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Report

Greying of black polished limestone - a case study to clarify the phenomenon

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Black polished limestone has been a fashionable decorative material particularly for tombstones since about 300 years. E.g., about 30 out of approximately 200 epitaphs from the 16th to the 19th century in the cloister of the Basel Cathedral (Switzerland) are from black limestone (fig. 1). Their local popular and trade name is Alpenkalk. As the stones are dense and polished they are popularly considered as marble. However, when exposed to the climatic influences on the outside, the polish and its black colour disappears. Today most of these stones look more or less pale grey unless they have been restored recently. In the following, this phenomenon of discoloration is called “greying” as a descriptive term which does not anticipate genetic implications.

Because “a single fault is in many cases due to a number of causes”, we basically assume that a variety of physical and chemical processes may contribute to similar visual appearance. In the considered case, such processes may be:

- the alteration of the stone surface itself e.g. by chemical leaching,
- the alteration of an artificial coating, e.g. microcracking of a varnish etc.,
- the formation of a surface covering, e.g. by a powdery efflorescence, a thin crust etc.

The history of the epitaphs in the cloister of the cathedral is complicated and only fragmentary known. All stones which are mounted on the walls are not in their original position. Some of them have possibly been moved several times. The same is true for original and later treatments for conservation. Inscriptions were originally painted or gilded. Some of the stones were possibly glazed or treated with waxes, oil etc. Therefore it is assumed that the actual grey surface of black stones has not necessarily resulted from the same set of processes. Accordingly, the time span of their formation varies greatly. Some stones have not been touched during more than one century (fig. 2), others have recently been treated with waxes and/or oil (fig. 3). The process of greying is particularly noticeable in its initial stage, i.e. when the dark polished surface starts to get brighter and dull. It is unaesthetic and disturbs the intentions of owner families and conservators who want the stones to stay black. Moreover, finely carved inscriptions get blurred.

The cathedral’s workshop being concerned with the stone restoration and conservation has undertaken attempts to remove or to inhibit the formation of such grey veils. They used e.g. pure water, EDTA (ethylenediaminetetraacetic acid), ammonium carbonate and other products in combination with brushing, steel wool, etc. However, the results were not yet satisfying. As long as the nature of greying is not clear, the success of its treatment remains rather a matter of luck. Therefore, the Expert Center for Conservation of Monuments and Sites in co-operation with the Institute of Monument Conservation at ETH Zurich was asked in 2002 to elucidate the nature and processes of greying. In order to develop appropriate methods for conservation, investigations were carried out and results reported in 2003. This article summarises them.

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Fig. 1: View of a wall in the cloister of the cathedral of Basel (Switzerland). The appended or inserted epitaphs of various stones are from the 17th to 19th century. The second stone from the lower left is from black Alpenkalk.
Occurrence and background of the phenomenon

Greying of black limestone is a widespread phenomenon. Apart from dense Alpenkalk which is investigated here, other dark limestone and marbles are affected similarly. Examples are Aachener Blaustein (Germany), Calcare di Varenna, Nero di Rove, and Grigio Carnico (Italy), Belge Noire (Belgium), Negro Marquiña (Spain) and many others. Such stones are still fashionable for decorative architecture elements. As a matter of course, their greying is a universal problem encountered at ancient and modern buildings (fig. 5 to 8). Alois Kieslinger has described it as bleaching (“Ausbleichen”, said of marble, which goes along with roughening of the surface). In dimension stone industry it is also referred as „chalking”. Interestingly, this phenomenon has not been commented by building stone experts like Winkler, and Ashurst and Dimes. It has been described by Benavente et al. using colour, gloss and roughness measurements.

As a note on exposure conditions greying of black limestone basically occurs where the stones are exposed to rain and other kinds of moisture, like mist, condensation etc. The phenomenon is equally noted on architecture and monuments, as on rocks in nature. Where the stones are in a dry environment, they remain black.

The geological provenance of Alpenkalk are Triassic and Jurassic limestone in the northern Alps of Switzerland. De Quervain characterizes St. Triphon limestone, a prominent variety of Alpenkalk, as follows: Macroscopically blackish grey, with a slightly glossy, shell-like fracture. Undulated clayey intercalations are parallel to the bedding or irregularly arranged and cause a nodular texture. These intercalations are less than 1 mm up to 3 mm thick and well linked to the massive stone. The limestone surface gets bright due to weathering. The petrographic structure is micritic (i.e. with a grain size between less than 10 up to 100 microns). The macroscopically black colour results from tiny amounts of black, finely dispersed organic, coaly matter. The limestone varies from purely calcitic to slightly dolomitic. It is very compact (with an accessible porosity of 1 - 2% and a water uptake of 0.07 - 0.15%), its compressive strength is 1000 - 1500 kg/cm². The stone easily takes a polish, whereby it gets a dark grey to deep black colour. Its weathering resistance is considered as generally very good. However, stones with abundant clay intercalations may deteriorate by breaking off spalls (fig. 4) or bigger scales when face- or edge bedded.

