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Construction and Building Materials 20 (2006) 355–365

Construction and Building MATERIALS

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Effects of thermal changes on Macael marble: Experimental study

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Received 13 May 2004; received in revised form 22 December 2004; accepted 31 January 2005
Available online 2 November 2005

Abstract

The continuous action of frequent thermal changes in conditions of extremes temperature is the main cause of the alteration of marble in monumental and artistic buildings. This is the case of the deterioration observed in the Court of the Lions in the Alhambra (Granada, Spain), the white marble of which columns are from Macael (Almería, Spain). In order to understand the effects of thermal stress on this type of material, samples of marble from the Macael quarry have been subjected to cycles of heating and cooling and determined their influence on the physical–mechanical characteristics of the material (ultrasonic transmission velocity, hydric behaviour, mechanical resistance and granular cohesion).

Keywords: Marble; Macael; Restoration–conservation; Thermal deterioration

1. Introduction

Marble is a material that is constantly found in building, either for structural (columns, floors, etc.) or decorative purposes (frieses, reliefs, statues, etc.). It is a noble material of particular beauty and easy manipulation, but it is susceptible to alteration by natural atmospheric agents or others resulting from urban and industrial activity. Given its abundant presence in buildings of historic and artistic value, this had led to special interest in understanding the alteration processes of marble and how to restore and preserve it. One of the most commonly described phenomena of deterioration is that resulting from its exposure to continuous, extreme changes of temperature, to which the anisotropic nature of calcite crystals also contributes. It is known [25] that under unirome heating such crystals dilate to different degrees according to the direction (maximum dilation along the crystallographic axis and even contractions along the directions perpendicular to this axis). It is therefore natural to suppose that continuous dilations and contractions of the calcite grains in different directions eventually weaken the interangular and intrangular cohesion forces, resulting in different, mainly superficial alteration phenomena in the form of microfractures, microfissures, pitting and loss of material through scaling or flaking or detachment.

The many studies of the anisotropic behaviour of calcite in marbles through tension caused by temperature variation (e.g. [3,4,7–9,21,25–27]) make direct reference to the formation of microfractures or microcracks as a result of expansion or residual deformation caused by even moderate, but continuous temperature variations in marble.

In Spain, Macael marble has been used since ancient times in works of art and monuments. Specifically, it is the material used in the famous Courtyard of the Lions in the Alhambra (Granada), that jewel of Nasrid Islamic art. The columns in this courtyard are affected by differing degrees of alteration, particularly in the form of superficial scaling and microcracks. The studies by Galán et al. [10,11] and Sáez [20] examine the intimate

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0950-0618/$ - see front matter
doi:10.1016/j.conbuildmat.2005.01.061

relation between the type and degree of deterioration presented by each column and the thermal gradient to which it is continuously exposed, as determined by the length of its exposure (approx. 500 years) to the sun. In order to confirm experimentally the previous hypotheses, and also to gain better understanding of the processes and mechanisms occurring in Macael marble in conditions of continuous, important temperature change, sample specimens of the material has been subjected to a different number of cycles of heating–cooling and determined the effects of these cycles on the physical and structural characteristics of the marble (ultrasonic transmission velocity, hydric behaviour, mechanical resistance) and examined the effects of the cycles on the granular cohesion of the material using an electron microscope.

2. Materials and methods

The marbles at Macael belong to the Nevado–Filabride Complex in the so-called Betic Internal Zone [12], where different units are developed that have undergone, in general, low thermal gradient, high pressure metamorphic processes, followed by other processes with higher thermal gradients. Both the metamorphism and the posterior deformations undergone by these units are Alpine in age. The geological units in which the marble quarries are located are the Nevado–Lubrin and Bedar–Macael, which in turn contain two different types of formations – the Huertecica Formation and the Las Casas Formation, the latter being where the quarries of Macael marble are located.

The characteristic materials of this formation are Late Triassic carbonated rocks, although these sometimes alternate with micaschists, calcareous micaschists, quartzite micaschists with garnet and quartzite micaschists with amphibole.

Generally speaking, two lithological sequences can be distinguished in this formation, one consisting mainly of carbonate rocks and the other of quartzite schists. From a stratigraphic point of view, the carbonate rocks are predominantly found in the uppermost and lowermost parts of the formations, with frequent pellitic layers in the central part.

The carbonate rocks, including the marble outcrops described above, are coloured white, blue, yellow and dark brown. Rocks can be found ranging from very white marble with high crystallisation to yellowish terrigenous limestone similar to calcarenite and between these two extremes a range of carbonate rocks (marbles with millimetric mica intercalations, ferruginous limestones, well crystallised, intense yellow limestones, etc.).

The material for testing was taken from the La Umbria quarry approximately 1500 m from Macael at the place known as Umbría de las Canteras (Fig. 1). It is white marble with some greyish banding. At first $50 \times 50 \times 15$ cm blocks were cut, from which specimens measuring $5 \times 5 \times 15$ cm were later cut. These dimensions were chosen in order to fit the highest possible number of normalisations into the tests. The sample blocks were cut so that the direction of the greyish banding followed the largest dimension and lay parallel to one of the lateral faces. We decided to denominate the direction of the longitudinal axis H. The direction perpendicular to H and parallel to the greyish bands as F and the direction perpendicular to the bands as L.

Fig. 1. View of “La Umbría” quarry from which the material tested in this paper was extracted.

Fig. 2. Detail of the groups of sample blocks established: (a) (absence of banding), (b) (intermediate banding) and (c) (abundant banding).

