



**HAL**  
open science

## **Progressive thermal decohesion in Carrara marble monitored with nonlinear resonant ultrasound spectroscopy**

Marie-Laure Chavazas, Philippe Bromblet, Jérémie Berthonneau, Jérémy Hénin,  
Cédric Payan

### ► **To cite this version:**

Marie-Laure Chavazas, Philippe Bromblet, Jérémie Berthonneau, Jérémy Hénin, Cédric Payan. Progressive thermal decohesion in Carrara marble monitored with nonlinear resonant ultrasound spectroscopy. *Bulletin of Engineering Geology and the Environment*, 2024, 83 (383), <10.1007/s10064-024-03875-8>. <hal-04690036>

**HAL Id: hal-04690036**

**<https://hal.science/hal-04690036v1>**

Submitted on 6 Sep 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

# Progressive Thermal Decohesion in Carrara Marble Monitored with Nonlinear Resonant Ultrasound Spectroscopy

Marie-Laure Chavazas<sup>1,2\*</sup>, Philippe Bromblet<sup>2</sup>, Jérémie Berthonneau<sup>2</sup>, Jérémy Hénin<sup>3</sup>, Cédric Payan<sup>1</sup>

<sup>1</sup> Aix Marseille Univ, CNRS, Centrale Marseille, LMA UMR 7031, Marseille, France

<sup>2</sup> Centre Interdisciplinaire de Conservation et de Restauration du Patrimoine, Marseille, France

<sup>3</sup> Ministère de la Culture, Laboratoire de Recherche des Monuments Historiques

\* Corresponding author. E-mail: [chavazas@lma.cnrs-mrs.fr](mailto:chavazas@lma.cnrs-mrs.fr). ORCID: 0000-0003-2680-5563

ORCID contributing authors: Philippe Bromblet: 0000-0002-8735-1481 / Jérémie Berthonneau: 0000-0003-2354-5567

## Acknowledgements

Authors wish to thank Alain Tonetto and Louis Godaert (PRATIM, Aix Marseille Univ, France) for their help with the SEM observations, Nathalie Gandolfo (CICRP, Marseille, France) for the thin section preparation, and Laurent Sabatier and Sophie Steinlin (LMA, Marseille, France) for their help with the uniaxial compressive strength tests.

## Author contributions

Cédric Payan, Philippe Bromblet and Jérémie Berthonneau contributed to the study conception and design. Material preparation, data collection and analysis were performed by Marie-Laure Chavazas and Jérémy Hénin. The first draft of the manuscript was written by Marie-Laure Chavazas and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

## **Abstract**

Marble has been used in sculpture and architecture since Antiquity. When exposed outdoors, it is subjected to physical, chemical, or biological weathering. Studies have shown that some deterioration (bowing, microcrack generation, thermal damage) can result from the exposure to cyclical thermal variations, but the actual temperature range triggering these phenomena remains unknown. Specifically, it is not yet understood if these phenomena are activated at a certain threshold temperature or by prolonged cyclic temperature exposure. In this work, the evolution of the mechanical state of Carrara Gioia marble samples under thermal stress is followed by means of Nonlinear Resonant Ultrasound Spectroscopy (NRUS). The results show, on the one hand, a progressive decrease of the linear parameter (resonant frequency) with heating temperature. This evolution agrees with results from previous works and with the consequent evolution of the microstructure. The (nonclassical) nonlinear parameter, on the other hand, exhibits an increase in the mild temperature range (40 – 85°C), followed by a decrease for the highest temperatures (85 – 250°C). This evolution of the NRUS parameters, as well as microstructural observations, depicts mild temperature induced degradation in Carrara marble. Carrara marble decohesion starts at the mesoscopic scale as evidenced by the initial increase in the nonlinear parameter, and then progressively expands to the macroscopic scale as highlighted by the resonant frequency evolution.

**Keywords:** Carrara marble; thermal weathering; nonlinear resonant ultrasound; nondestructive testing

# 1 Introduction

Carrara marble is a well-appreciated and well-known marble variety used in sculpture and architecture since Antiquity (Primavori 2015). It can undergo diverse deteriorations during its aging such as sugaring, thermal damage, bowing, microcrack generation, loss of mechanical resistance. Many studies have shown the significant role of temperature variations in marble degradation (Kessler 1919; Lord Rayleigh 1934; Mahmutoglu 1998; Ferrero and Marini 2001; Siegesmund et al. 2008; Peng et al. 2019; Sena Da Fonseca et al. 2021). The sensitivity of marble to thermal weathering is generally explained by the anisotropy of the thermal dilation coefficient of calcite, the main mineralogical component of calcitic marble (Siegesmund et al. 2000a; Grelk et al. 2004; Malaga-Starzec et al. 2006). The anisotropic expansion/contraction of calcite crystals during heating/cooling cycles generates intergranular decohesion between calcite grains. Such phenomenon has classically been recreated in laboratories by applying artificial weathering on fresh marble by means of thermal degradation between 100 and 500 °C (Ferrero and Marini 2001; Koch and Siegesmund 2004; Sassoni et al. 2017; Sena Da Fonseca et al. 2021). Yet, the study of thermal weathering induced by exposure to mild temperatures is particularly relevant as these temperatures are often recorded on the surface of marble exposed outdoors. From an onsite monitoring campaign and a comprehensive literature review, Schouenborg et al. (2007) concluded that the maximum temperature reached on white Carrara marble surface was about 60 °C. Besides, the environmental monitoring made on marble in the central Namib desert for three years by Viles (2005) showed that marble surface temperature reaches 55 °C, with a maximum air temperature of 37 °C. Some studies already indicate marble deterioration in the mild temperature range (Malaga et al. 2002; Schouenborg et al. 2007; Gherardi et al. 2019; Waragai 2023). For instance, Schouenborg et al. (2007) recommended to condition marble at 40 °C rather than 70 °C since a considerable loss of mechanical strength was observed for temperatures lower than 70 °C. Besides, Malaga et al. (2002) suggested that intergranular decohesion could occur between 40 and 50 °C for some marble varieties, based on porosity measurements on calcitic and dolomitic marbles heated between 40 and 200 °C.