Fig. 2: Epitaph ‘Ursula Reber’ (†1844) from black polished Alpenkalk, showing an intensely greyed surface. This stone has probably never been restored.

Fig. 3: Epitaph ‘Peter Bischoff’ († 1836) from black Alpenkalk. It has been treated with linseed oil about 5 years ago. In the meantime, grey veils have developed again.

Fig. 4: Detail of epitaph ‘Martin Wenck’ († 1830) from St. Triphon limestone, a variety of black Alpenkalk (width 30 cm). The finely carved and originally gilded inscription is hardly visible against the bright surrounding colour. In addition, stone spalls have been detached along clayey intercalations, which is a typical deterioration feature of this stone.
Nature and formation of greying

Laboratory investigations have been carried out by binocular microscope, polarising light microscopy, micro-chemistry and scanning electron microscopy on small spalls from epitaphs situated in the cloister of the Basel cathedral, as well as on weathered samples from other locations. The results are summarised subsequently and illustrated in Figure 9.

The grey stone surface is a thin layer of powdery, disaggregated stone material. It passes gradually into the sound, dense structure underneath. The grey looking altered surface zone has a thickness of a few tens of microns as in the case of investigated epitaphs, up to 1 mm and more in the case of surfaces which were rain exposed during about 100 years and more. What appears grey is in fact a rim of the fissured, porous limestone structure. In this superficial zone, calcite grains show clear effects of chemical dissolution. Hence the colour of suchlike altered stone surface represents the colour of disaggregated or "pulverised" stone matter 15. In addition, the surface is partly covered by a thin crust of gypsum and dust in sheltered areas.

According to our investigations, greying turns out to be a weathering process by chemical leaching. So the initially black, dense limestone gets fissured and porous in a superficial zone. This leaching process corresponds to chemical dissolution of limestone when exposed to rain. In areas sheltered from direct rain such as the cloister of the cathedral, the process is slower and more complicated. As usual in polluted atmospheres, chemical dissolution is controlled by the deposition of acid aerosols (particularly sulphuric acid) and the accumulation of gypsum, which is indicated by the observed presence of gypsum crusts. In addition, cleaning actions with the use of acids may have caused accelerated leaching in the past.

The grey appearance of the stone is recognised as a microscopic disintegration of the primary dense micritic structure. The involved optical effects can be interpreted as schematically illustrated in Figure 10. The polished surface gets dull and grey as the surface is porous, so that incident light is superficially scattered and refracted. A transparency which is similar to the original state can be partly regained when the gaps of the porous structure are filled with a medium of similar optical properties like the stone minerals, i.e. the stone. This is in practice achieved by impregnating the porous surface with oil, wax or other appropriate mediums.

Various causes and processes may alternatively contribute to effect a similar greying of black limestone. In the cloister...
of the cathedral of Basel, powdery efflorescence of gypsum have been identified\textsuperscript{16}, as well as blooming, tarnishing and chalking of deteriorated paint films and artificial coatings. Impacts by thermal dilatation on the other hand seem to be irrelevant as there is no obvious relation to sun exposure. Neither a significant microbiological activity has been observed until now.