The sample blocks were then classified into three groups according to the abundance of the banding. In group A the greyish banding is not present or can scarcely be detected, group B has medium abundance of banding and group C has the most banding (Fig. 2). The total number of blocks tested was 75 (25 per group).

3. Thermal cycles (heating/cooling)

The 75 specimens ($15 \times 5 \times 5$ cm) of the three types of material (A, B and C) were subjected to cycles of heating (100 °C) and cooling (−20 °C). The samples spent 6 h in the oven, then 2 h at room temperature and were then placed in a freezer for 6 h and, after 10 h at room temperature, were again placed in the oven.

We have considerated series of 50, 100, 150 and 200 cycles, with 5 specimens of each of the three types for each series, for not to extend unnecessary the test, but with the possibility if it was necessary to do more number of cycles in accordance with the results obtained.

Before starting the cycles and after each series of 50 cycles, the specimens were weighed and their physical state examined. Any alterations in physical state were duly recorded.

4. Mineralogical and chemical analyses

The mineral phases of the marble were determined using polarised light microscopy and X-ray diffraction (XRD). Thin sections were prepared for the microscopic study and the XRD analysis was carried out using the disoriented crystalline powder method. In both cases, two types of samples were analysed: a white specimens one with no grey banding and a grey one with abundant banding.

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Atomic Absorption Spectrometry were used for the chemical analyses.

On completion of the heating/cooling cycles established for each series, their effects were examined using the procedures detailed below.

5. Ultrasonics

One of the most commonly used non-destructive tests (NDT) in studies of artistic buildings and monuments is the propagation of elastic waves (ultrasonics) and, specifically, the determination of their transmission velocity in the material. As mentioned above, this methodology, developed in detail by [22] can be used to provide a physical characterisation of different materials, including stone.

In a solid the transmission velocity of elastic waves is dependent on several factors such as: material density, quantity of hollows or pores and amount of humidity found in the material's porous structure. Propagation velocity therefore depends on the nature of the medium through which they are transmitted, i.e., its compositional and textural characteristics. The variations in propagation velocity through the material under study can be interpreted to provide data on the quality and durability of the stones in historic buildings and in quarries, such as their mechanical resistance, porosity and fissuring, as well as evaluating the degree of alteration of the material and the effectiveness of

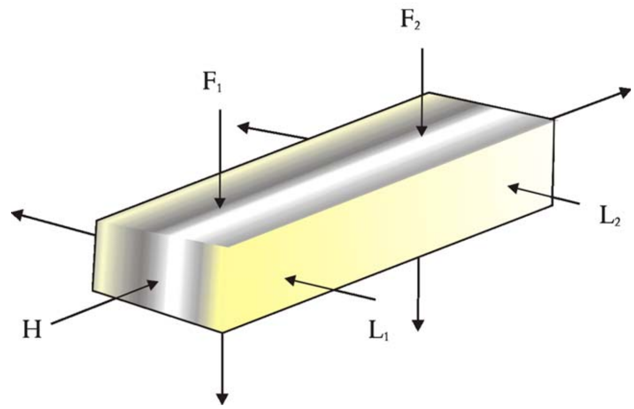

Fig. 3. Diagram of ultrasonic propagation velocity directions measured in each block.

restoration techniques. [20] provides a substantial recopilation of the literature on this technique applied to historic buildings.

Of the three possible measurement methods (direct, diagonal and surface transmission), the method used was the direct transmission of ultrasonic impulses. We followed the recommendations of Spanish standard UNE 83-308-86 [24] and NORMAL 22/86 [15]. The procedure specifically consisted in directly measuring the ultrasonic transmission velocities along the three orthonormal directions of the $5 \times 5 \times 15$ cm blocks (Fig. 3). We used Steinkamp BP V ultrasonic equipment. Given the dimensions of the blocks ($15 \times 5 \times 5$ cm) we used cylindrical, 100 kHz frequency transductors. Measurements in the group A blocks were taken along the H (longest) direction, but were randomly measured also in the F and L directions when the banding was completely unappreciable.

6. Hydric tests

The hydric properties of materials used in buildings, particularly of an historic nature, can be considered characteristics of primary importance. The possible use, durability, resistance, etc., of a material does in fact depend on its hydric behaviour.

Water is present in many of the alteration processes of stone, which is why it is necessary to understand and establish quantitatively the material's behaviour in its presence. In addition, the hydric behaviour of a material varies according to its state and the type of alteration, so that verification of this behaviour will represent a determination of the degree of alteration. For this reason the quarry material was tested without subjecting it to heating/cooling cycles, while the sample blocks were tested after their respective cycles of thermal stress.

7. Desorption tests

Absorption (free absorption of water by total immersion) (1)

Desorption (free desorption of water: evaporation) (2).

The usefulness of these tests is shown by the numerous studies which have used this technique in the characterisation and evaluation of the alteration of stone material, such as [19,17,1,18,2,5,6].

7.1. Absorption (1)

The absorption tests were carried out using plastic containers with a perforated aluminum tray placed at the bottom to prevent contact between the blocks and the plastic, thus ensuring optimal access of water to the entire surface of the blocks' faces.

We obtained the Dmass-t (min) absorption curves for the material (specimens with and without cycles) and the maximum imbibing value IA according to the specifications of NORMAL 7/81 [14].