The evolution of marble thermal degradation can be monitored by various techniques. Mechanical properties are usually evaluated by destructive testing: Brazilian test, uniaxial compression test, flexural strength test (Mahmutoglu 1998; Ferrero and Marini 2001; Marini and Bellopede 2007, 2009; Siegesmund et al. 2008). Due to their destructive nature, these tests do not allow following the evolution of damage in one sample during thermal weathering. However, mechanical properties can also be probed using nondestructive methods. For example, ultrasound-based techniques have been developed to characterize marble degradation. Ultrasonic pulse velocity allows monitoring the deterioration of the same sample all along the ageing process (Weiss et al. 2002; Malaga-Starzec et al. 2006; Marini and Bellopede 2007, 2009; Siegesmund et al. 2021; Zhang et al. 2022; Wu et al. 2023; Sáez-Pérez et al. 2024). Ultrasound tomography can provide a mapping of the inner degradation state of samples without damaging them during the experiment (Siegesmund et al. 2021). Resonance methods also enable probing and monitoring the mechanical state of materials. In fact, Resonant Ultrasound Spectroscopy (RUS) method (Migliori and Sarrao 1997) was developed in the early 2000s and successfully applied for characterization of rocks (Ulrich et al. 2002; Remillieux et al. 2015). The Nonlinear Resonant Ultrasound Spectroscopy (NRUS) method was also developed in the same period when it was found that noticeable nonlinear phenomena occurred in rocks when increasing vibration amplitude. Rocks and geomaterials fall in the nonclassical class of nonlinear media which exhibit features such as hysteresis, slow dynamics, end-point memory (Ten Cate and Shankland 1996; Guyer and Johnson 1999; Ostrovsky and Johnson 2001a; Johnson et al. 2004; Johnson and Sutin 2005). These nonlinear phenomena are found to be highly sensitive to any change (microcracks, relative humidity, etc.) at the microstructural scale. Nonclassical nonlinearity has been investigated in diverse rock types such as sandstone (Ten Cate and Shankland 1996; Van Den Abeele 2002; Johnson et al. 2004; Rivière et al. 2015) and carbonate rocks like marble, limestone and chalk (Van Den Abeele 2002; Johnson et al. 2004; Johnson and Sutin 2005; Averbakh et al. 2017).

However, specific studies on the impact of marble heating on its NRUS response are very limited and present very few data. Johnson et al. (2004) studied the nonclassical nonlinearity in a white Asian marble (from

