Staining of white marble

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Abstract

White marbles have been a popular building material since Greek and Roman times. Recently, the long-term aesthetical aspect of white marbles has been questioned. In this paper, the results of our research on the development of stains on different types of white marbles (seven Italian and one Greek marble) are presented. The staining of white marbles has been studied by using different microscopic techniques and staining methods. In addition, a new optimised staining technique is proposed for artificially staining of white Carrara marble. An objective normalised measuring method is also developed for quantifying the discolouration of natural materials. Although the inclusions of organic material in crystals in marbles are often suggested to be responsible for staining, this investigation illustrated that they have little or no influence on the discolouration of the natural stones. Systematic investigation showed that the presence of pyrite and hematite crystals plays a dominant role for the development of discolouration.

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1. Introduction

White marbles have been very popular since Greek and Roman times. This is illustrated by its numerous building applications. Nowadays, white marbles are still specified for traditional construction as well as in innovative applications (such as in combination with glass for structural sealant glazing systems). Although the technical quality of the white marbles is not questioned, nowadays, more and more discussion arises about the problems concerning the long-term aesthetical aspect. After application, some marbles often show a yellow–brownish diffuse discolouration (Fig. 1), which is very difficult to remove. Although staining is one of the most common problems regarding natural stone, this type of discolouration is certainly damaging for the image of stone.

Although the processes responsible for this type of staining are well known in theory, the specific conditions that cause discolouration remain undetermined. For example, in-situ observations have shown no systematic relation of the staining with:

– the type of application (walling, flooring, …)
– the way the stone elements are put in place (mortar, glue, …).

This implies that other factors play a role in the staining of marbles. Many case studies of the BBRI (Belgian Building Research Institute) allow us to state that even when the practice codes for placing the marble
elements are carefully followed by the building contractor, no guarantee can be given concerning the later appearance of these yellow–brownish diffuse discolourations. This lack of knowledge often results in confusion in the attribution of responsibilities in the frame of disputes. As a consequence, the work of the craftsman is generally implicated. For this reason, the BBRI was asked by the Belgian stone sector to carry out practical research in order to answer the following questions:

– Which are the important parameters explaining this type of staining?
– Are some marbles more sensitive than others?
– Can preventive surface treatments be a solution?
– Which are the most efficient techniques for stain removal?

This article reports the microscopic aspects of this research, namely:

– The identification and quantification of possible stain-causing constituents (iron-bearing minerals or organic matter) by microscopic analysis of thin sections and polished sections and by Scanning Electron Microscopy (SEM).
– The development of laboratory tests to replicate the phenomenon, in support of the microscopic analysis (thin and polished sections of stained marbles).
– The use of image analysis of photos of stained marble to analyse the relation between the structure (for example the grey “veins” in Carrara marble) and the discolouration.

Three major types of stains can be identified in natural stones. The first type is formed by the oxidation of iron-bearing minerals present in the stone. These minerals are mainly iron sulphides (e.g., pyrite, marcasite), iron carbonates (siderite) and ferromagnesian silicates (biotite, hornblende). These accessory minerals occur dispersed or concentrated along veins in the natural stone. Staining forms when iron is transported by water to the surface of the tile, where it is precipitated as coloured iron hydroxide (limonite). This kind of staining develops after placement of the stone elements (after 8 to 12 months). Staining does not occur when the elements are placed close to heating- or hot water piping [1]. The discolouration not only affects the aesthetic appearance of the stone, it can also result in physical damage of the stone. Fissures appear to result from volume expansion of the oxidised and hydrated minerals [2]. The stains of this first type are non-soluble and are, therefore, difficult to remove.

The second type of staining is caused by the reaction of organic matter, which is trapped during sedimentation and lithification of the rock, and alkalis that originate from the cement. The structure of the organic matter can be compared to humus [1]. Organic matter is soluble in water and is coloured (generally brown–yellow) or develops a colour on reaction with alkalis. During drying of the floor, water that originated from the mortar or the screed beneath, reacts with organic matter and migrates to the evaporation surface. The amount of water which migrates through the stone, is a function of the mode of placing (Table 1). This water also transports the soluble fraction of the alkalis present in cement, which in turn react with the organic substances within the stone. The coloured reaction products will be carried along to the stone surface, where they will concentrate and form more or less marked and homogenous stains. These stains develop within a few days or weeks after positioning the stones. However, since the reaction products are water-soluble, the stains are easy to remove.