**Concepts for conservation**

The cathedral’s workshop has used several reportedly traditional treatment concepts on epitaphs of dense limestone: (1) re-polishing of originally polished stones, (2) treatments with resins, oils and waxes and combinations of these products\textsuperscript{17}, (3) treatment with oils (particularly linseed oil and turpentine), glazing with pigmented oil, (4) treatment with soft soap. Experiments with these methods have revealed that re-polishing (by hand) is not only very time-consuming but also creates a wavy surface (fig. 11) and produces an excessive loss of original surface. This method has therefore been abandoned. Wax treatments (beeswax or paraffin mixed with oil) have the disadvantage that a grey surface remains grey, because the sticky liquid does not penetrate into the finely porous grey surface layer. Moreover, inhomogeneity of the stone structure and weathering intensity cause a patchy appearance of dark and bright areas. Similar negative effects have been experienced by treatments with soft soap. More satisfying results are produced by treatments with linseed oil which is variably mixed with turpentine. By the way this is a common traditional maintenance practice on buildings, particularly on dense black limestone which are exposed to rain\textsuperscript{18}. However, it has often been disregarded in the last decades. Oil treatments should be repeated every 10 years or so, depending on the weather exposure. This method does not work when thick disintegrated zones have developed. For such cases, an interesting new concept has been introduced by the cathedral’s workshop in Basel: In a first treatment step, the disintegrated stone surface is “re-consolidated” with limewater. Lime-water is applied by brush or by compress. Since the amount of precipitated calcium carbonate is small at a time, this procedure is repeated several times. In a second step, the dry...
Fig. 9: a) Fracture edge of St. Triphon limestone from the main station of Zurich. The bright grey weathered stone surface (above) passes into dark and dense stone structure underneath (width 5 mm). The stone has been exposed to rain for about 100 years. b) Thin section through the surface zone of this sample viewed in the polarising microscope (crossed nicols, width 1 mm). The dense stone structure to the right gets gradually porous to the weathered surface on the left. c) Detail of the surface zone viewed by scanning electron microscopy (SEM). Calcite grains show intense dissolution shapes (width 20 microns). d) Weathered grey stone surface from an epitaph in the cloister of the cathedral of Basel. The surface is partially covered by a thin crust of gypsum and dust on the upper zone. Calcite grains underneath show clear dissolution shapes (marked with arrows, SEM image width 50 microns). e) Weathered zone near to the surface of the same sample. The calcite grains are separated by narrow fissures due to leaching (SEM image width 50 microns). f) Detail of the same sample in the dense stone structure about 1 mm beneath the surface (SEM image width 100 microns).

Fig. 10: Schematic illustration of optical surface effects on an originally dense and dark stone in various conditions. a) On the polished surface of a dense and dark stone, the incident light is mostly absorbed. b) On the weathered and therefore porous stone surface, incident light is scattered and refracted by the grain boundaries. In consequence, the surface takes more and more the colour of disintegrated material which is also the colour of its powder. Transparency is lost and the surface gets dull. c) When the weathered stone surface (as in b) is treated with a liquid such as oil, the pores are filled with a medium of similar optical properties as the minerals of the stone. In consequence, the light is absorbed and reflected in a similar way as in a) and the surface appears dark again.

Surface is impregnated with linseed oil. The result is shown in Figure 12 and 13.

Aiming at sustainable care, further options should be considered, one of which is the relocation to an environment which is free from acid deposition and condensation. Finally, one has to challenge the concept of removing or hiding the grey surface. A historical argument is to consider the trace of an ageing process as valuable information per se, as it would be for a patina. A scientific-technological argument is that the grey surface has apparently no accelerating destructive effect. Therefore, instead of comprehensive protection or of regaining the illusion of an original state by restoration, greying can be regarded as a relevant feature of authenticity. This leads to the basic questions in monuments conservation which must be answered for each individual case: To what operative and financial extent should appropriate care develop? Which degree of damage progress as well as present and future risk is acceptable for a piece of art?
Abstract

In a case study at the Basel Cathedral (Switzerland), grey coverings on epitaphs from black, originally polished limestone have been investigated in order to determine suitable methods for conservation. The grey superficial discoloration has been identified as the result of chemical dissolution, which corresponds to the natural weathering process occurring on limestone which are exposed to rain. In the shelter of the cloister, moisture impact is due to mist and occasional condensation events, combined with sulphuric aerosols. In order to regain the black surface of epitaphs, recent attempts with a pre-treatment by lime water followed by an impregnation with linseed oil show best results. As the greyed surface has apparently no accelerating effect on the weathering process, it can also be preserved as a patina.

Zusammenfassung

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Notes

2 In geological and petrographic terms, marble is a metamorphic limestone.
4 A synonym is "corrosion", a term that is rather used with materials such as metal and glass.
5 The coating thereby is getting dull and "blind".
6 Alternative terms are "blooming", "veiling", "chalking" etc.
8 Personal communication with Prof. Dr. Lorenzo Lazzarini, University of Venice IUAV, Italy.
10 Personal communication with Peter Eckardt, Eckardt Natursteine AG, Volketswil, Switzerland.
15 This feature is analogous to the so called "streak colour", the colour of a scratched line on unglazed ceramics, a determining feature used to characterise minerals.
18 E.g. in the monastery of Engelberg, cp. fig. 6. Personal communication by Paul Arnold, architect.