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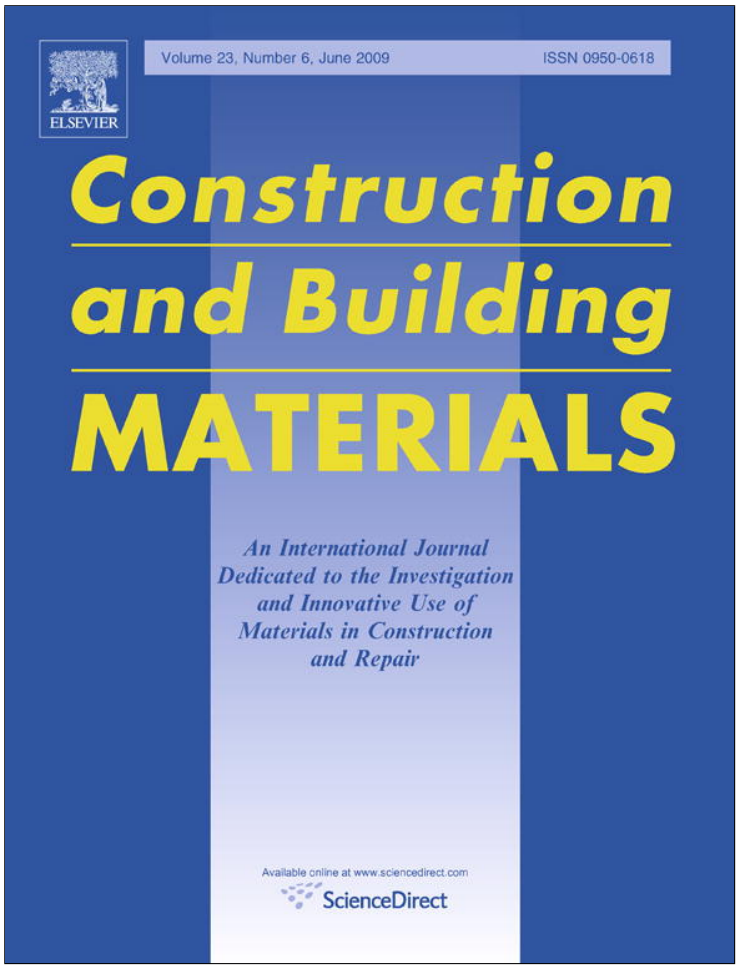

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Review

Structural and compositional anisotropy in Macael marble (Spain) by ultrasonic, x-rd XRD and optical microscopy methods

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ABSTRACT

By using the non-destructive technique of ultrasonic transmission, this paper undertakes a study of the compositional and structural discontinuities in marble from Macael (Almería, Spain), which is the material of the columns in the Court of the Lions in the Alhambra (Granada, Spain), in order to contribute to understanding of the processes of deterioration and conservation affecting them. Thermal stress is responsible for alterations in the columns, and is affected by scaling, loss of substance, stains, etc. The results allow us to establish that, apart from the discontinuities in the mineralogical composition of the marble, the preferential orientation of the calcite crystals has an important effect on its anisotropic reaction. This preferential orientation is confirmed by textural studies using X-ray diffraction and determinations using a petrographic microscope equipped with universal stage.

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1. Introduction

The presence of discontinuities and structural defects in the stone materials of artistic and monuments explains many of the phenomena and typologies of their alteration. The existence of such discontinuities and defects is in many cases perfectly clear to the naked eye, showing their position, directions and size. In other cases, however, such anomalies and flaws are not immediately apparent nor can their profusion and extent be estimated. In such cases we must turn to study techniques that provide information on these structural aspects and their quantification. Of the techniques available, the artistic and historical nature of these materials naturally forces us to use those that are non-destructive (NDT). One of the non-destructive physical methods with most acceptance and applications in the study of the structural characteristics and state of conservation of stone materials in historic and artistic buildings is by determination of the propagation velocity of ultrasonic waves. The velocities and variations in propagation of these ultrasonic pulses through stone are related to its quality and durability and represent a way to evaluate its mechanical resistance, porosity, fissuring, discontinuities, etc., as well as the results of restoration and conservation treatments. The presence of cracks, fissures and granular schistose structure, or veined areas of different or anomalous mineralogical composition affect the material's behaviour regarding the propagation of ultrasonic pulses through it, depending on whether the directions are parallel or perpendicular to the schistose development, cracks, fissures or areas of different composition.