The third type of staining is caused by external agents of several sub-types. The first sub-type is when the stain is attached on the surface, e.g., gum or simply dust. The second and most important sub-type is related to the susceptibility of the floor covering and occurs when substances penetrate the material. This discolouration can result from two different causes: a chemical reaction,
In the literature, it is often mentioned that white marbles contain organic matter, which is interpreted to be the main cause of the diffuse brown–yellow stains [4, 5]. Others propose the presence of pyrite minerals as the main cause of the discolouration in natural stone. Therefore, the aim of our investigation is to find out which of these two is the main cause of the change in the appearance of white marbles.

2. Experimental investigation of marbles

Based upon their well-known staining behaviour, the Carrara marbles (Italian marble) and Thassos White (Greek marble) were selected for experimental investigation. According to the number of complaints recorded by BBRI, staining of the Carrara marble is a more frequent problem than for the Thassos marble. Essentially no incidences of staining have been reported for this latter type of marble. It should, however, be borne in mind that Carrara marble is the most frequently used. Therefore, several Carrara types have been selected for this study and their differences and similarities have been examined (Table 2). The samples have been supplied by the Italian company “La Internazionale Marmi e Machine Carrara SpA” (or IMM Carrara) as reference pieces. The list was composed in co-operation with the Technical Committee “Natural Stone” representing all the concerned federations in Belgium.

3. Petrographic investigation

3.1. Macroscopic description

The Blanco Carrara marble (three sub-types) has a fairly homogeneous colour, ranging from white to off-white up to grey. In some cases, the ground mass is interrupted by slightly fading greyish veins, which are usually isolated and limited in length. The sub-type C of the Blanco Carrara is characterised by a white ground mass, with uniform (though not marked) spots and veins. It can be distinguished from subtype C/D by its clear and regular ground mass. Sub-type C/D is also characterised by an inferior whiteness compared to sub-type C. Sub-type D combines uniform non-marked spots and a greyish ground mass.

Arabescato Corchia has a white to off-white ground mass, with an irregular pattern of grey–yellowish veins. These veins have a tendency to follow a given direction and often cut across one another. The Calacata Oro marble has a pure white ground mass with light yellow, sometimes light greyish veins. The veins are, however, more visible and more common compared with the Statuario marble, and are present as irregular wavy lines. The grain size is fine to medium. Statuario Macchia Oro consists of a pure white, verging to ivory white, ground mass, showing minute yellowish to greyish veins of limited length embedded into the ground mass in isolated areas. In these latter zones pyrite crystals can be recognised. The grain size of the ground mass is very fine to medium. The Bianco P marble is considered to be the best of the different Carrara marbles investigated, due to its very white ground mass and few spots and inclusions [6].

The Greek Thassos White marble is characterised by its pearly white homogenous colour and its lack of any spots or veins.

3.2. Methodology

Optical investigation, done with a Reichert-Jung microscope, of the non-opaque minerals in transmitted light and opaque minerals in reflected light allows the characterisation of the mineralogy and the description of the morphology of the minerals. The porosity and cracks are analysed with thin sections under fluorescent light. For this investigation, the stone samples were surrounded and impregnated under vacuum by a fluorescent epoxy resin. The preparation and finishing of the thin sections and polished sections were done according to EN 12407. The thin sections had a thickness of 25 to 30 μm and a surface of 3 × 5 cm. The polished sections have the same surface and are used for the microscopic analysis by reflected light as well as for the investigation with a Scanning Electron Microscope (SEM) (Philips XL-30) fitted with an EDAX DX-4i system. The SEM analysis was carried out with a BSE detector. The specific conditions used are mentioned on each individual picture. Additional characterisation of the mineralogy has been carried out with powder X-ray
diffraction (XRD) (Bruker AXS D8-advance diffractometer). The stone samples were crushed and pulverized. The resulting powder was pressed into a special holder and placed in the diffractometer. The rotating (speed of 30,000 rpm) sample is irradiated with CuKαradiation (40 kV and 40 mA). The analysis is executed with a divergence slit of 1° and covers a 2θ-area of 10° to 75° with a step size of 0.02° (1 s per step).

3.3. Microscopic description

Different mineral grains with black “dots” were observed in all marbles examined (Fig. 2). SEM investigation identified the mineral grains as dolomite ((Ca,Mg)(CO₃)₂, Fig. 3). The concentration of the dolomite crystals is too low to be identified by XRD analysis. These minerals are interpreted as secondary minerals formed by the dolomitisation of the original limestone. The black “dots” in these dolomite crystals are interpreted as inclusions, which were trapped in the crystals during the dolomitisation.