7.2. Desorption (2)

Once the absorption test is finished and with the blocks completely saturated, they were weighed at regular intervals (following a logarithmic progression) in order to establish the progress of water loss from the material. To this aim the blocks were placed on a plastic grid and were left to dry in the laboratory at room temperature and pressure until a constant weight was obtained, as in the previous experiment.

Using the values obtained we calculated the water content present in the rock following the considerations described in NORMAL 29/88 [16], using a mathematical process very similar to the previous experiment and obtaining the desorption curves and the drying index ID.

8. Mechanical resistance. Elastic module

This test was conducted according to standard UNE 22-187-85 (Marbles and ornamental limestones. Elastic module) [23], 45 specimens were tested, distributed in series of 15 blocks (3 per cycle) for each of the three groups studied (A, B and C) and subjected to the different cycles of thermal stress.

Two extensiometric bands (TML PFL 10-11) were used to measure deformation, placed parallel to the axis on opposite sides of the block, providing the mean value of both deformations. The bands were stuck with adhesive (Cioanocrilato TML CN, for non-porous surfaces) to the surface polished with 1000 grain (mesh) sandpaper and taking care not to touch the surface with bare fingers.

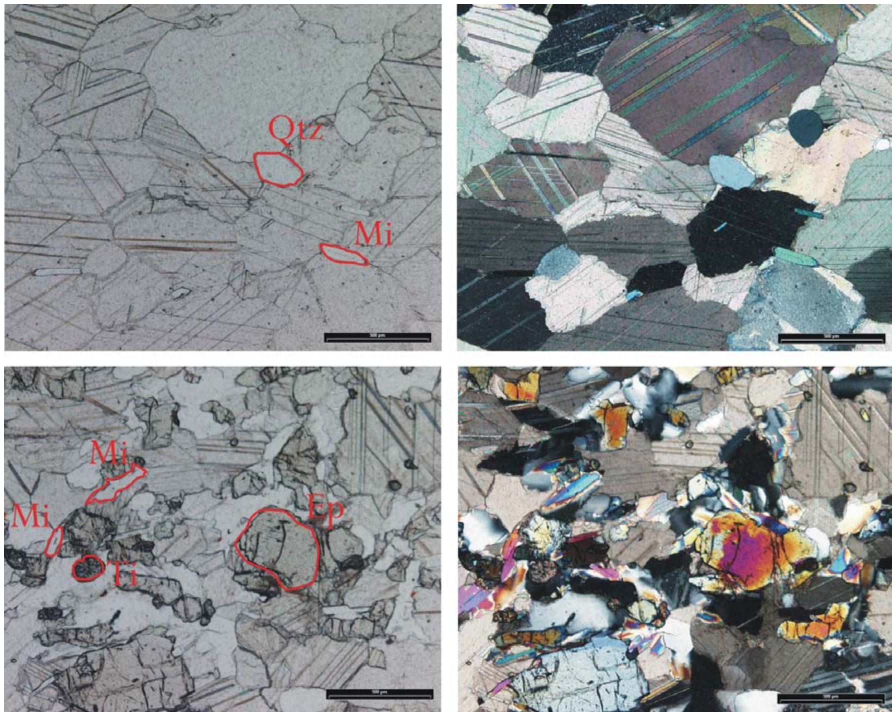

Fig. 4. (Upper part) Detailed view of accessory minerals (quartz and mica). Note the coinciding lengthening of the colourless mica and calcite crystals. (Left) one polariser, (right) crossed polarisers. (Lower part) General view of the concentration of accessory minerals (mainly epidote and titanite) in dark levels of the grey sample. (Left) one polariser, (right) crossed polarisers.

The press used for this test was an Ibertest MEH 2000 CO. This equipment has charge characteristics that can be varied from 2 to 2000 kN and offers a continuous record of stress (MPa) and deformation (mm/m) until the sample block breaks. The charge velocity applied was ≈0.7 MPa/s.

8.1. Scanning electron microscope

The scanning electron microscope allowed us to study the stone without any prior treatment, specifically its morphology and the size of the calcite crystals, as well as other questions concerning porosity, fissuring, banding, etc. Equally, and as in the case of the other techniques used, our intention was to carry out an evolutionary study of the material after subjection to the different cycles of thermal stress, in order to obtain exhaustive information on the behaviour and evolution occurring in aspects relating to loss of intergranular cohesion, changes or differences between outer and inner

Table 2
Minority elements (ppm) in samples of White and Grey quarry material

Sample	Li	Rb	Cs	Sr	Ba	Sc	V	Cr
White	1.4	0.9	0.1	145	<10	1.8	1.2	4.4
Grey	7.3	23.8	1	111	35	4.9	22.9	19.6
	Co	Ni	Cu	Zn	Y	Nb	Ta	Zr
White	<1	14.7	5.3	17.3	2.7	0.2	0.1	<10
Grey	1.6	24.6	5.3	32.3	5.1	3.4	0.3	27
	Hf	Mo	Pb	U	Th	La	Ce	Pr
White	0.1	0.3	1.4	0.2	0.1	2	0.8	0.3
Grey	0.2	0.3	1.4	0.7	1.6	5.8	11.5	1.4
	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er
White	1.4	0.4	0.1	0.4	0.1	0.4	0.1	0.2
Grey	5.2	1	0.2	0.9	0.1	0.8	0.2	0.5
	Tl	Tm	Yb	Lu	Sn	Ga		
White	<0.1	<0.1	0.3	<0.1	9.9	0.2		
Grey	0.1	0.1	0.4	0.1	9.9	4		

The contents of S, Be, B, Mn, Ag, Au, Cd, W, Ge, As, Sb and Br were below the detection limit of the respective analytical techniques.

