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Mineralogical and chemical methods in investigations of decay of the Devonian black “marble” from Dębnik (S Poland)

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Optical microscopy, scanning electron microscopy with energy dispersive spectrometry (SEM-EDS), X-ray diffraction (XRD), IR spectroscopy (FTIR), Rock-Eval pyrolysis and gas chromatography in combination with mass spectroscopy (GC-MS) were used to examine deterioration of the architectonic details made of the black limestone from Dębnik near Cracow. Due to its unique, deep black colour and good polishing properties, the rock is called the “Dębnik marble”. This stone have been widely used since Baroque times. It is possible to find a lot of architectonic details made of the Dębnik “marble”, mainly at the churches, monasteries, chapels and cemeteries (altars, baptismals, portals, balustrades, columns, monuments, tombstones and headstones) not only in Cracow, Poland, but also in Europe (Frankfurt am Main, Vienna, Graz, Salzburg).

The historical quarries of this black limestone are located about 20 km of Cracow in the “carmelite” quarry in the Dębnik village. The stone is compact and occurs in three varieties: the homogeneous, micritic limestone, the micritic limestone with fossils and the nodular limestone, occurring in the form of horizontal layers separated by discontinuities filled with clay minerals. Non-carbonate components include K-feldspar, smectite, illite, subordinate pyrite and organic substance, as well as traces of detrital quartz and hydromuscovite. The black colour of the Dębnik limestone is thought to be caused by an admixture of bitumens or pyrite.

The results of current investigations have indicated the organic matter to be mainly aliphatic hydrocarbons (infrared analyses). The GC-MS study confirms the presence of aliphatic hydrocarbones (C_{16}–C_{18}) and other compounds, mainly methyl esters.

The correlation between hydrogen (HI) and oxygen (OI) indices points to organic matter to be the type III kerogen (Rock-Eval pyrolysis). Two populations of crystals represent pyrite: 1 – those of very small sizes (0.00X–0.04 mm), and 2 – cuboidal with larger sizes, reaching 2 mm. The total amount of pyrite in the Dębnik limestone is about 2 wt.%.

Physico-mechanical properties of the Dębnik limestone are good and give the stone good resistance to atmospheric parameters, although some alterations of the stone surface can usually be observed. They affect mainly the original black colour, which changes to grey or even white. Polishing of the surfaces returns the stone to its proper, black colour.

The differences in the degree of damage of the architectonic details studied depend on the texture of the Dębnik limestone used, their orientation to bedding, and their localization in respect to atmospheric conditions. The samples were taken from different monuments exposed to natural and anthropogenic conditions and natural outcrops as well. Surface exfoliation is one of the signs of the damage and results in the formation of irregular or lensoidal fractures in the nodular limestones with admixtures of clay matter (marly limestones). The surfaces of undulatory or nodular lamination are the ways of penetration of aggressive, atmospheric waters. The fractures become filled with gypsum, a product of reaction of these waters with the calcium carbonate of the rock. The stone elements cut out of the stone without sedimentary textures are more resistant to water penetration: gypsum was observed only sporadically on the surfaces of both the micritic limestones and the micritic limestones with fauna. The results of SEM-EDS analyses have been corroborated by XRD and IR investigations that showed the presence of calcite only. The mineral occurs in the form of fine crystals with sizes from several to fifteen or so micrometers and shapeless aggregates as well. Beside gypsum, other anthropogenic components found on the stone surfaces include spherical particles that represent either aluminosilicate glass or iron oxides, the latter with characteristic, dendritic shell.

Architectonic elements exposed to external conditions show decolouration of the outer stone layer. The methods involved in finding the reason of these changes have not been conclusive and allow stating that whitening of the Dębnik limestone is probably associated with oxidation of organic matter.

The final conclusion is that the discontinuities in the Dębnik limestone provide an easy access for rainwater. Being exposed to the SO_2-containing atmosphere, in reaction of acid rains with calcite they become filled with hydrated calcium sulphate. Crystallization of gypsum leads to alveoling or cracking and exfoliating of the otherwise compact material. The way of cutting the stone blocks controls their further

destruction. When the stone is cut along the discontinuities, its destruction results in exfoliating and cracking, while perpendicular cutting gives rise to the formation of alveoles.

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