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Recent examples of studies on ultrasonic methods in conservation of stone methods or characterization of stones are [1–10].

This technique is used here to study the marble from Macael with a double objective – to test the technique's validity as a method for detection and evaluation of the structural and compositional anomalies in the material and also to determine the directions and size of structural anomalies in the samples in which this phenomenon is not visually perceptible.

This marble was chosen as it is the same as that of the columns, lions and fountain of the famous Court of the Lions in the Alhambra (Granada, Spain). Authors such as [11,12] and more recently [13] have described the deterioration of the marble in these columns, which in some parts is increasingly intense, requiring further research into its causes and factors in order to proceed with restoration and conservation.

In order to evaluate the incidence of chemical as well as structural anomalies, we studied marble both with and without varying degrees of greyish veining. Additionally, in order to compare the data on the ultrasonic propagation velocity, as well as determining the chemical and mineralogical composition of the greyish veins, an optical-petrographic microscope (with universal stage) was used together with X-ray diffraction analysis of textures to study the possibility of preferential orientation of the calcite crystals.

2. Materials and methods

The study was carried out using white marble from Macael, located in the Nevado–Filabride Complex, specifically, the Las Casas Formation (IGME 1975) [14]. From a regional point of view, these carbonate rocks are predominantly found in the uppermost and lowermost parts of this formation. In general terms, this is a metamorphic rock with equidimensional granoblastic texture and a rather simple mineralogical composition. The white variety consists almost exclusively of coarse carbonate minerals, with some white mica, albite, quartz and occasionally pyrite, as well as other minerals such as biotite, epidote, tremolite, zoisite and bluish-green amphiboles. The quarry where the samples were taken is known as the "Cantera de la Puntilla" located at the "Bancada de la Reina", with similar mineralogical and chemical characteristics to the marble of the Court of the Lions [13].

The selected material was classified into three groups: group A is marble with scarce or zero presence of greyish veining or any other flaw. Group C contains the material with higher density of grey veining and group B contains intermediate material. The marble in the different groups was cut into blocks measuring $5 \times 5 \times 15$ cm. (NORMAL 22/86 document and Spanish UNE 83-308-806 norm) [15,16]. The blocks in groups B and C were cut so that the grey veining was parallel to the block's length. In all 75 blocks were measured, 25 for each of the three groups established.

Regarding the determination of transmission velocity of ultrasonic waves through the blocks, we chose direct transmission (*P* waves), measuring the transmission velocity in the block's three dimensions. Fig. 1 shows the different measuring points, defined as follows for groups B and C: VPz measurement – opposing faces along the length of the block and parallel to the plane of the veining. VPx1 and VPx2 measurements – taken at 1/3 and 2/3 of the block's length, parallel to the direction of the planes of veining visible in the samples. VPy1 and VPy2 measurements – taken at 1/3 and 2/3 of the block's length, perpendicular to the direction of the planes of veining visible in the samples. For the group A samples the VPz measurement was also taken along the length of the block, but VPx and VPy were random, as the greyish veining planes are generally not perceptible.

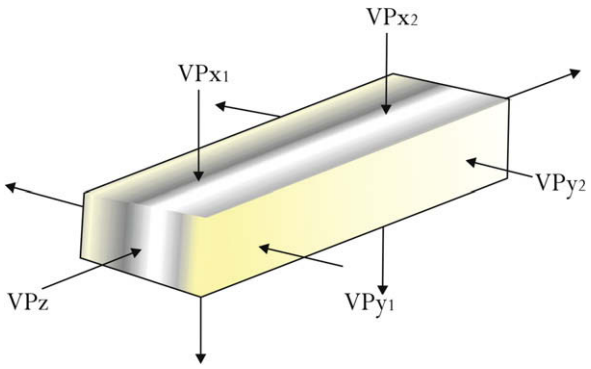

Fig. 1. Diagram of the directions of the ultrasonic propagation velocities measured in each block.

