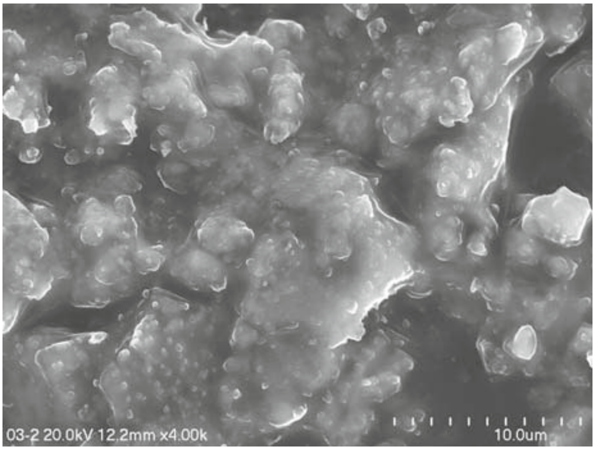

Fig. 6.6 SEM micrograph of outer, weathered part of the stone, revealing fine grains of calcium carbonate only and signs of leaching

fine-grained sugar. Under a scanning microscope the grains from the surface were distinctly loosened, standing out of the compact, massive rock typical of the sections unaffected by weathering. The transition from these almost loose grains into the massive, uniform rock was always smooth and gradual. The thickness of the loosened layer depends on the size of the grains and the cohesion of the rock. The layer could be even some millimetres thick if weathering was advanced (personal communications from J. Wrzak, M.Sc., a speleologist).

The study of the TOC, HI and OI (Rock Eval) parameters can be summarized as follows. These indices are higher in weathered layers than in unweathered (inner) parts of the stone (Table 6.2). Those differences could be connected with the presence of microorganisms on the surface of the stone. The presence of bioactivity was

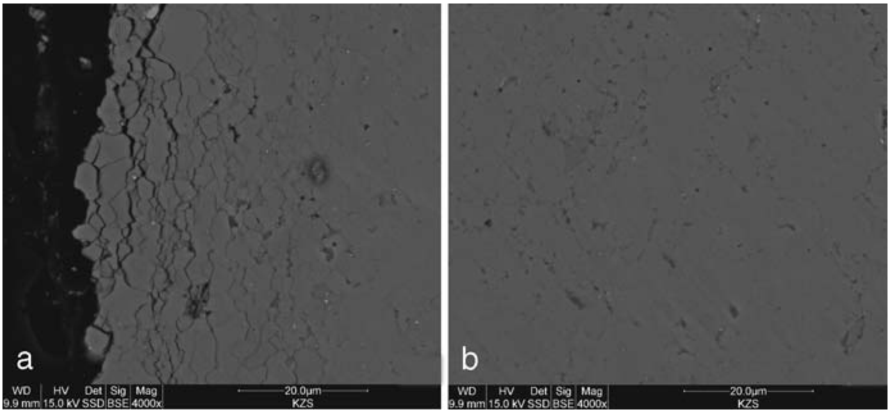

Fig. 6.7 SEM micrograph of a black limestone transversal section: **a** highly fractured weathered black limestone surface, **b** inner part of the black limestone, highlighting a compact structure of the stone and low porosity

Table 6.2 Rock-Eval data measured in the unweathered and weathered samples of black Dębnik limestone

Sample	TOC	T_{max}	S_1	S_2	S_3	PI	HI	OI
KB/04a	0.19	–	0.06	0.03	0.51	0.75	15	268
KB/04b	0.18	–	0.08	0.05	0.54	0.67	27	300
KW/04a	0.23	431	0.18	0.62	0.77	0.22	269	334
KW/04b	0.22	431	0.16	0.61	0.72	0.21	277	327

TOC – total organic carbon, T_{max} – temperature, S_1 – mass of the hydrocarbons, released at 300°C (mg HC/g), S_2 – mass of the hydrocarbons, released at 300–600°C (mg HC/g), S_3 – mass of CO_2 (mg CO_2/g), PI – index = $S_1/(S_1+S_2)$, HI – hydrogen index (mg HC/g TOC), OI – oxygen index (mg CO_2/g TOC)
KB – bulk sample of Dębnik limestone; KW – weathering layer

confirmed by scanning electron microscopy, which showed traces of lichen activity and microorganisms on the Dębnik limestone surface (Fig. 6.8).