Table 1
Majority elements (% oxides) in samples of White and Grey quarry material

Sample	CaO	SiO_2	Al_2O_3	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	P_2O_5
White	56.1	0.27	0.08	0.75	0.02	0.02	0.06	<0.01	<0.01
Grey	49.1	6.12	3.05	0.89	0.04	0.72	0.89	0.15	0.03

areas of the blocks, porosity, fissures, cracks and other textural modifications that might have occurred during application of the cycles. A total of 10 polished thin (stratigraphic) sections were used after the different cycles of heating–cooling. We also examined fragments ("mushrooms") of material from group A after 0 and 200 cycles. The equipment used for visualisation and photography was a Zeiss DSM 950 equipped with a Likn QK 2000 microanalyser.

Table 3
Mean values, standard deviation of weight loss for blocks groups A, B and C after different numbers of cycles (50, 100, 150 and 200)

No. cycles	Group	Weight loss (%)	Standard deviation
50	A	0.03	0.11
	B	0.03	0.14
	C	0.04	0.09
100	A	0.03	0.13
	B	0.03	0.14
	C	0.04	0.11
150	A	0.06	0.09
	B	0.05	0.15
	C	0.06	0.15
200	A	0.06	0.09
	B	0.06	0.16
	C	0.06	0.18

9. Results and discussion

The examination by polarised light microscope shows that the material in the type A blocks consists almost exclusively of calcite, minority amounts of quartz and muscovite and some isolated crystals of feldspar. The microstructure is granoblastic, ranging from equigranular,with large-size grains, to medium to fine grain heterogranular.

In addition to the minerals mentioned above, the sections with a high proportion of grey banding also contained epidote, titanite and opaque metallic veins (mainly pyrite), concentrated on parallel levels of millimetric thickness. Fig. 4 illustrates these features.

No variations in mineralogical composition or differences in grain distribution, possible fractures, intergranular separations, etc., were observed in the thin sections of quarry material subjected to the different cycles of thermal stress (only the SEM showed differents textures).

The results of the study of the White and Grey samples by X-ray diffusion (powder method) coincide with those

Table 4
Mean values, standard deviation and variations as material not subjected to cycles (total and percentage) of ultrasonic transmission velocity (m/s) for sample groups A, B and C and the different series of cycles to which they were subjected

Group	No. cycles	PV_H	Std.	Δ	%	PV_F (m/s)	Std.	Δ	%	PV_L (m/s)	Std.	Δ	%
A	0	6203	141			5531	191			5172	245		
	50	3506	149	2689	43.3	2758	331	2773	50.13	2409	344	2763	53.4
	100	3514	152	2660	42.9	2839	362	2692	48.6	2322	334	2850	55.1
	150	3646	162	2557	41.2	2846	390	2685	48.5	2324	304	2848	55.1
	200	3671	124	2532	40.8	3108	421	2423	43.8	2535	259	2637	51
B	0	6023	153			5133	212			5100	181		
	50	3472	334	2551	42.3	2754	298	2379	46.3	2262	302	2838	55.7
	100	3787	403	2236	37.1	2864	363	2269	44.2	2484	354	2616	51.3
	150	3568	171	2455	40.8	2721	320	2412	47	2457	205	2643	51.8
	200	3663	124	2360	39.2	2794	383	2339	45.6	2555	146	2545	49.9
C	0	5971	216			5179	224			4927	231		
	50	3733	296	2238	37.5	2912	227	2267	43.8	2508	294	2419	49.1
	100	4043	239	1928	32.3	3001	262	2178	42.1	2676	296	2251	45.7
	150	3502	120	2469	41.4	2877	214	2302	44.4	2512	186	2415	49
	200	3581	203	2390	40	2838	248	2341	45.2	2458	196	2469	50.1

PV, standard notation for longitudinal waves in ultrasonics methods.
Std. Standar deviation.
Δ, increase.

Table 5
Mean values of breaking point and elastic module for each group of blocks after different cycles of thermal stress

No. cycles	A		B		C	
	Failure load (kN)	Elastic module (MPa)	Failure load (kN)	Elastic module (MPa)	Failure load (kN)	Elastic module (MPa)
0	215	70	186	64	153	58
50	167	55	169	53	150	44
100	155	50	159	45	161	48
150	180	51	154	41	142	48
200	148	44	180	47	158	46

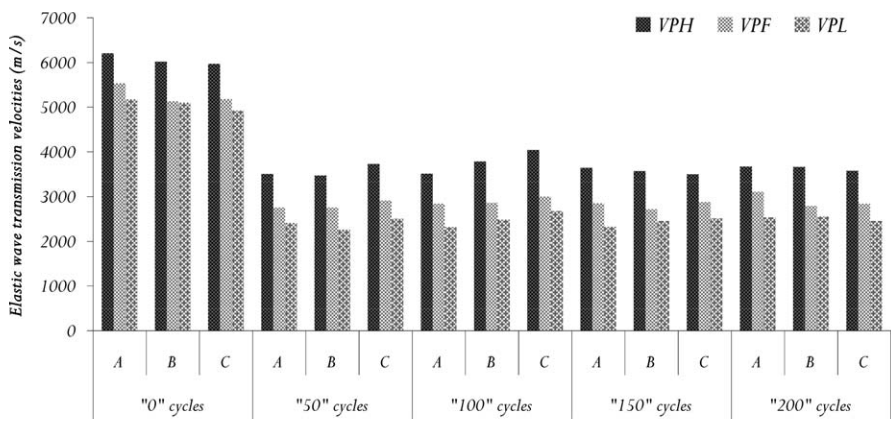

Fig. 5. Variability of elastic wave transmission velocities in the material for each of the groups (A, B and C) according to the three directions analysed (PV_H, PV_H and PV_H) for each series of cycles (0, 50, 100, 150 and 200).