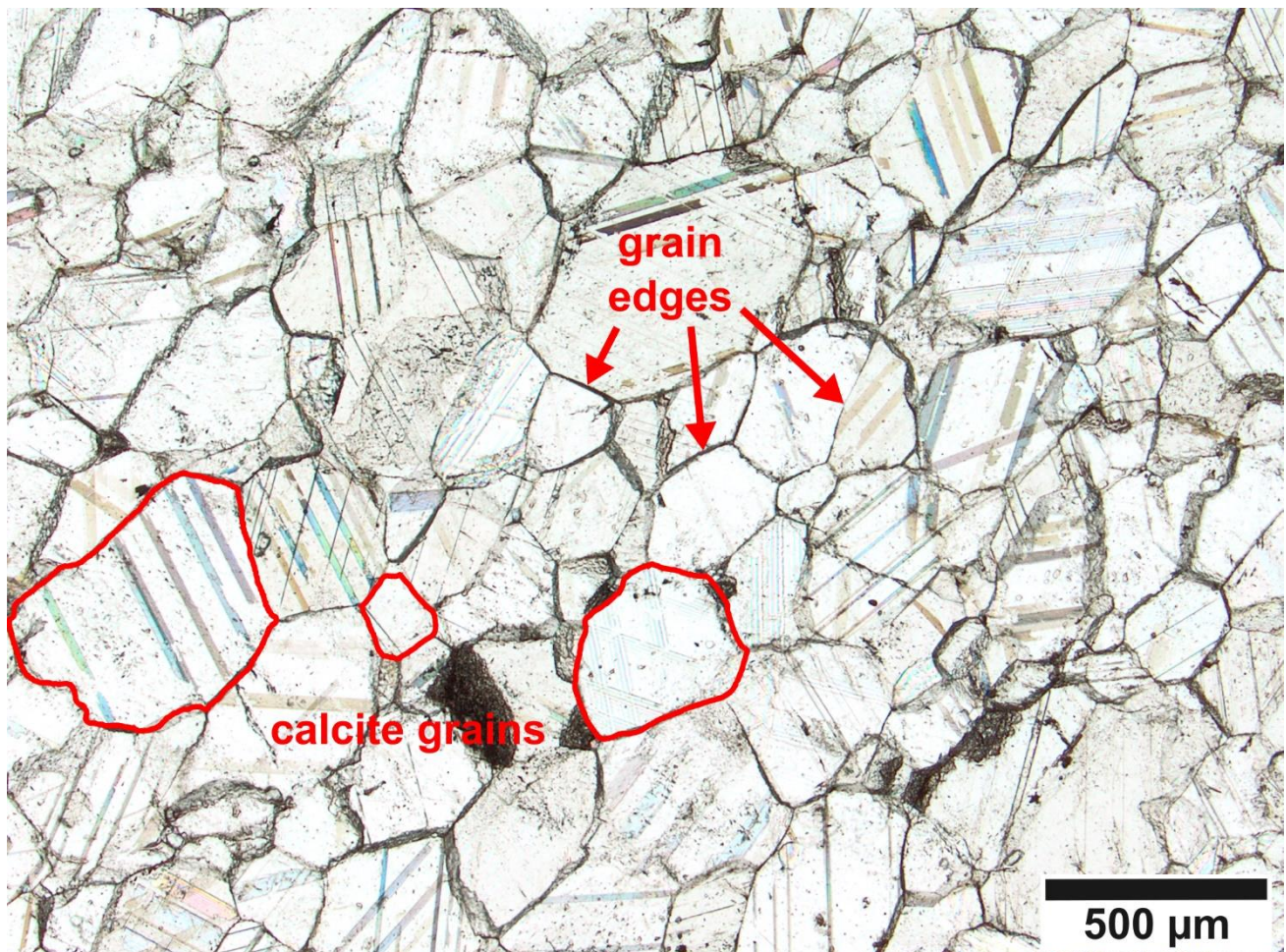
Turkey) under varying conditions. In their work the nonlinear parameter was first measured in ambient conditions, then after the sample was heated at 200 °C. The 44% drop of the nonlinear parameter value (from 27,006 to 15,251) was interpreted by the authors as an ability of Asian marble to heal itself during the heating process. Yet, no other studies have supported this hypothesis so far and the temperature at which such mechanism may be triggered is unknown, especially within the mild temperatures (40 – 85 °C). The impact of exposure to mild temperatures can be critical for marble artefact preservation. However, this temperature range has not yet been investigated by NRUS even though this technique can bring further information on the underlying degradation mechanisms compared to traditional techniques such as destructive mechanical tests and ultrasonic pulse velocity. Indeed, NRUS does not only probe the macroscopic scale of materials as traditional methods but also the mesoscopic scale, and accounts for other phenomena.

This work aims at investigating further the impact of thermal damage on the NRUS response of Carrara marble, especially at mild temperatures and until its complete granular disintegration, and thus linking the evolution of the NRUS parameters to the changes occurring in marble microstructure. To this end, Carrara marble samples are heated at different temperatures between 40 and 500 °C. Their degradation is then evaluated with NRUS by following the evolution of linear (resonant frequency) and nonlinear (nonclassical parameter) parameters. The nonclassical nonlinear parameter exhibits an unexpected evolution with thermal damage compared to other granular materials. Microstructural and mechanical characterizations are also carried out to investigate the evolution of marble microstructure due to thermal damage.

## 2 Materials and methods

### 2.1 Carrara marble samples

A block (45 cm x 45 cm x 20 cm) of fresh Carrara Gioia marble (provided by Logica SRL, Carrara, Italy), a calcitic white veined marble, was used in this study. This variety of Carrara marble was chosen since it has a granoblastic equigranular-polygonal microstructure (Malaga-Starzec et al. 2003; Siegesmund et al. 2008, 2021; Menningen 2020; Menningen et al. 2021). Marbles with this microstructure are expected to be more sensitive to thermal weathering (Royer-Carfagni 1999; Grell et al. 2004; Åkesson et al. 2006). The microstructure of the studied block is illustrated in Fig. 1. This marble is mainly composed of equigranular monocrystals of calcite (calcium carbonate,  $\text{CaCO}_3$ ). The average size of the calcite grains is ca. 300  $\mu\text{m}$  and the grain boundaries are mostly straight.



**Fig. 1** (Color online) Optical microscope image of a sample of fresh Carrara Gioia marble, magnification x25, plane light. Some calcite grains are circled in red, and some calcite grain edges are indicated by red arrows

The condition and isotropy of the marble block were first checked by measuring ultrasonic pulse velocity. Core samples of 20 cm in height and 4 cm in diameter were then drilled from the block. At this point, reference NRUS measurements (see section 2.2 for details on this technique) were made on each core sample before they undergo any thermal treatment.

To evaluate the influence of temperature on marble weathering, samples were heated in an oven up to various setpoint temperatures. The heating rate was set to  $1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  to allow the homogeneous heating of the

material (Weiss et al. 2002; Sassoni et al. 2017; Siegesmund et al. 2021). The setpoint temperature was maintained for 6 h as in Siegesmund et al. (2021). The cooling down to room temperature was left free. After heating, the samples were stored in a temperature-controlled oven maintained at 23 °C, and they also remained in this oven during the NRUS testing. The setpoint temperatures were the following: 40, 65, 85, 105, 150, 200, 250 and 500 °C. Four core samples were heated per setpoint temperature, and four unheated samples (stocked at 23 °C) were used as references. This temperature set was chosen to explore the impact of natural (40 – 85 °C) (Viles 2005; Schouenborg et al. 2007) as well as artificial (105 – 500 °C) (Ferrero and Marini 2001; Koch and Siegesmund 2004; Sassoni et al. 2017; Sena Da Fonseca et al. 2021) weathering conditions. The interval between each temperature point was first set low to study the influence of several natural heating conditions to evaluate the impact of exposure to climatic conditions on marble alteration. The temperature point at 105 °C was preferred to 100 °C to go beyond the water evaporation point. The highest temperatures (105 – 500 °C) enabled to continue a progressive artificial alteration of marble until its complete granular disintegration (500 °C).