6.3.3 Weathered Surfaces of Monuments—Cracow City

Historical elements exposed to a polluted atmosphere reveal the presence of the bleached surface as well (Fig. 6.9), but the composition of the surface is different from that of the rock surface in the natural outcrops. Some elements are covered by gypsum layers and contain other anthropogenic particles, mainly aluminosilicate glass spherules, iron oxides, partly coked carbon particles. In some architectonic details alveoles or surface exfoliation are developed. Their presence depends on the texture of the Dębnik limestone variety used, its orientation towards the bedding, and localization in respect to atmospheric factors.

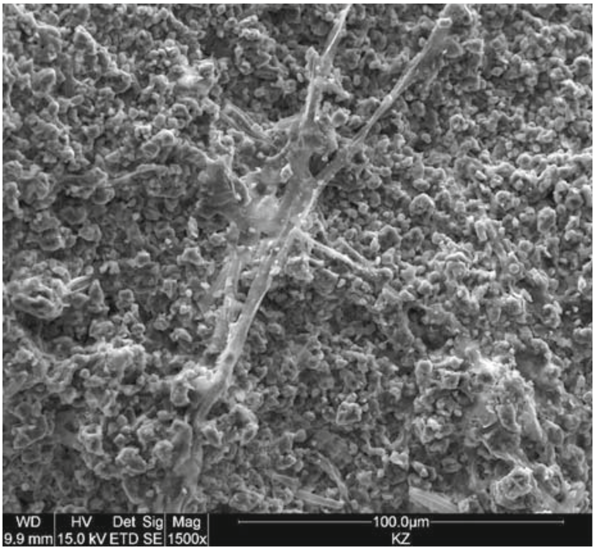

Fig. 6.8 Bio-activity on the black limestone surface—SEM micrograph

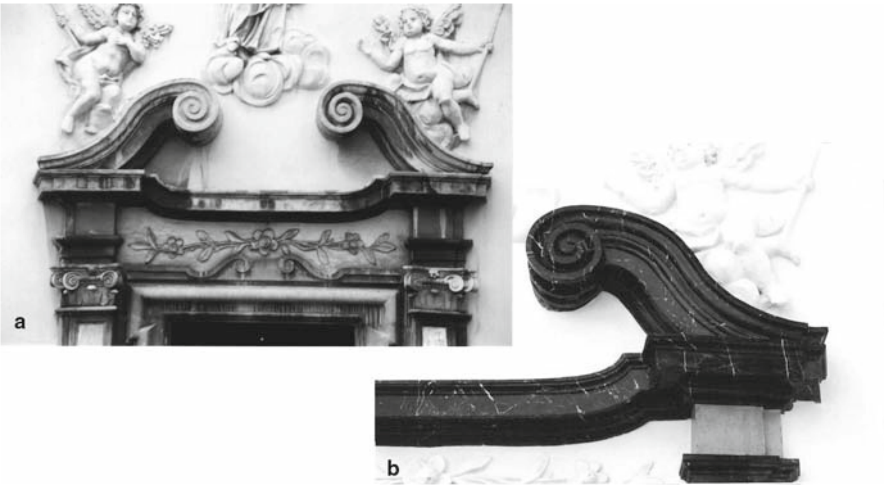

Fig. 6.9 Upper part of the portal constructed from Dębnik limestone—at St. Adalbert Church in Cracow **a** before and **b** after cleaning

The way the stone blocks are cut controls their further destruction:

- along discontinuities—results in exfoliating and cracking;
- perpendicular to discontinuities—gives rise to the formation of alveoles.

The processes of weathering of the black Dębnik limestone visible in architectonic details were discussed in Kozłowski and Magiera (1989) and in more detail by Marszałek (2004, 2007), and Marszałek et al. (2006).