The marbles of Bianco Carrara (sub-types C and D) have granoblastic calcite crystals with an average size of 350 μm. The grey colour in the ground mass of sub-type D can be explained by the presence of small inclusions (of a few micrometers) in the calcite crystals. The macroscopically observable grey veins are microscopically difficult to distinguish from the ground mass since the size of the calcite crystals is approximately the same in the ground mass as in the veins. Calcite in the veins seems to contain more inclusions. The veins of sub-type C show crystals with a size of ~20 μm. The veins also contain a lot of inclusions (Fig. 4). Polygonal pyrite crystals are principally found along the edges of the calcite crystals and have a size varying between 2 μm and 50 μm. Hematite can be found randomly distributed (Figs. 5 and 6). This marble has a low porosity. Only
microcracks along the calcite minerals can be observed. It also shows that the veins, in sub-type C with the small crystals, are no more porous than the rest of the marble. The Arabescato Corchia marble consists of calcite and contains small amounts of dolomite, quartz and feldspar. No inclusions occur in the ground mass of the Arabescato marble. The ground mass consists of granoblastic calcite crystals with an average size of 200 μm. The veins contain smaller and more irregular crystals than the ground mass and contain inclusions (Figs. 7 and 8). Pyrite crystals are concentrated along these veins. Pyrite is found as isolated polygonal crystals or as irregular aggregated crystals, oriented parallel to the orientation of the vein (Figs. 7, 8 and 9). Hematite can be found randomly distributed (Figs. 10 and 11). Microcracks are present along the crystal edges in the ground mass as well as in the veins. Small intragranular pores are also observed in the veins, which makes them more porous than the rest of the marble. The calcitic ground mass of the Calacata Oro marble consists of granoblastic crystals with an average size of 350 μm. Only a few crystals were observed to contain inclusions. The green–yellowish veins can be microscopically identified as a mixture of smaller calcite crystals (average size of 50 μm), pyrite (20–100 μm) and hematite grains. In general, this marble shows a relatively small amount of pyrite and hematite. The veins are more porous than the ground mass, which has a low porosity (intergranular porosity along the crystal edges). The Statuario Macchia Oro marble has a ground mass of granoblastic calcite (400 μm) and minor quartz and feldspar grains (125 μm). No crystals with inclusions were observed. Microscopically, it is not possible to
distinguish the green or yellow veins from the ground mass. Pyrite minerals occur as solitary crystals (50 μm) or as aggregates (up to 2.5 mm), located in intergranular cavities in the ground mass. Iron oxides, such as hematite, were also observed. The porosity is defined by microcracks along the calcite crystals and scattered intergranular pores.

The homogeneous white marble Bianco P consists of granoblastic calcite minerals (average size of 150 μm), with scattered groups of crystals containing inclusions. The minerals with inclusions are associated with intergranular pores. The porosity is defined by microcracks. Pyrite appears as solitary polygonal crystals, homogeneously dispersed in the calcitic ground mass (Fig. 12).

The Thassos White marble has a different petrography than the Carrara marbles. The ground mass consists of xenoblastic, anhedral dolomite crystals with a size that varies between 120 μm and 1.75 mm (Fig. 13). The presence of dolomite is confirmed by XRD analysis. Many dolomite crystals contain inclusions, but the amount of these inclusions is not always the same. Iron sulphides were not observed in the sample examined. An intergranular (crystal edges) and an intragranular porosity can be observed. In the dolomite crystals microcracks along crystallographic planes are present.

4. Artificial staining tests

Staining tests were developed to determine whether the natural stone is susceptible to the development of a particular type of staining. To artificially produce staining by the oxidation of iron-rich minerals, two different tests were developed and applied: a thermal shock test and an alkaline water test. These two testing methods result in accelerated oxidation and staining of

Fig. 10. Pyrite (= P) and hematite (= H) in Arabescato Corchia (microscopic analysis with reflected light — crossed polars).

Fig. 11. Pyrite (= P) and hematite (= H) in Arabescato Corchia (microscopic analysis with reflected light — plane polars).

Fig. 12. Two pyrite crystals on a different level in the calcitic ground mass of Bianco P (microscopic analysis with plane polarized light).