## 2.2 Nonlinear Resonant Ultrasound Spectroscopy (NRUS)

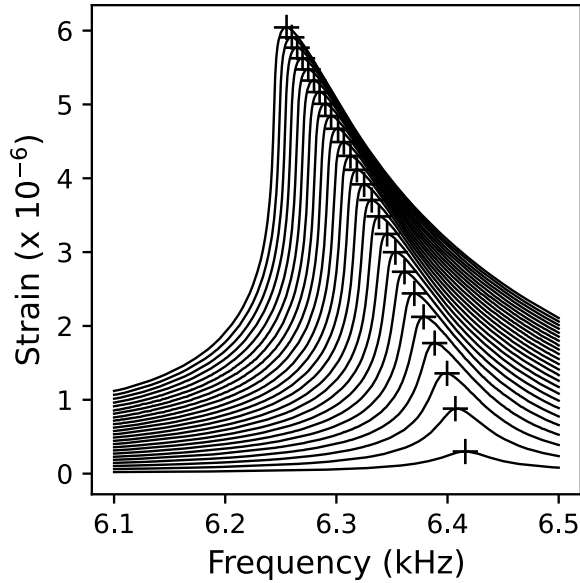
NRUS consists in exciting a sample at several increasing drive amplitudes to study the evolution of the resonant modes. For linear materials the resonant frequency of a given mode remains constant as the drive amplitude increases, whereas for nonlinear media a shift towards the low frequencies is observed. Geomaterials, such as marble, exhibit a nonclassical nonlinear behavior. Their modulus  $K$  is expressed as (Guyer and Johnson 1999; Van Den Abeele 2002; Johnson et al. 2004; Johnson and Sutin 2005):

$$K = K_0[1 + \beta\varepsilon + \delta\varepsilon^2 + \dots + \alpha(\Delta\varepsilon, \dot{\varepsilon})] \quad (1)$$

where  $K_0$  is the elastic modulus,  $\beta$  and  $\delta$  are the classical nonlinear coefficients and  $\alpha$  is the nonclassical nonlinear parameter. In nonclassical nonlinear materials, the relative shift in frequency is proportional to the strain amplitude  $\Delta\varepsilon$  of the sample:

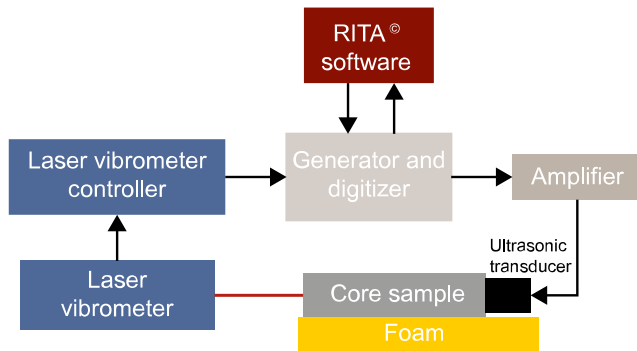
$$\Delta f/f_0 = \alpha \Delta\varepsilon \quad (2)$$

where  $\Delta f = f_0 - f$  with  $f_0$  the linear resonant frequency obtained for the lowest drive amplitude and  $f$  the resonant frequency for higher drive amplitudes. In this work, only the first longitudinal resonant mode of the core samples is studied. The detection of this mode is facilitated by the sample geometry (cylinders with a large height over diameter ratio). Fig. 2 shows an example of an NRUS scan, obtained for an unheated core sample of Carrara Gioia marble with a resonant frequency  $f_0$  of  $6.42 \pm 0.03$  kHz and a nonlinear parameter  $\alpha$  of  $(5.0 \pm 0.4) \times 10^3$ .



**Fig. 2** NRUS curves obtained for an unheated sample of Carrara Gioia marble with a resonant frequency  $f_0$  of  $6.42 \pm 0.03$  kHz and a nonlinear parameter  $\alpha$  of  $(5.0 \pm 0.4) \times 10^3$

Linear and nonlinear parameters extracted from NRUS scans provide information on the mechanical state of a sample. The resonant frequency (linear resonant frequency extracted for the lowest drive amplitude) is related to the stiffness and density of the macroscopic sample. The nonlinear parameter  $\alpha$  finds its origin in nonlinear phenomena occurring at the mesoscopic scale of the material, such as opening/closing of microcracks, capillary effects, friction, contacts, dislocations, etc. (Rasolofosaon et al. 1997; Ostrovsky and Johnson 2001a, b; Payan et al. 2014). Therefore, the mesoscopic scale is ranging between the grain contacts and the grain assemblage. Thus, the two parameters account for different phenomena occurring at different scales in the material.