The phenomena of the bleaching of black compact limestones were studied over the last few years by Marinoni et al. (2002, 2007); Benavente et al. (2006); and Zehnder (2006). All these authors emphasize colour changes of a variety of black compact limestone from black to grey or even white during exposure to climatic influences and they explain the changes as being optical effects taking place on the weathered, porous surfaces of the stone. On the polished surface of the dense and dark stone, the light is mostly absorbed, opposite to the weathered one, where light is reflected from the porous surface and scattered by the grain boundaries. As a result, the surface takes the colour of the disintegrated powder material, known to mineralogists as streak; and the streak of calcite, disregarding its colour, is white. When treating such an uneven surface with a liquid such as oil (e.g., linseed oil with an index of refraction 1.48), the pores become filled with a medium of optical properties similar to the minerals of the stone (calcite with indices of refraction $n_\varepsilon = 1.486$ and $n_\omega = 1.658$) and the original black colour of the stone comes back. It is a novel approach to the problem of colour changes, bearing in mind that most common explanations involve such phenomena as the weathering of organic matter and pyrite or the formation of secondary mineral phases on the stone surfaces.

Generally, the methods applied by the authors mentioned above in studying the processes of greying of black limestone are rather similar. On the whole, the results obtained do not provide clear-cut evidence to explain the chromatic weathering (i.e., greying, whitening) of the black “marbles”.

6.4 Conclusions

The variety of Dębnik limestone used widely in the Baroque period in small-scale architecture in Poland is a black, homogeneous, micritic rock with fossils and white calcite veins and nests. Besides calcite, the limestone contains subordinate amounts of feldspars, clays, pyrite and organic matter of the kerogen type, and traces of quartz and hydromuscovite.

Both the artifacts made of the Dębnik limestone and the rocks exposed in the quarry show patches or zones whose original colour fades to grey or even white. In the quarry the depth of these changes reaches a fraction of a millimetre. Of the components present within the rock, its black colour is imparted by pyrite and organic matter. Weathering of these two is commonly blamed for the decolouration of the black limestone, but no new mineral phases have been observed in Dębnik. This rather excludes pyrite and suggests that the changes may be associated with alterations of organic compounds. On the other hand, the changes of rock cohesion in the topmost layer with a thickness of 20–30 μm may cause some optical phenomena resulting in colour changes. They may include scattering of the light on the rough rock surface, i.e., on the grain boundaries, with simultaneous lowering of light absorption. Nevertheless, the problem remains open.

The reasons for the colour changes observed in the architectonic elements made of the same stone in Cracow are more complex. Newly formed gypsum is commonly present in surface layers of the Dębnik limestone; and the surfaces themselves are usually covered by particulate matter. Both these components are of anthropogenic origin and effectively hinder full explanation of the phenomenon. The presence of the gypsum layer on the surface of limestone is so common in the polluted urban atmosphere that most authors dealing with the problem of colour changes limit themselves to precipitates and particulates of anthropogenic origin.

Acknowledgements This study was supported by the AGH–University of Science and Technology project No. 11.11.140.158. Authors’ thanks go to C. Saiz-Jimenez and B. Hermosin of the Instituto de Recursos Naturales y Agrobiologia (Sevilla, Spain) for GC-MS analyses. The help of A. Gaweł, M. Kotarba, S. Olkiewicz, S. Siwulski of the AGH–University of Science and Technology (XRD, Rock-Eval pyrolysis, FTIR, colorymetry) is very much appreciated. We are also grateful to M. Wójtowicz for XRF analyses.