The ultrasonics equipment used was a STEINKAMP BP V with a low power impulse generator and high power emission and reception transducers and a capacity to generate impulses of 50 and 100 KHz. Given the size of the blocks we used 100 KHz frequency waves. Vaseline was used as interface between the transducers and the rock, given the smoothness of the block surfaces. After setting up the equipment with the PVC standard sample as indicated, five measurements were taken from each block following the directions indicated in Fig. 1. Regarding the thermal-hygrometric conditions, the measurements were taken in an atmosphere at approximately 20 °C with 40–50%. relative humidity (RH).

The mineral phases of the marble were determined using polarized light microscopy and X-ray diffraction (XRD). Thin sections were prepared for the microscopic study and a polarising optical microscope was used with transmitted and reflected light. The XRD analysis was carried out using the disoriented crystalline powder method. The procedure used consisting in milling the samples in an agate mortar to less than 0.053 mm (A.S.T.M. mesh 270). The powder obtained was mounted on an aluminium sample holder. Care was taken not to exert pressure that could give the crystals a preferential orientation. The equipment used for XRD was a difractometer Philips PW 1710 equipped with automatic slit.

Inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS) were used for chemical analysis of types of samples. The samples were previously dissolved by acid digestion under pressure in a teflon capsule containing HNO_3 and HF and finally dissolved in 4% HNO_3. The sulphur content was obtained by combustion in an oxygen current (LECO method) and the O_2C and volatile contents by precision scale weighing after calcination at 1100 °C (LOI).

The equipment used in ICP-MS was a PERKIN Elmer Sciex-Elan 500 spectrometer and for AAS was a PERKIN Elmer 5100 model with graphite camera. 75 samples were tested, distributed in 25 blocks for each of the groups (A, B and C).

Two methods were used to establish calcite crystal orientation: the optical-petrographic microscope with universal stage and XRD (the relative intensities of different reflections). There follows a brief description of the methods mentioned above.

a) Using the universal stage or Turner's dynamic analysis, we can determine textural and crystallographic orientations in the minerals present on the basis of twin determination size and their corresponding orientation density diagrams. A large number of petrofabric studies on limestone and marble have provided greater reliability in the determination of the orientation of the *c* axis of the calcite crystals in the rock using a petrographic microscope with universal stage. Several papers on marble material exemplify the usefulness of the method, such as [17–21].
b) Analysis of the relative intensities of reflections (102), (104), (113), (110) and (202) and their deviations from the theoretical values. The indexes *hkl* (104, e.g.) of every plane they correspond with the Miller's indexes, and indicate the inverse of the crystallographic distances or periods of translation to which intercut to the crystallographic axes *x*, *y* and *z*, respectively. The intensities of these reflections were measured on a 001 or basal section ($5 \times 5 \times 1$ cm) cut from the original block ($5 \times 5 \times 15$ cm). The equipment and instrumentals conditions have been the same than in mineralogical analysis. The sample preparation was carried out using the disoriented crystalline powder method.

In addition, the diffractometric data obtained by these textural studies allowed us to obtain the degree of crystallinity of the calcite grains in the blocks. Based on the consideration of the width of the beams diffracted by the crystalline matter, the method provides the *D* parameter or crystallinity index by Scherrer's formula [22], which takes into account the width of beam diffracted (β in radians), wavelength (λ) of the incident X-ray, the 2θ angle at which the diffracted beam appears and a constant (K), whose value in our case is 1.

$$D = \frac{\lambda \times K}{\beta \times \cos\theta} \tag{1}$$

Finally, we obtained the total structural anisotropy coefficient ΔM (%) and the Relative Anisotropy Coefficient Δm (%) of the marble material from the mathematical relations between the ultrasonic propagation velocities, following the equations of [23], modified for our case according to the three directions of the sample.

$$\Delta M\ (\%) - \left[1 - 2\left(\frac{\mathrm{VPy}}{\mathrm{VPz} + \mathrm{VPx}}\right)\right] \times 100 \tag{2}$$

$$\Delta m\ (\%) = \left[2\left(\frac{\mathrm{VPz} - \mathrm{VPx}}{\mathrm{VPz} + \mathrm{VPx}}\right)\right] \times 100 \tag{3}$$