Fig. 13. Dolomite crystals of Thassos White (microscopic analysis with plane polarized light).
different types of stone, which contain a different amount and type of sulphide.

4.1. Thermal shock test (prEN 14 066) [7]

In this test, natural stone tiles (20 cm × 20 cm × 1–2 cm) are submitted to 20 cycles of 6 h in a bath of demineralised water at 20±5 °C, followed by heating in an oven at 105±5 °C for 18 h.

After the 20 thermal cycles, only the stones with iron-rich minerals visible on the surface of the tile showed oxidation stains. However, the marble tiles did not display staining comparable with natural staining. In addition, the use of this test on different types of stone proved that the finish of natural stone elements plays a role in the intensity of oxidation. For example, granite with a polished finish shows less oxidation stains than does one with a flamed finish. The differences in staining after thermal shock seem minor between a polished and a honed tile.

4.2. Alkaline water test

Since the thermal shock test did not result in staining on Carrara Bianco C and this marble is actually known to be sensitive to staining (dispersed beige–brown stains in Fig. 1), another staining test was developed.

As indicated by the petrographic analysis, the presence of pyrite (FeS2) is identified in a number of these marbles. It has been proven that the rate of oxidation of pyrite is higher in an alkaline environment than in a neutral or acid one [8]. Hence, the new test consists of 20 cycles of 6 h in an alkaline solution (1 M), obtained by dissolving NaHCO3 in water, followed by 18 h in an oven at 55±5 °C.

This test produced stains similar to those observed in naturally discoloured Carrara Bianco C marbles. It should be mentioned that none of the other natural stones tested showed stains. Consequently, this test seems to be relevant for marbles containing finely dispersed pyrite minerals [9]. With this staining test for white marbles optimised, the different marble types mentioned in Table 2 were subjected to staining.

4.3. Results of petrographic investigations with the alkaline water test

The Carrara Bianco marbles (sub-type C, C/D, D) all show a diffuse discolouration of the ground mass and the veins (Fig. 14). However in a few tiles there are regions that have the same colour as before the test and no discolouration can be observed.

The ground mass of Arabescato Corchia exhibits a lightly yellowish colour, but the bright white areas are not discoloured. More remarkable is the brown colour in the original dark grey veins (Fig. 15), where the pyrite is concentrated.

The difference in colour before and after the stain test for the Calacata Oro marble is small. Only the veins are little more accentuated, due to the oxidation of the iron-rich minerals. It should be mentioned that not all the pyrite crystals observed by the naked eye show oxidation signs. The same observations can be made for Statuario Macchia Oro marble. It should be noted that one of the five Statuario tiles tested showed a diffuse yellow staining in the ground mass. In this marble type, pyrite has been found in cavities in the ground mass.

The uniformly white Bianco P marble turned into a uniformly yellow–orange marble. The whole tile shows

Fig. 14. A Bianco Carrara C tile before the alkaline water test (left) and a tile after the test (right) (not the same tiles).
one diffuse stain (Fig. 16). In this marble, pyrite is found dispersed in the ground mass of the marble. No discolouration was observed for the Thassos White marble, Figs. 17 and 18.

Based on these observations, it should be noted that the different marbles exhibit different discolouration behaviour. In addition, it is clear that the discolouration of the marbles is discontinuous and is often associated with the veins. Petrographic observations have indicated that these veins are characterised by the presence of pyrite and/or hematite crystals.

Polished sections of a discoloured marble were investigated. In zones with no staining, pyrite was not found by microscopic investigation. Table 3 gives a summary of the relation between the discolouration and the presence of pyrite (the variation of the observed sizes and the appearance) and illustrates the importance of iron sulphides for the discolouration of marbles.

5. Use of image analysis as a tool to quantify the discolouration

Every scientific investigation dealing with aesthetical problems needs to be supported by a method beyond the human eye to characterise objectively and numerically the aesthetical properties of a surface. Therefore, normalised methods are needed to obtain reproducible results.

Standard colorimeters or spectrophotometers are available for quantitative measurements of colours, but are useless for a detailed identification of relatively large surfaces (for example, a tile of 30 cm × 30 cm). In this research, a practical method was used to objectively quantify the discolouration and staining. Recent technological advances in digital image acquisition and computing offer powerful tools to develop quantifying methods. In the ornamental stone sectors, many applications of such systems have already proved their
efficiency, for example for the classification of tiles according to their texture [10,11].