**Fig. 3** (Color online) Scheme of the experimental set-up used for the NRUS tests

Fig. 3 illustrates the experimental set-up for the NRUS experiments. The signal generation is managed by RITA<sup>®</sup> software coupled with a generator (NI PXIe-5406) and an amplifier (NF Electronic Instruments 4005 High Speed). The vibrations are generated in the core sample thanks to an ultrasonic piezoelectric transducer (Beijing Ultrasonic, resonant frequency of 40 kHz) placed at one sample extremity. The piezoelectric transducer was non-permanently glued with phenyl salicylate (also called salol) and unglued between each NRUS scan. The out-of-plane velocity is measured at the other sample extremity with a Polytec laser vibrometer (OFV-505 Single Point Sensor Head and OFV-5000 Controller,  $\lambda = 633$  nm (He-Ne), power < 1 mW). The signal acquisition is also managed by RITA<sup>®</sup> software coupled with a digitizer (NI PXIe-5122). During the signal recording, the tested sample was placed on foam to minimize the attenuation or modification of the vibration modes due to the rigid support. As shown by Fig. 2, the resonant frequency  $f_0$  is directly accessible from the

output signal data provided by the laser vibrometer. However, to calculate the nonlinear parameter  $\alpha$  by means of Eq. ( 2 ), amplitude strain  $\Delta\varepsilon$  reached at resonance must be evaluated from the out-of-plane particle velocity amplitude  $A$  recorded by the vibrometer at resonance. It is calculated as follows (Remillieux et al. 2016; Mechri et al. 2019):

$$\Delta\varepsilon = \frac{A}{2 * L * f_0} \quad ( 3 )$$

where  $L$  is the sample length and  $f_0$  is the (low amplitude) resonant frequency.

### 2.3 Microstructural and mechanical characterizations

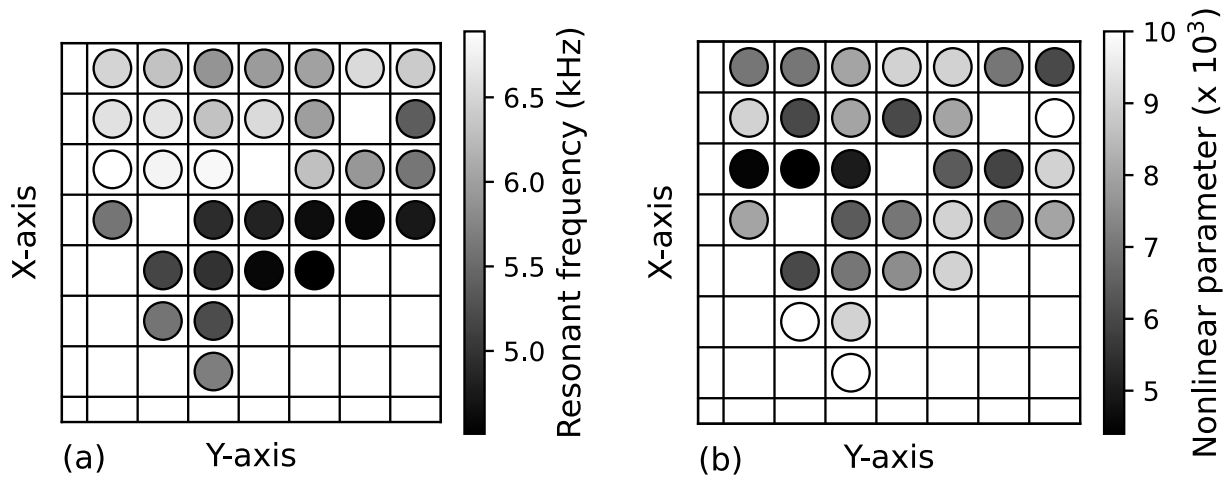
For each setpoint temperature, two 8 cm long cylinders and centimetric fragments were extracted from one core sample. One fragment was used to characterize marble microstructure with Mercury Intrusion Porosimetry (MIP) using a AutoPore IV 9500 (Micromeritics) working with a maximal pressure of 210 MPa, thus probing pores between 0.01 and 360  $\mu\text{m}$ . Mercury intrusion was measured at 111 increasing pressure points. Another fragment was used to prepare thin sections to perform a petrographic description using a polarized light microscope (Olympus BX-51). The thin sections as well as the remaining freshly cut fragments were also characterized under a Scanning Electron Microscope (SEM, ZEISS EVO 15). The two 8 cm long cylinders were used to measure Uniaxial Compressive Strength (UCS). Uniaxial compression tests were performed on a MTS 809 Axial / Torsional Test System, at a constant displacement rate of 0.24 mm.min<sup>-1</sup>. Two discs of Teflon™ of 1 mm thick and 5.4 cm in diameter were placed on the top and bottom of the sample to correct the lack of strict parallelism of the sample faces and limit edge effect.

## 3 Results

### 3.1 Degradation state and variability in the fresh Carrara marble block

Ultrasonic pulse velocity was measured on the whole Carrara marble block, at different points, in the three orthogonal directions. The mean velocities were  $3.9 \pm 0.1 \text{ km.s}^{-1}$ ,  $4.4 \pm 0.2 \text{ km.s}^{-1}$  and  $3.8 \pm 0.4 \text{ km.s}^{-1}$ , respectively along the X, Y and Z directions. Based on these values, the block may be considered as a class I marble (Köhler 1991). All core samples were drilled along the same direction (Z).