of the optical study. The White sample was found to contain calcite and some quartz, while the diffractogram of the Grey sample also showed the presence of mica (the technique does not permit detection of very minority phases). Table 1 shows the results of the chemical analysis of majority elements in the six samples of material detached from the columns in the Alhambra and also in the samples of White and Grey material from the quarry.

Table 2 summarises the minority element contents of the two types of sample.

These results confirm that in all cases this is very pure, scarcely dolomitic marble. The differences between the samples can be explained by the presence of quartz, micas, epidote and veins in the Grey sample.

10. Heating/cooling cycles

Regarding the changes observed, the most outstanding was a slight loss of material as powder, together with rounding of edges and corners of the sample blocks. The mean values of weight loss (Table 3) show that loss rises as the number of cycles increases. This rise is similar in the three groups and occurs in a non-uniform manner. After 50 cycles approximately 50% of loss occurred, there is little loss between 50 and 100 cycles and between 150 and 200 cycles it rises once more.

11. Ultrasonics

Table 4 shows the mean values of PV_H, PV_F and PV_L with their respective standard deviations for each of groups A, B and C and for the groups of cycles established (0, 50, 100, 150 and 200). The Table also shows the difference as regards the velocity at 0 cycles and this difference in %. Fig. 5 illustrates these results.

The data and their graphic representation show an important and similar decrease in ultrasonic transmission velocity (approximately 40%) after the first 50 cycles of heating/cooling in the three types of samples and in any of the three directions measured. The importance of the following series of cycles is in general not so significant, particularly when taking into account the dispersion of the transmission values, with standard deviations, that are higher than the differences found

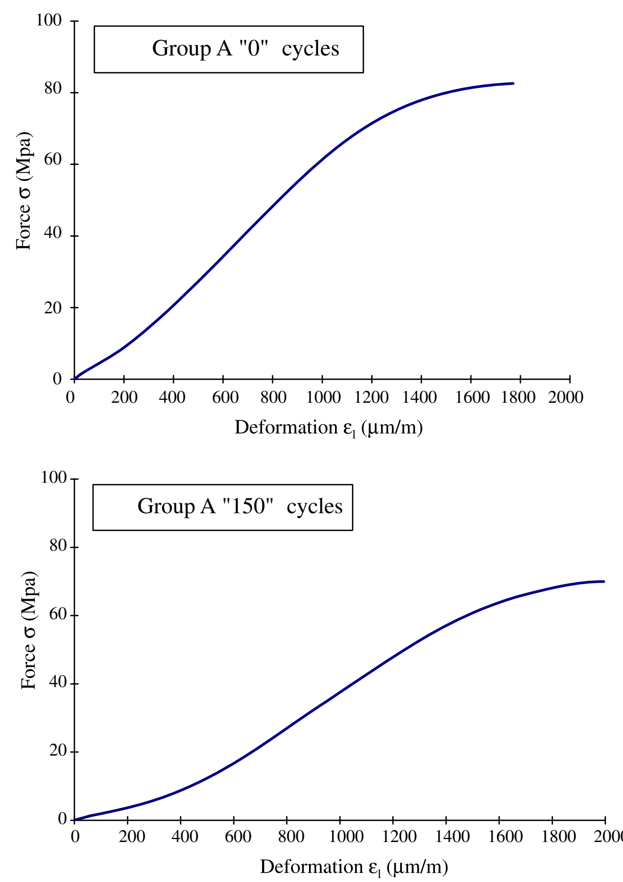

Fig. 6. Force–deformation curves for Group A blocks not subjected to cycles and after 150 cycles.

between transmission speeds after 100, 150 or 200 cycles and the first 50 cycles, respectively.

Despite this dispersion of values, and with the corresponding reservations, a number of trends can be observed. The different velocities of the three types of sample blocks seem to fall into a $V_A > V_B > V_C$ order, between directions the order also seems to be $V_H > V_F > V_L$ and, finally, the data seems to suggest that after 200 cycles the velocity in the L direction (perpendicular to the grey bands) decreases the most in percentage terms, while the H direction is that which is least affected in percentage terms. These trends could indicate some effect of the greyish mineralisation on ultrasonic propagation velocities in the marble.

12. Mechanical resistance. Elastic modulus

A total of 45 blocks from the three groups (A, B and C) subjected to the different thermal cycles were tested using compression to determine the elastic modulus. Table 5 summarises the mean values of breaking point and elastic modulus for each of three blocks from the same group subjected to the same number of thermal cycles.

In each of the three groups, we can observe a considerable decrease in elastic modulus after 50 cycles. This value continues to decrease gradually for the group A blocks as the number of cycles grows and, generally speaking, the blocks from group B behave in a similar fashion. The "increase" after 200 cycles could be attributed to the degree of variability implicit in the method. The values of the elastic modulus seem to stabilise after 50 cycles for the C type material.