This digital image analysis technique was used in this research in order to:

– quantify the level of the observed discolourations, especially before and after oxidation tests.
– characterise locally their distribution on the surfaces.

All the image acquisitions have been made by the MICA laboratory (Mineral Georesources and Geological Imaging, University of Liège, Belgium) that specialises in this field of investigation.

Image acquisition is comparable to a standard scanner, and consists of a linear displacement system moving under a linear acquisition area, on which the lighting and the sensor are focused. To reproduce a given surface, quantification stages making up the visual system have to be reproduced. Thus the lighting and the acquisition system have been characterised in order to provide corrected and calibrated images.

A ‘daylight’ fluorescent tube (Philips TLD965) and a trilinear CCD camera (Dalsa Trillium 02K25) were employed. Non-uniform lighting and device dependence are eliminated by using a white profile reference and a colour test pattern (Kodak Q-14). The image is then saved in a usable CIE-compliant standardized colour space [12].

5.1. Results

A set of 10 tiles (40 cm × 40 cm) of Carrara Bianco sub-type C was submitted to the alkaline water test. Images of the same tiles before (Fig. 17) and after (Fig. 18) the test were acquired and calibrated according to the method described above.

The results of the test show a general yellow–brownish diffuse discolouration (Fig. 18), visually homogeneously spread on the surface. Chromatically, this discolouration is characterised by a shift between the pixels of the red and blue channels (Figs. 19 and 20); the distribution of the green channel remained unchanged.

<table>
<thead>
<tr>
<th>Marble</th>
<th>Pyrite</th>
<th>Discolouration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrara Bianco C</td>
<td>2–50 μm dispersed in ground mass</td>
<td>Ground mass</td>
</tr>
<tr>
<td>Arabescato</td>
<td>3–300 μm concentrated in veins</td>
<td>Brown veins</td>
</tr>
<tr>
<td>Calacata Oro</td>
<td>20–100 μm ground mass and veins (concentration a bit higher)</td>
<td>Little discolouration</td>
</tr>
<tr>
<td>Statuario Macchia</td>
<td>50 μm–2.5 mm ground mass</td>
<td>Little discolouration</td>
</tr>
<tr>
<td>Bianco P</td>
<td>7–20 μm dispersed in ground mass</td>
<td>Uniform yellow–orange colour</td>
</tr>
<tr>
<td>Thassos White</td>
<td>None observed</td>
<td>No discolouration</td>
</tr>
</tbody>
</table>
In order to map the quantitative colour variation of each pixel before and after the test, the calibrated RGB (Red, Green, Blue) values were transformed into a $L^*a^*b^*$ system, which allows the calculation of the difference between two measured colours according to the following relationship:

$$\Delta E_{\text{lab}} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

where $L^*$ is the value of brightness, and $a^*$ and $b^*$ are the values of, respectively, the red–green saturation and the yellow–blue saturation. $(\Delta L^*)$, $(\Delta a^*)$ and $(\Delta b^*)$ in Eq. (1) are the pixel-to-pixel differences within each of the $L^*$, $a^*$, $b^*$ channels before and after the oxidation test. This result is then mapped into a new image (Fig. 21), in which the intensity of each pixel is proportional to the calculated $\Delta E_{\text{lab}}$ (black colour corresponds to zero and white colour to the maximum).

By thresholding this image according to a certain level of perceptibility (chosen here as $\Delta E_{\text{lab}} < 5$), the oxidised and non-oxidised regions on the surface of the tiles can be distinguished. On Fig. 22, the non-oxidised regions are shown in blue.
6. Conclusions

The combination of microscopic analysis and staining techniques clearly illustrates that the typical diffuse brown–yellow stains appearing on white marbles are influenced by the presence of pyrite and hematite minerals. The marbles may also contain organic matter, as inclusions in ground mass crystals. However, investigation has shown that these latter inclusions have no significant influence on the discoulouration.

An accelerated alkaline water staining test was developed to predict the behaviour of the appearance of a white marble in time. This test is easy to carry out and takes little time (about a month), compared with results obtained by previous methods.

The development of an objective normalised measuring method to quantify discolouration of natural materials has made it possible to distinguish a discoloured zone from a non-discoloured zone in a natural stone tile, based on parameters of an investigator’s own choice.

These results will be further elaborated to develop practical recommendations for the use of marble as a building material, including:

– preventive treatments
– maintenance
– guidelines for the proper application.

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