A first set of NRUS measurements was performed on the drilled core samples before any heating (temperature of  $23 \pm 0.1^\circ\text{C}$ ). The results show some variability among the samples in both resonant frequency  $f_0$  and nonlinear parameter  $\alpha$  values. The minimum and maximum values for the resonant frequency  $f_0$  are  $4.5 \pm 0.2 \text{ kHz}$  and  $6.9 \pm 0.2 \text{ kHz}$ , respectively. For the nonlinear parameter  $\alpha$ , the minimum and maximum values are  $(4.4 \pm 0.7) \times 10^3$  and  $(10 \pm 4) \times 10^3$ , respectively. The NRUS parameters values acquired at  $23^\circ\text{C}$  are displayed in Fig. 4. The grid is a scheme of the top view of the marble block with each square corresponding to the original sample position. One can note that the resonant frequency value tends to decrease along the X-axis, and that the nonlinear parameter  $\alpha$  also exhibits some variability. This variability in the NRUS parameters values does not, however, seem to follow any pattern across the marble block. Nonetheless, the drilled core samples were randomly assigned to the setpoint temperatures to account for this variability and avoid any influence of their original location in the marble block.

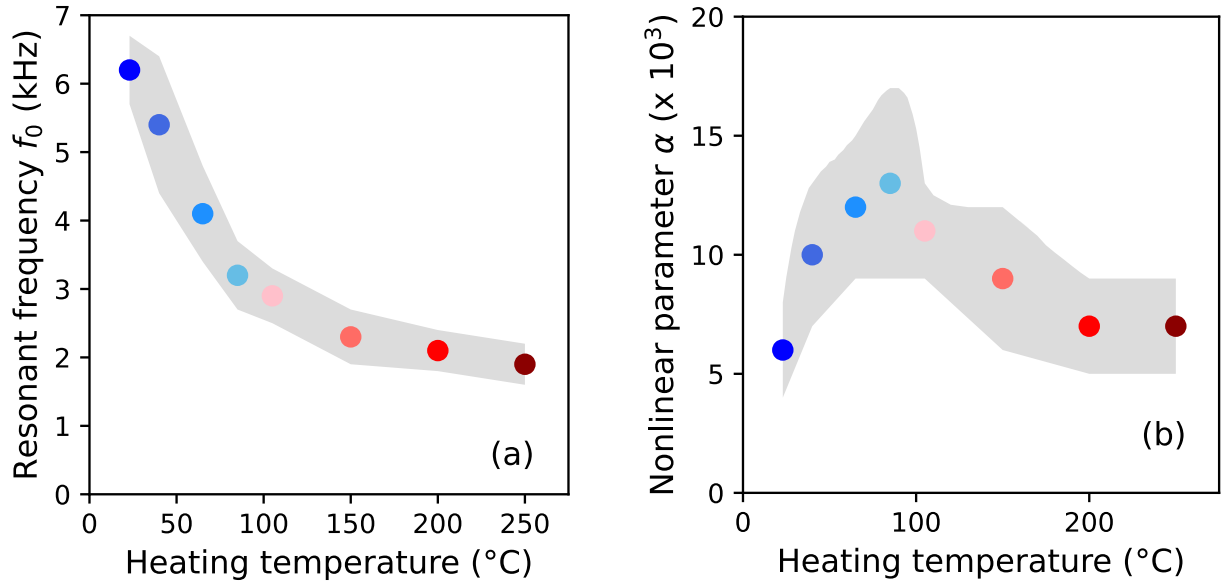


**Fig. 4** (a) Resonant frequency and (b) nonlinear parameter values of the tested Carrara samples prior to their heating. The grid schematizes the top view of the marble block. Each square corresponds to the initial position of a core sample in the block

### 3.2 Influence of heating temperature

32 core samples were used to study the influence of thermal damage on the NRUS response of Carrara marble. 4 samples remained unheated to be used as reference. The other 28 samples were heated up to 7 different setpoint temperatures (4 samples heated at each temperature of 40, 65, 85, 105, 150, 200 and 250 °C). All samples were then stored and tested with NRUS in a temperature-controlled oven maintained at  $23 \pm 0.1$  °C. At least three NRUS scans were acquired per sample removing and reattaching the transducer on the sample (using phenyl salicylate) each time. 4 samples were also heated at 500 °C but suffered complete disintegration after the heating, therefore they could not be scanned with NRUS.

The resulting evolutions of the resonant frequency  $f_0$  and of the nonlinear parameter  $\alpha$  with heating temperature are displayed in Fig. 5 (a) and (b), respectively. Each point shown on Fig. 5 corresponds to the average value for all NRUS measurements made on all four samples heated at a given temperature. The uncertainties displayed in these figures (shaded areas) correspond to one standard deviation.



**Fig. 5** (Color online) Evolutions of (a) resonant frequency  $f_0$  and of (b) nonlinear parameter  $\alpha$  with heating temperature for Carrara Gioia marble. Filled circles correspond to average values of the NRUS parameters. Shaded areas denote one standard deviation

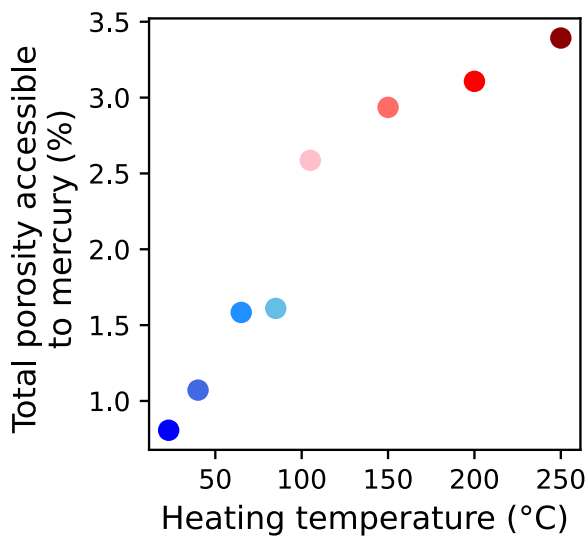
Fig. 5 (a) clearly shows that the resonant frequency  $f_0$  decreases with increasing heating temperature. This parameter ranges from an average of  $6.2 \pm 0.5$  kHz for the unheated samples to an average of  $1.9 \pm 0.3$  kHz for the samples heated at 250 °C, thus exhibiting a global decrease of 69%.