It can also be seen that the elasticity values in the "fresh" material (0 cycles) decrease as the amount of greyish banding increases (A > B > C), although the effect of the thermal stress cycles eventually homogenises this behaviour and even inverts it.

The strain deformation lines for the material not subjected to thermal cycles are steeper and more linear than

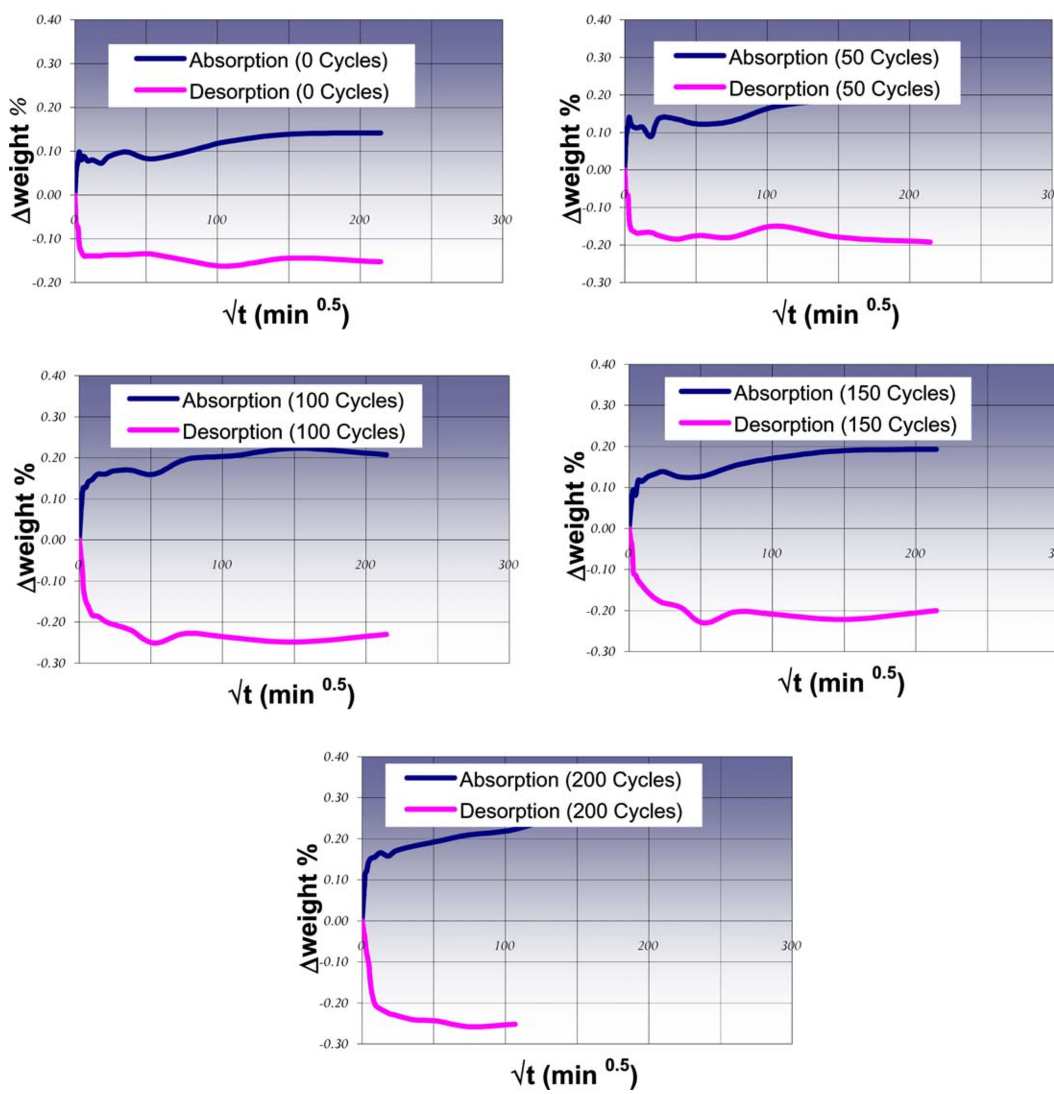

Fig. 7. Absorption and desorption curves for material from groups A and C after the series of cycles established.

Table 6
Mean values of absorption indices (AI) and desorption indices (DI) for groups A, B and C of blocks in the different series of cycles (0, 50, 100, 150 and 200)

No. cycles	AI			DI		
	A	B	C	A	B	C
0	0.12	0.12	0.15	0.29	0.24	0.36
50	0.17	0.2	0.21	0.38	0.38	0.32
100	0.21	0.26	0.24	0.35	0.38	0.36
150	0.19	0.23	0.21	0.38	0.37	0.39
200	0.28	0.27	0.31	0.4	0.38	0.38

after being subjected to thermal stress. After 50 or more cycles, the material shows a considerable change in slope in the plastic area (Fig. 6).

Finally, the failure values incompression for the material not subjected to cycles are approximately 86 MPa, which coincides completely with other values obtained for Macael marble (81–87 MPa, according to [13]).

13. Absorption–desorption

A total of 60 blocks were tested, 20 from each of the three groups of material (A, B and C) subjected to different heating–cooling cycles (4 per cycle).

Fig. 7 illustrates the absorption and desorption curves for Group A and C blocks subjected to the different cycles of heating–cooling. The values for the different types of material (A, B and C) subjected to the thermal cycles confirm the observations made above.