3. Results and discussion

Regarding the ultrasonic study, Table 1 summarises the values of the propagation velocity of the ultrasonic pulses in the three

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types of blocks. Given the high number of samples and, therefore, of parameters measured, this table only contains the mean values for each group, with their corresponding standard deviations (the VPx and Vpy values correspond to the mean values of VPx1 and VPx2 and Vpy1 and Vpy2, respectively). For the Vpx and Vpy values in group A, the *x* and *y* directions are basically random. However, given that VPx is systematically higher than Vpy in all the blocks of this group, we have chosen to consider Vpy as the minimum velocity value for the samples type A (Table 1). Mean values and standard deviation of ultrasonic transmission velocity (m/s) for sample groups A, B and C.

3.1. The data reveal several facts

Considering each group of samples, it can be seen that VPz is considerably higher in all groups than propagation velocity in the *x* and *y* directions. Similarly, and in average terms, VPx is higher than VPy in groups B and C, although in this case the differences are considerably lower. The propagation velocity in any direction (VPz, VPx, VPy) decreases slightly in general terms from group A to B to C.

To consider groups B and C, the mean differences in velocity between directions *z* and *y* are 923 and 1044 m/s for B and C respectively, the differences between *z* and *x* are 890 and 792 m/s and the differences between *x* and *y* are 33 and 252 m/s. Considering that both *z* and *x* are directions parallel to the areas of greyish mineralisation, it is not immediately obvious why both directions should have different velocities, and so these differences must be caused by another factor other than the veining. In addition, given that the VPz − VPy difference is higher than that between VPx and VPy, we should consider that the "shared effect" of the zoning or greyish mineralisation is what is determined by the VPx − VPy value, which seems to be suggested by the fact that these differences are higher in samples of group C than group B. Consequently, the difference in behaviour of the ultrasonic waves in the *x* and *y* directions as regards the *z* direction must be due not only to the anisotropy of the greyish veins, but also to other structural or crystallographic anisotropies (preferential orientations of the calcite grains, of their crystallographic axes, etc.) which, we suggest, would be determined by the VPz − VPx differences. This is confirmed by the fact that these differences are also detected in the group A samples.

Table 1
Mean values and standard deviation of ultrasonic transmission velocity (m/s) for 75 samples (25 of each group A, B and C).

Group	VPz (m/s)	Std.	VPx (m/s)	Std.	VPy (m/s)	Std.
A	6.203	141	5.531	191	5.172	245
B	6.023	153	5.133	212	5.100	181
C	5.971	216	5.179	224	4.927	231

Regarding the mineralogical composition of the type A material without greyish veining, the optical microscope examination showed the presence of quartz and muscovite and some isolated feldspar crystals apart from calcite. In the type C material the greyish zones also included epidote, titanite and opaque metallic veins, probably of pyrite (Photo 1). The XRD (powder method) study of these greyish veins also showed the presence of mica, quartz, epidote and titanite, whereas in the diffractograms of the type A material only some quartz was detected apart from the calcite (the technique does not detect very minority phases).

Regarding the chemical composition, Table 2 summarises the data of the chemical analysis of majority elements in type A, B and C blocks (in the latter case we have chosen a sample with high abundance of greyish veining). This table also includes the OCa and O_2C contents calculated for an ideally pure calcite. These results confirm that the type A material is a very pure calcitic marble. The compositional differences between the samples type A and the type B and C are explained by the above-mentioned presence of quartz, micas, epidote and veins in the C sample.

3.2. Study of the preferential orientation of the calcite grains

We now present the data on possible morphological and crystallographic orientations obtained from optical-petrographic microscope with universal stage and XRD.

