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, 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.

Keywords: marble, stain, discolouration, pyrite.

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 rises about the problems concerning the longterm aesthetical aspect. After application, some marbles often show a yellow-brownish diffuse discolouration (Figure 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.



Figure 1: case of discolouration of a marble

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 causes 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 a later appearance of these yellow-brownish diffuse discolouration. 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 to 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 Microscope (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 hydroxides (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 (Dugniolle & Muzzin, 1997). The discolouration does not only affect 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 (Winkler, 1973). The stains of the first type are non-soluble and, 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 (Dugniolle & Muzzin, 1997). 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 function of the mode of placing (Table 1). This water also transports the soluble fraction of the alkalis present in cement, which on their 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.

Mode of placing	Amount of water (litre/m ²)
Traditional placing (mortar bed)	5 - 7
Placing in fresh screed	10 - 13

0.7 - 1

Placing with adhesive mortar on hardened screed

Table 1: Amount of water that can be absorbed by the stone, is a function of mode of placing

The third type of staining is caused by external agents. 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, e.g. acids damaging marble surfaces, or a purely physical alteration of gloss, e.g. the infiltration of oil in gneiss (Fahrenkrog, 2002). In 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 (Dugniolle, 1987, Bassie, 1990). 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 of aspect of white marbles.

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. Nearly no cases are 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 is composed in co-operation with the Technical Committee "Natural Stone" representing all the concerned federations in Belgium.

Table 2: Seven Carrara marbles and one Thassos White marble were selected for experimental investigation.

Origin	Marble type
Italy	Bianco Carrara C
	Bianco Carrara C/D
	Bianco Carrara D
	Arabescato Corchia
	Calacata Oro
	Statuario Macchia Oro
	Bianco P
Greece	Thassos White

Petrographic investigation

Macroscopic description

The *Blanco Carrara* marble 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 sub-type 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, 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 minuscule 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 (Bradley, 1998).

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

Methodology

Optical investigation, done by a Reichert-Jung microscope, of the nonopaque 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 are surrounded and impregnated under vacuum by a fluorescent epoxy resin. The preparation and finishing of the thin sections and polished sections are done according to EN 12407. The thin sections have a thickness of 25 to 30 µm and a surface of 3 x 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 the Scanning Electron Microscope (SEM) (Philips XL-30) fitted with a EDAX DX-4i system. The SEM analysis is carried out with a BSE detector. The specific used conditions 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 are crushed and pulverished. The obtained powder is pressed into a special holder and placed in the diffractometer. The rotating (speed of 30.000 rpm) sample is irradiated with CuKaradiation (40 kV and 40 mA). The analysis is executed with a divergence slit of 1° and covers an 2 θ -area of 10° to 75° with a stepsize of 0,02° (1 s per step).

Microscopic description

Different mineral grains with black "dots" were noticed in all examined marbles (Figure 2). SEM investigation identified the mineral grains as dolomite $((Ca,Mg)(CO_3)_2)$, Figure 3). The presence of 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.



Figure 2: dolomite crystal with inclusions – Bianco P (microscopic analysis with plane polarized light)



Figure 3: SEM image of a dolomite crystal (= D) in a calcitic ground mass (= C)

The marbles of *Bianco Carrara* (sub-type C & D) have granoblastic calcite crystals with an average size of 350 μ m. 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 macroscopic 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 μ m. The veins also contain a lot of inclusions (Figure 4). Polygonal pyrite crystals are

principally found along the edges of the calcite crystals and have a size varying between 2 μ m and 50 μ m. Hematite can be found randomly distributed (Figure 5 and 6). The 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 not more porous than the rest of the marble.



Figure 4: detail of a vein in Carrara Bianco C (microscopic analysis with plane polarized light)



Figure 5: pyrite (= P) and hematite (= H) in Carrara Bianco D (microscopic analysis with reflected light – crossed polars).

Figure 6: pyrite (= P) and hematite (= H) in Carrara Bianco D (microscopic analysis with reflected light – plane polars).

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 μ m. The veins contain smaller and more irregular crystals than the ground mass and contain inclusions (Figures 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 (Figures 7, 8 and 9). Hematite can be found randomly distributed (Figures 10 and 12).

Microcracks are present along the crystal edges in the ground mass as well as in the veins. Also small intragranular pores are observed in the veins, which makes them more porous than the rest of the marble.



Figure 7: Detail of the veins in Arabescato Corchia, containing smaller crystals and pyrite (microscopic analysis with plane polarized light)

Figure 8: Detail of the veins in Arabescato Corchia, containing smaller crystals and pyrite (microscopic analysis with plane polarized light)



Figure 9: pyrite minerals oriented parallel to the orientation of the vein in Arabescato Corchia (microscopic analysis with reflected light).



in Arabescato Corchia (microscopic analysis with reflected light - crossed polars).

Figure 10: pyrite (= P) and hematite (= H) Figure 11: pyrite (= P) and hematite (= H) in Arabescato Corchia (microscopic analysis with reflected light - plane polars).

The calcitic ground mass of the Calacata Oro marble consists of granoblastic crystals with an average size of 350 µm. Only few crystals with inclusions were observed. The green-yellowish veins can be microscopically identified as a mixture of smaller calcite crystals (average size of 50 μ m), pyrite (20 - 100 μ m) 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 μ m) and minor quartz and feldspar grains (125 μ m). No crystals with inclusions were identified. 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 homogenous 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 micro cracks. Pyrite appears as solitary polygonal crystals, homogenously dispersed in the calcitic ground mass (Figure 12).