It can be seen that the cycles of thermal stress have a considerable effect on the hydric behaviour of the material. Absorption- and, naturally, desorption-increases with the number of cycles in all cases and groups. Indeed, after 200 cycles the material has an even greater absorption capacity than that shown by the experiment, as this had to be concluded early.

The data also indicate a certain effect of the amount of greyish mineralisaiton on the hydric behaviour of the marble. Absorption and desorption are invariably lower in group A than in groups B or C. In any case the effect seems to be less significant than the number of cycles.

Other than in the first stages, the desorption rate is higher than that of absorption. Moreover, no water appears to be retained when the number of cycles is less than 200.

Finally, Table 5 summarises the values of the absorption (AI) and desorption (DI) indices.

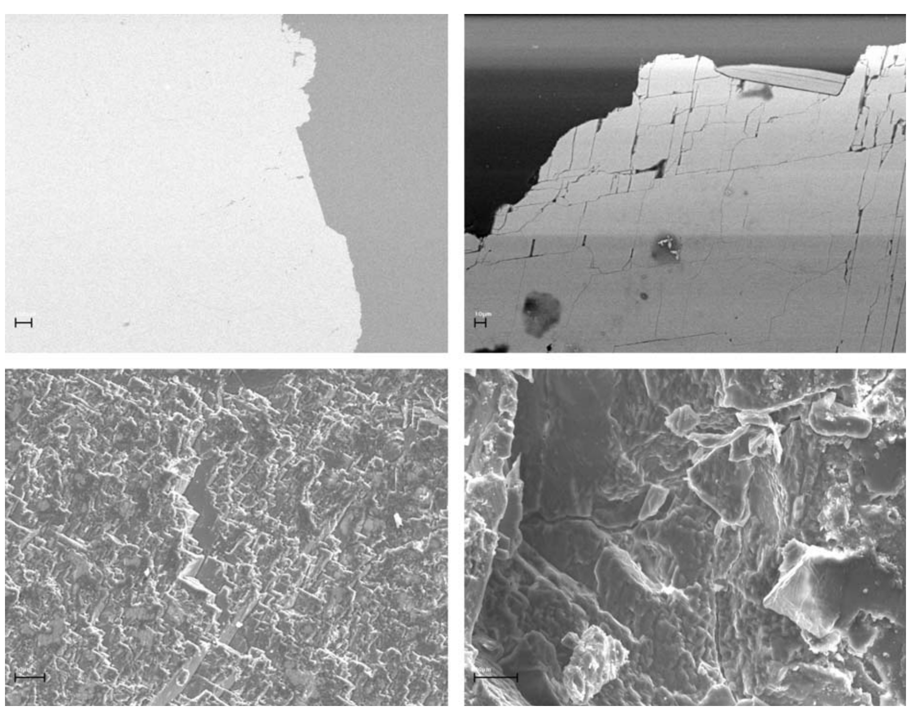

Fig. 8. (Upper left) SEM image of thin section from block (0 cycles) – considerable homogeneity can be observed. (Upper right) SEM image of thin section from block (200 cycles) – rhombohedral exfoliation of calcite crystals is especially noticeable in the external zone. (Lower left) – SEM image of fragment from block (0 cycles) – the homogeneous nature of the sample is noticeable. (Lower right) SEM image of fragment from block (200 cycles) – microfracturing and disaggregation are noticeable.

14. Scanning electron microscope

The scanning electron microscope (SEM) study has shown that for the samples studied the secondary electron images (SEI) obtained on thin sections and fragments of samples provide information complementary to that obtained by optical microscope, revealing more subtle textural differences in the samples that may result from the treatments to which they had been subjected (see Table 6).

The images of specimens not subjected to thermal cycles show fairly homogeneous surfaces in which hardly any geometric traces are visible, whereas the images of specimens subjected to 200 cycles show calcite grains with a clear, characteristic rhombohedral exfoliation as well as some grain edges and microfractures in the parts of the thin section corresponding to the outer faces of the sample. These features become more obvious as the number of cycles increases.

The secondary electron images obtained from fragments show a compact state of the calcite grains in the untreated material, which develops towards microfracturing and disaggregation when the material has been treated with thermal stress, which follows the grain edges. Fig. 8 illustrates some of these aspects.

It should be mentioned that the features described could in part be masked by a similar effect caused by the cutting of the samples to obtain the sample blocks and, particularly, the thin sections, especially when the cutting was not done with sufficient care.

15. Conclusions

As shown above, the effects of the heating–cooling cycles on the Macael marble and similar results were obtained on both their mechanical and hydric behaviour. After 200 cycles, the data on mechanical resistance, ultrasonic transmission velocity, absorption–desorption and hardening (by sclerometric method) indicate an appreciable decrease in mechanical resistance and compacity. This is confirmed by the 20–50% variations detected by the above techniques between untreated samples and samples subjected to 200 thermal cycles.

In general, the samples without greyish banding (Group A) have slightly better characteristics than those with abundant mineralisation. However, as the number of cycles increases, the characteristics of both types of material become similar in many cases.

It can be clearly seen that there is a sharp variation in values in the different tests after 50 thermal cycles. The later evolution of the material up to 200 cycles is less marked, as if there were a "structural accommodation" of the material tested.

The main mechanism of decay is scaling, as shown by the electron microscope images. Disaggregation by loss of intergranular cohesion is clearly appreciable in the images of samples after 200 cycles. This is the expression of the residual dilation resulting from the extreme anisotropy of the calcite's thermal expansion coefficient and its location demonstrates that degradation and loss of cohesion in the sample preferentially affect the most external zones.