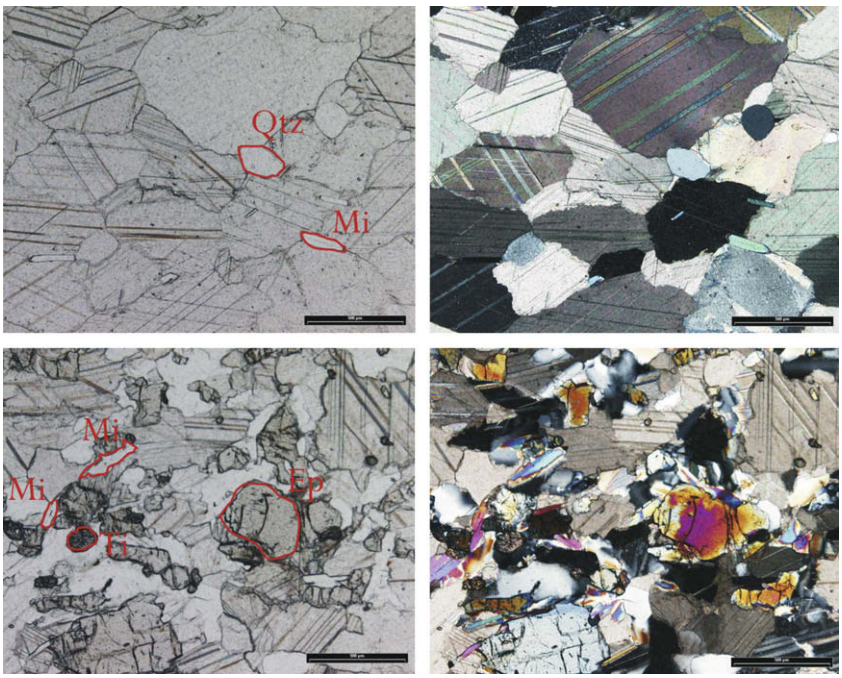

Photo 1. (Upper) Detailed view of accessory minerals (quartz and mica), note the coincidental lengthening of the crystals of colourless mica and calcite. (Left) Polarized light (right) Crossed polars. (Lower) General view of the concentration of accessory minerals (mainly epidote and titanite)in dark areas of the grey sample. (Left) Polarized light (right) crossed polars.

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Table 2
Majority elements (% oxides weight), sulphur content and loss by calcinations (LOI) corresponding to the A, B and C quarry samples and a 100% pure calcite. Detection limit (0.01%). ICP method: P_2O_5, Al_2O_3, SiO_2, TiO_2; AAS method: CaO, MgO, Na_2O, K_2O, Fe_2O_3.

Sample	CaO	SiO_2	Al_2O_3	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	P_2O_5	S (LECO)	LOI	Total
A	56.1	0.27	0.08	0.75	0.02	0.02	0.06	<0.01	<0.01	<0.01	42.01	99.34
B	53.1	2.5	1.15	0.7	0.02	0.3	0.52	0.05	0.01	<0.01	40.2	99.26
C	49.1	6.12	3.05	0.89	0.04	0.72	0.89	0.15	0.03	<0.01	38.12	99.12
Pure calcite	56.00	–	–	–	–	–	–	–	–	–	44.00	100.00

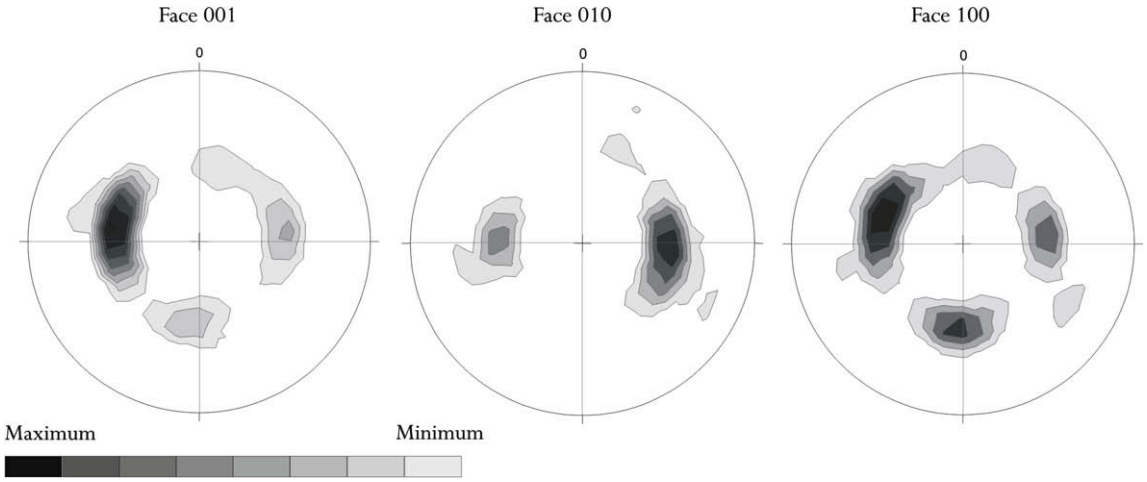

Fig. 2. Density diagram of the *c* axes measured in thin sections taken from each of the (001), (010) and (100) faces of the sample block.