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

The Thassos White marble has a different petrography than the Carrara marbles. The ground mass consists of xenoblastic, anhedral dolomite crystals with a size, varying between 120 µm to 1,75 mm (Figure 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. No iron sulphides were observed in

the examined sample. An intergranular (crystal edges) and an intragranular porosity can be noticed. In the dolomite crystals are micro cracks along crystallographic planes present.



Figure 13: Dolomite crystals of Thassos White (microscopic analysis with plane polarized light).

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 applied and developed. The two testing methods result in an accelerated oxidation and staining of different types of stone, which contain a different amount and type of sulphide.

Thermal shock test (prEN 14 066)

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

After the 20 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, application 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, a granite with a polished finish shows less oxidation stains than the one with a flamed finish. The differences in staining after thermal shock seem minor between a polished and honed tile.

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 Figure 1), another staining test has been developed.

As indicated by the petrographic analysis, the presence of pyrite (FeS_2) is identified in these marbles. It is known and proved that the rate of the oxidation of

pyrite is higher in an alkaline environment than in a neutral or acid one (Brown & Jurinak, 1989). The new test consists of 20 cycles of 6 hours in an alkaline solution (1 M), obtained by dissolving NaHCO₃ in water, followed by 18 hours in an oven at 55 ± 5 °C.

This test produced stains, similar to these observed in naturally discoloured Carrara Bianco C marbles. It should be noticed that no other tested natural stone type investigated showed stains. Consequently, this test seems to be relevant for marbles containing fine dispersed pyrite minerals. (Bams & de Barquin, 2004). With this staining test for white marbles optimised, the different marble types mentioned in Table 2 were subjected to staining.

Results

The Carrara Bianco marbles (sub-type C, C/D, D) all show a diffuse discolouration of the ground mass and the veins (Figure 14). However in a few tiles there are regions that have the same colour as before the test and no discolouration can be observed (Figure 18).



Figure 14: an Bianco Carrara C tile before the alkaline water test (left) and a tile after the test (right) (not the same tiles).

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



Figure 15: an Arabescato Corchia tile before the alkaline water test (left) and a tile after the test (right) (not the same tiles).

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 shows 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 one diffuse stain (Figure 16). In the Bianco P, pyrite is found dispersed in the ground mass of the marble. No discolouration has been observed for the Thassos White marble.



Figure 16: a Bianco P tile before the alkaline water test (left) and a tile after the test (right) (not the same tiles).

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 observation has indicated that these veins are characterised by the presence of pyrite and/or hematite crystals.

Polished sections of a discoloured marble have been investigated. In zones with no staining (see also Figure 22), no pyrite can be found by microscopic investigation. Table 3 below 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.

Table 3: Summary of quality of discolouration related to the occurrence of pyrite in samples investigated.

marble	pyrite	discolouration
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Carrara Bianco C, C/D,	- 2 – 50 μm	- ground mass
D	- dispersed in ground mass	- veins (especially the
		less marked ones)
Arabescato Corchia	- 3 – 300 µm	- brown veins
	- concentrated in veins	
Calacata Oro	- 20 – 100 μm	- little discolouration
	- ground mass and veins	- veins a bit more
	(concentration a bit higher)	accentuated
Statuario Macchia Oro	- 50 µm – 2,5 mm	- little discolouration
	- ground mass	- veins a bit more
		accentuated
Bianco P	- 7 – 20 μm	- uniform yellow-orange
	- dispersed in ground mass	colour
Thassos White	- none observed	- no discolouration

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 substituting 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 x 30 cm).

In this research, a practical method is described 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 (Dislaire & Pirard, 2004, Bruno & Pitavy, 2004).

This digital image analysis technique has been used in this research in order

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

to:

All the image acquisitions have been made by the MICA laboratory (Mineral Georessources and Geological Imaging, University of Liège, Belgium) that is specialised 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, where the lighting and the sensor are focusing. 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) are employed. Non-uniform lighting and device dependence are removed 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 (Lebrun et al., 2004).

Results

A set of 10 tiles (40 cm x 40 cm) of Carrara Bianco sub-type C has been submitted to the alkaline water test. Images of the same tiles before (Figure 17) and after the test have been acquired and calibrated according to the method described above.

The results of the test show a general yellow-brownish diffuse discolouration (example in Figure 18), visually homogeneously spread on the surface. Chromatically, this discolouration is characterised by a shift between the pics of the red and blue channels (Figures 19 and 20), the distribution of the green channel remaining unchanged.



Figure 17: a Carrara Bianco C tile before the alkaline water test

Figure 18: a Carrara Bianco C tile after the alkaline water test



Figure 19: RGB distribution of one Carrara Bianco C tile before the alkaline water test

Figure 20: RGB distribution of the same Carrara Bianco C tile after the alkaline water test

In order to map the quantitative colour variation of each pixel before and after the test, the calibrated RGB values have been transformed into a L^*a^*b system, which allows the calculation of the difference between two measured colours according to the following relationship:

$$\Delta E_{lab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$
(1)

With L the value of brightness, a and b the values of respectively the redgreen saturation and the yellow-blue saturation. (ΔL^*) , (Δa^*) and (Δb^*) in Equation 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 (Figure 21), in which the intensity of each pixel is proportional to the calculated ΔE_{lab} (black colour corresponds to zero and white colour to the maximum).



Figure 21: Distribution of the ΔE_{lab} values related to Figures 17 and 18.

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



Figure 22: The non-oxidized regions of the tile, shown in Figure 18, are marked in blue.

Conclusion

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 dominant influence on the discolouration.

An accelerated stain 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 it made possible to distinguish a discoloured 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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