References

Baliński A (1989) Biostratygrafia górnego dewonu antykliny Dębnika. (Upper Devonian biostratigraphy of the Dębnik anticline). In: Rutkowski J (ed) Przewodnik LX Zjazdu PTG (LX Meeting of Polish Geological Society). Kraków, pp 30–34

Bednarczyk J, Hoffmann M (1989) Wapienie dębnickie (Dębnik limestone). In: Rutkowski J (ed) Przewodnik LX Zjazdu PTG (LX Meeting of Polish Geological Society). Kraków, pp 40–46

Benavente D, Bernabéu A, Fort R, Martínez-Martínez J, García del Cura MA (2006) The decolouration of breciated black marbles used in heritage monuments of Alicante. In: Fort R, Alvarez de Buergo M, Gomez-Heras M, Vazquez-Calvo C (eds) Heritage, weathering, and conservation, vol 1. Taylor Francis, London, pp 205–210

Bromowicz J (2001) Ocena możliwości wykorzystania skał z okolic Krakowa do rekonstrukcji kamiennych elementów architektonicznych (Application of the building stones of the Cracow area for the masonry reconstructions—evaluation of preferences). Gospodarka Surowcami Mineralnymi 17/1:16–73

Gradziński R (1972) Przewodnik geologiczny po okolicach Krakowa (Geological Guide of Cracow region). Wydawnictwo Geologiczne, Warszawa

Hermosin B, Gavino M, Saiz-Jimenez C (2004) Organic compounds in black crusts from different European monuments: a comparative study. In: Saiz-Jimenez C (ed) Air pollution and cultural heritage. Balkema, London, pp 47–55

Kozłowski R, Magiera J (1989) Niszczenie wapieni dębnickich i pińczowskich w zabytkach Krakowa (Deterioration of the Dębnik and Pinczów limestones in Cracow monuments). In: Rutkowski J (ed) Przewodnik LX Zjazdu PTG (LX Meeting of Polish Geological Society). Kraków, pp 204–208

Lewandowska A (1998) Mineralogia skarnów magnezowych grzbietu Dębnika (Mineralogy of Mg-scarns of the Dębnik hill). PhD thesis, Jagiellonian University. Kraków

Marinoni N, Pavese A, Bugini R, Di Silvestro G (2002) Black limestone used in Lombard architecture. Journal of Cultural Heritage 3:241–249

Marinoni N, Pavese A, Riva A, Cella F, Cerulli T (2007) Chromatic weathering of black limestone quarried in Varenna (lake Como, Italy). Building and Environment 42:68–77

Marszałek M (2004) Deterioration of stone in some monuments exposed to air pollution: a Cracow case study. In: Saiz-Jimenez C (ed) Air polution and cultural heritage. Balkema, London, pp 151–154

Marszałek M (2007) Mineralogical and chemical methods in investigations of decay of the Devonian black "marble" from Dębnik (S Poland). In: Prikryl R, Smith B (eds) Building stone decay: from diagnosis to conservation. Geological Society, London, pp 109–115

Marszałek M, Muszyński M (2001) Authigenic K-feldspars in Dębnik limestone (S Poland). Mineralogia Polonica 32(1):49–61

Marszałek M, Skowroński A, Gaweł A (2006) Składniki antropogeniczne w zwietrzałych wapieniach dębickich z krakowskich zabytków (Antropogenic components in weathered Dębnik limestones from Cracow historic sites). Gospodarka Surowcami Mineralnymi 22(3):450–459

Narkiewicz M, Racki G (1984) Stratygrafia dewonu antykliny Dębnika (Devonian biostratigraphy of the Dębnik anticline). Kwartalnik Geologiczny 28(3–4):513–546

Niemcewicz P (2005) Konserwacja wapienia dębnickiego (Conservation of the Dębnik limestone). Wydawnictwo Uniwersytetu Mikołaja Kopernika, Toruń

Rajchel J (2004) Kamienny Kraków (Stony Cracow—Stone in Cracow architecture). AGH – Uczelniane Wydawnictwa Naukowo-Dydaktyczne, Kraków

Wilczyńska-Michalik W (2004) Influence of atmospheric pollution on the weathering of stones in Cracow monuments and rock outcrops in Cracow, Cracow-Częstochowa upland and the Carpathians. Wydawnictwo Naukowe Akademii Pedagogicznej, Kraków

Winkler EM (1997) Stone in architecture. Properties, durability. Springer, Wien, New York

Zehnder K (2006) Greying of black polished limestone—a case study to clarify the phenomenon. Zeitschrift fur Kunsttechnologie und Konservierung 2:361–367