Regarding the results obtained using the universal stage, the stereographic projection of the orientations of the *c* axis of the calcite grains in the three sections studied shows a distribution indicative of maxima coinciding with an angle of slightly more than 45° to the 001 axis. This axis was taken as a random reference for the samples studied, as shown in the density diagrams (Fig. 2), where areas of minima can be seen that are of little importance and are normal in the dispersion presented by the orientations of some measured grains.

It is therefore clear that the calcite crystals making up the material studied have an important degree of preferential orientation. The *c* axis of these crystals is predominantly oriented along directions closer to the *xy* plane than the *z* (longitudinal) direction of the sample block.

The results of the XRD studies are shown in Table 3, which summarises the mean values of the relative intensities of the (102), (104), (113), (110) and (202) reflections for the 25 sections of each of groups A, B and C. Table 3 also shows the differences (in %) from the theoretical intensities where there is no preferential orientation and the mean values of the intensities for each reflection for the total of 75 sections and the mean value of the difference from the theoretical value. The number of diffractograms is high enough for the data considered here to be significant in qualitative terms at least.

It can be seen in the results both sorted by groups and in the total of 75 sections that all the reflections have higher intensities than the theoretical values with the exception of the (104) reflection, which is lower than the theoretical value (100%) in the absence of preferential orientation.

Fig. 3 gives a schematic representation of the directions of the (102), (104) and (202) planes responsible for the corresponding reflections as regards the *x* and *c* crystallographic axes. The directions of the (110) planes would be contained in the *xy* plane of the crystallographic axis system.

In order to relate the crystallographic directions to the directions of the sample block we must consider, on the one hand, that if certain reflections in a diffractogram are stronger than others, this is indicative of a higher number of planes corresponding to the stronger reflections. In our case the stronger reflections are those corresponding to (202) planes whose directions intersect tend to be located more along the *xy* plane, or, in other words, along the basal plane of the sample block (it should be remembered that the X-rays incide on the *xy* surface of the section, perpendicular to the *z* direction), the data on the relative intensities of the different reflections or diffracted beams indicate a predominant orientation of the calcite crystals in the marble, so that their *c* crystallographic axis would tend to coincide with the *xy* plane, or close to it, but not with the *z* direction.

Table 3
Mean values of relative intensity (%) of the (102), (104), (113), (110) and (202) reflections, standard deviation and the differences in % from the theoretical intensity for 75 samples (25 of each group A, B and C).

Group	102 (It = 12)			104 (It = 100)			113 (It = 14)			110 (It = 18)			202 (It = 18)		
	True I (%)	Δ (%)	Std.	True I (%)	Δ (%)	Std.	True I (%)	Δ (%)	Std.	True I (%)	Δ (%)	Std.	TrueI (%)	Δ (%)	Std.
A	13	12	2	74	−26	5	45	223	6	32	77	4	51	76	6
B	17	43	3	80	−20	7	44	213	5	45	150	6	57	91	7
C	11	−8	3	92	−8	8	29	108	3	38	113	5	54	84	7
Mean	14	16	3	82	−18	7	39	181	5	38	113	5	54	84	7

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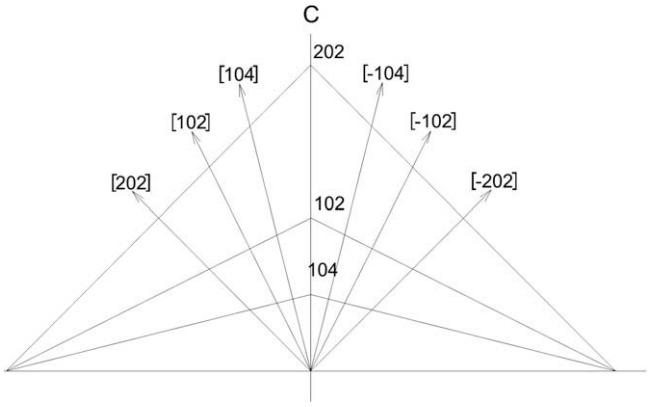

Fig. 3. Diagram of directions of (102), (104) and (202) planes as regards the *x* and *c* crystallographic axes.