The evolution of the nonlinear parameter  $\alpha$  with heating temperature (Fig. 5 (b)) differs from the resonant frequency evolution. For heating temperature between 23 and 85 °C, the nonlinear parameter  $\alpha$  increases from an average of  $(6 \pm 2) \times 10^3$  to an average of  $(13 \pm 4) \times 10^3$ . Then, it decreases down to an average of  $(7 \pm 2) \times 10^3$  for the samples heated at 250 °C.

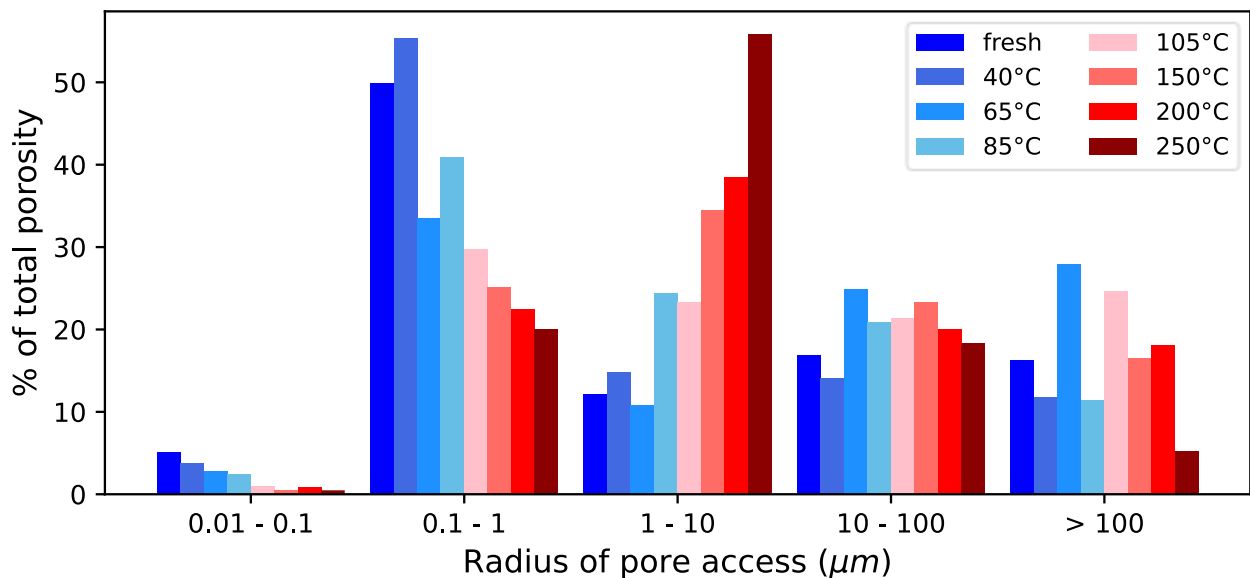
Aside from these general trends, the collected data display significant uncertainties, especially for the nonlinear parameter  $\alpha$  (Fig. 5 (b)). This could be explained by diverse factors such as the significant variation in the nonlinear parameter values between samples (even prior to thermal treatment as shown on Fig. 4), the reattachment of the piezoelectric transducers on the samples between each NRUS scan with the use of a reversible glue (phenyl salicylate), or by the fact that air relative humidity was not controlled during the NRUS scans. Nonetheless, the measured variations are still greater than the uncertainties, and the global tendencies are thus robust.

### 3.3 Microstructural and mechanical evolutions

Microstructural and mechanical characterizations were then performed on the samples to understand the evolution of the NRUS parameters with heating temperature. First, the evolution of porosity and pore size distribution with temperature was probed through Mercury Intrusion Porosimetry (MIP). Fig. 6 presents the total porosity accessible to mercury as a function of the heating temperature of the sample. Fig. 7 indicates the contribution of different porosity classes to the total porosity of each sample.



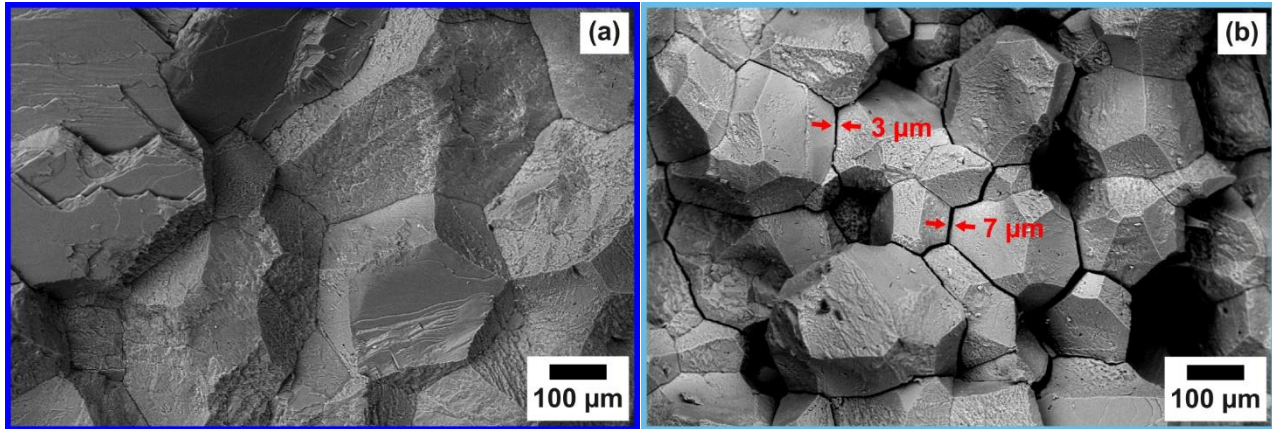
**Fig. 6** (Color online) Total porosity (accessible to mercury) of Carrara marble samples heated at different temperatures