Acknowledgements

This research received financial support from Research Group RNM 172 of the Junta de Andalucía. The chemical analysis data were obtained at the Centre for Scientific Instrumentation (CIC) of the University of Granada.

References

[1] Alonso FJ, Esbert RM, Ordaz J. Comportamiento hídrico de calizas y dolomías. Boletín Geológico y Minero 1987;TXCVIII-IV:555–76.
[2] Alonso FJ, Ordaz J, Pérez A, Esbert RM. Laboratory study of a treated dolostone subjected to thermal cycles. In: 7th international congress on deterioration and conservation of stone, Lisbon; 1992. p. 745–51.
[3] Battaglia S, Franzini M, Mango F. High sensivity apparatus for measuring linear thermal expansion: preliminary results on the response of marbles. Il Nuovo Cimento 1993;16: 453–61.
[4] Bertagnini A, Franzini M, Gratziu C, Spampinato M. Il marmo cotto in natura e nei monumenti. Rendiconti Società Italiana di Mineralogia e Petrologia 1984;39(1):39–46.
[5] Bello MA, Martín L, Martín A. Decay and treatment of macael white marble. Stud Conserv 1992;37:193–200.
[6] Durán Suárez J, García Casco A, Rodríguez Gordillo J. Evaluación de compuestos protectores para material pétreo poroso. Aplicación a calcarenitas. Boletín Sociedad Española de Mineralogía 1998;21:61–75.
[7] Franzini M, Gratziu C, Spampinato M. Degradazione del marmo per effectto di variazioni di temperatura. Rendiconti Società Italiana di Mineralogia e Petrologia 1984;39(1):47–58.
[8] Galán Huertos E. Influence of temperature changes on stone decay. In: Weathering and air pollution. Acts. First Course: C.M.U. Univ. School Monument Conservation, Lago di Garda; 1991. p. 119–29.
[9] Galán E, Guerrero MA, Vázquez MA, Zezza F. Progressive deterioration of marble columns by thermal changes in relation to their state of superficial decay. In: 7th international congress on deterioration and conservation of stone, vol. 1, Lisboa; 1992. p. 905–13.
[10] Galán Huertos E, Zezza F. Diagnóstico del estado de conservación del Patio de los Leones de la Alhambra de Granada. Informe para el Patronato de la Alhambra y Generalife, Granada; 1990.
[11] Galán E, Guerrero MA, Vázquez MA, Zezza F. Progressive deterioration of marble columns by thermal changes in relation to their state of superficial decay. In: 7th international congress on deterioration and conservation of stone, vol. 1, Lisboa; 1992. p. 905–13.
[12] IGME 1975. Mapa Geológico 1:50.000, MAGNA, Hoja no 1013 (Macael).

[13] López Mesones F. Mármoles de Macael. Diseño y colocación. Fundación Macael, editor; 2000. 103 p.
[14] NORMAL 7/81 CNR-ICR. Assorbimento D'Acqua per Inmersione Totale. Capacitá di Imbibicione, Roma; 1981. 5 p.
[15] NORMAL 22/86 CNR-ICR. Misura della Velocitá di propagazione del Suono, Roma; 1986. 7 p.
[16] NORMAL 29/88 CNR-ICR. Misura Dell'Indice di Asciugamento (Drying Index), Roma; 1988. 9 p.
[17] Peruzzi R, Bugini R. Eficacia di alcuni protettivi per il marmo di Candoglia. Rendiconti Societá 3 Italiana di Mineralogia e Petrología 1984;39(1):71–80.
[18] Punuru AR, Chowdhury AN, Kulshreshtha NP, Gauri KL. Control of porosity on durability of limestone at the great sphinx. Egypt Environ Geol Water Sci 1990;15(3):225–32.
[19] Ritter HL, Drake LC. Pore-size distribution in porous materials, pressure porosimeter and determination of complete macropore-size distribution. Ind Eng Chem (Analytical ed) 1945;17:782–6.
[20] Sáez Pérez MP. Estudio de elementos arquitectónicos y composición de materiales del Patio de los Leones. Interacciones en sus causas de deterioro. Ed. Servicio de Publicaciones de la Universidad de Granada; 2004. 429 p.
[21] Siegesmund S, Ullemeyer K, Weiss T, Tschegg EK. Physical weathering of marbles caused by anisotropic thermal expansion. Int J Earth Sci 2000;89:170–82.
[22] Thompson BR, Thompson DO. Ultrasonic in non-destructive evaluation. Proc IEEE 1985;73:1716–55.
[23] UNE 22-187-85. Mármoles y calizas ornamentales. Ensayo de módulo elástico; 1985. 2 p.
[24] UNE 83-308-86. Ensayos de hormigón. Determinación de la velocidad de propagación de los impulsos ultrasónicos; 1986. 12 p.
[25] Winkler EM. Properties of marble as building veneer. Int J Rock Mech Min Sci 1996;33(2):215–8.
[26] Zezza U, Previde Massara E, Massa V, Venchiarutti D. Effect of temperature on intergranular decohesion of the marbles. In: Vth international congress on deterioration and conservation of stone, vol. 1, Lausanne; 1985. p. 131–40.
[27] Zezza U, Massa V, Bortolaso G. Non destructive on site spectrometric color testing building stones. In: 3rd Int. conf. non-destructive testing, microanalytical and environmental evaluation for study and conservation of work of art, Viterbo; 1992. p. 539–53.