Table 4
Mean values and standard deviation of crystallinity index (*D*) for the A, B and C groups of sample blocks from (102), (202) and (104) reflections measured in 75 samples (25 in each group).

hkl	(102) Group			(202) Group			(104) Group		
	A	B	C	A	B	C	A	B	C
Mean values	651	1054	520	555	423	467	596	547	594
Std.	205	448	120	46	42	35	47	111	85

Table 5
Mean values and standard deviation of anisotropy index (DM: total anisotropy index in %; Dm relative anisotropy index in %) for 75 samples (25 of each group A, B and C).

	A	Std.	B	Std.	C	Std.
$\Delta M(\%)$	11.84	3	8.57	3	11.62	3
$\Delta m(\%)$	6.71	2	0.64	0	4.99	2

3.3. Crystallinity index and anisotropy index study

The study of the 75 diffractograms of the 001 sections (perpendicular to the *z* direction) from the marble samples (method b) provided data on the crystallinity index of the grains.

Table 4 summarises the values of the crystallinity index (*D*) obtained using the Scherrer formula on the (102), (202) and (104) reflections of the 25 samples in each of the three groups.

Concerning the anisotropy index, Table 5 summarises the values obtained by relating the differences between the ultrasonic propagation velocities perpendicular (VPy) and parallel to (VPz and VPx) the planes of grey mineralisation, using Eqs. (2) and (3). Despite the dispersion of the values, the resulting anisotropy is of the same order as that obtained by [12] and [24] for Macael marble (15.4 for $\Delta M\%$ and 3 for $\Delta m\%$).

4. Conclusions

The foregoing analysis and discussion on the data obtained lead to the following general conclusions.

First of all, we can conclude that the ultrasonic technique is suitable and accurate enough to detect chemical and structural anomalies and discontinuities in marble material such as that studied here. In the case in hand, we can see that the transmission velocity of the ultrasonic waves in any of the directions considered decreases as the degree or proportion of greyish veining increases in the samples, thus indicating a decrease in propagation velocity determined by the zoning effect or compositional anisotropy. Loss of velocity is greater for those directions in which the wave moves perpendicular to the veining (VPy), which confirms the influence of this compositional anisotropy.

In addition, analysis of the differences in ultrasonic propagation velocities in the different directions of the sample blocks reveals a preferential orientation of the crystals in the material. This was confirmed by the studies of crystallographic orientation, that indicate the *c*-axis of calcite crystals shows a preferential orientation at an intermediate position between a *z* and *x* directions of the sample blocks, in agreement with the data on ultrasonic propagation velocity.

We can therefore conclude that the resulting degree of orientation for the material studied with XRD technique is significant. Indeed, if we take into account that the maximum density of links in the calcite structure is located on the plane perpendicular to the *c* axis, which is also where the planar groups of $CO3^{=}$ are located whose C–O bond is four times stronger than the O–Ca bond [25], and considering also a relation between ultrasonic velocity and mechanical resistance and compacity of the material, this explains that the ultrasonic velocity is higher along the longitudinal direction of the sample blocks (*z*) than along the two lateral directions (*x* and *y*).

The values of the ultrasonic velocities also lead to establishing the anisotropy indices, revealing the importance of the preferential crystalline orientations on the anisotropy of the material. This indicates the undoubted influence of these preferential orientations on the physical–mechanical behaviour of stone material and at the same time the similarity in the $\Delta M\%$ values for the three groups indicates little influence of greyish mineralisation veins on this index.

Finally, with some caution, we can say that a higher crystallinity index, given the dispersion of the values obtained, seems to correspond to higher purity (less greyish veining) of the marble.

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