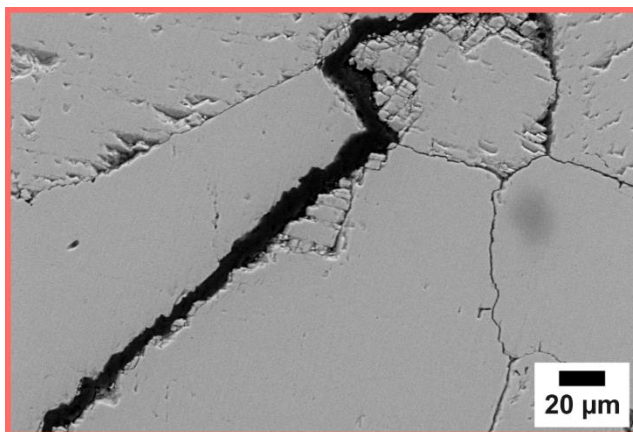
**Fig. 7** (Color online) Porosity classes for Carrara marble samples heated at different temperatures

The total porosity accessible to mercury increases with heating temperature, from 0.81% for the unheated sample to 3.39% for the sample heated at 250 °C (Fig. 6). The contribution of five porosity classes to the total porosity was analyzed: radius of pore access between 0.01 and 0.1  $\mu\text{m}$ , between 0.1 and 1  $\mu\text{m}$ , between 1 and 10  $\mu\text{m}$ , between 10 and 100  $\mu\text{m}$ , and above 100  $\mu\text{m}$ . The porosity class with radius of pore access between 0.01 and 1  $\mu\text{m}$  exhibits a tendency to decrease as heating temperature increases whereas the porosity class between 1 and 10  $\mu\text{m}$  tends to increase with heating temperature. The contribution of pore access with a radius between 10 and 100  $\mu\text{m}$  is relatively steady from heating temperature of 65 °C and is lower for the unheated and 40 °C heated samples. The contribution of pores with access radius above 100  $\mu\text{m}$  is quite variable with heating temperature but does not show a clear evolution pattern.

SEM observations were then performed on thin sections and fracture plans to follow the evolution of intergranular spaces. Fig. 8 presents images of fracture plans for the unheated sample and the sample heated at 85 °C, at magnification x100. One can note the widening of the intergranular spaces between the unheated sample and the sample heated at 85 °C. Fig. 9 presents a SEM image of a thin section of marble heated at 150 °C, at magnification x400. It shows that localized microcracking can be found along some grain edges.

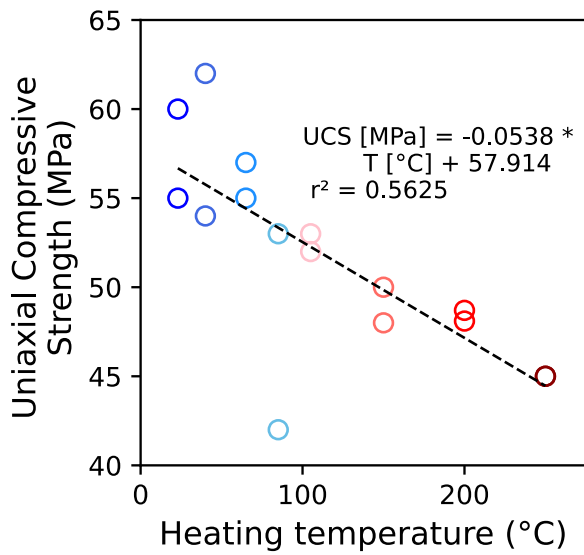


**Fig. 8** (Color online) SEM images (magnification x100) on fracture plans of Carrara Gioia for (a) the unheated sample and for (b) the sample heated at 85 °C. Some cracks are indicated between red arrows, along with their width



**Fig. 9** SEM image (magnification x400) on a thin section of Carrara Gioia marble heated at 150 °C: localized microcracking along grain edges is visible at the center and at the top right of the image

Eventually, mechanical properties of marble samples were destructively probed through uniaxial compression tests. Fig. 10 shows the evolution of Uniaxial Compressive Strength (UCS) with heating temperature. Empty circle data points correspond to the UCS values extracted from two measurements at each heating temperature. The data points were linearly fitted: the linear trend is shown as the dashed line and the fitting parameters are given in the figure. UCS exhibits an overall tendency to decrease with heating temperature, from 57 MPa at 23 °C to 45 MPa at 250 °C in average. Only one of the two measurements made on the sample heated at 85 °C does not follow the linear trend. No specific reason for this behavior was found: NRUS measurements on this sample did not give scattered values of linear or nonlinear parameters compared to the three other samples heated at 85 °C.

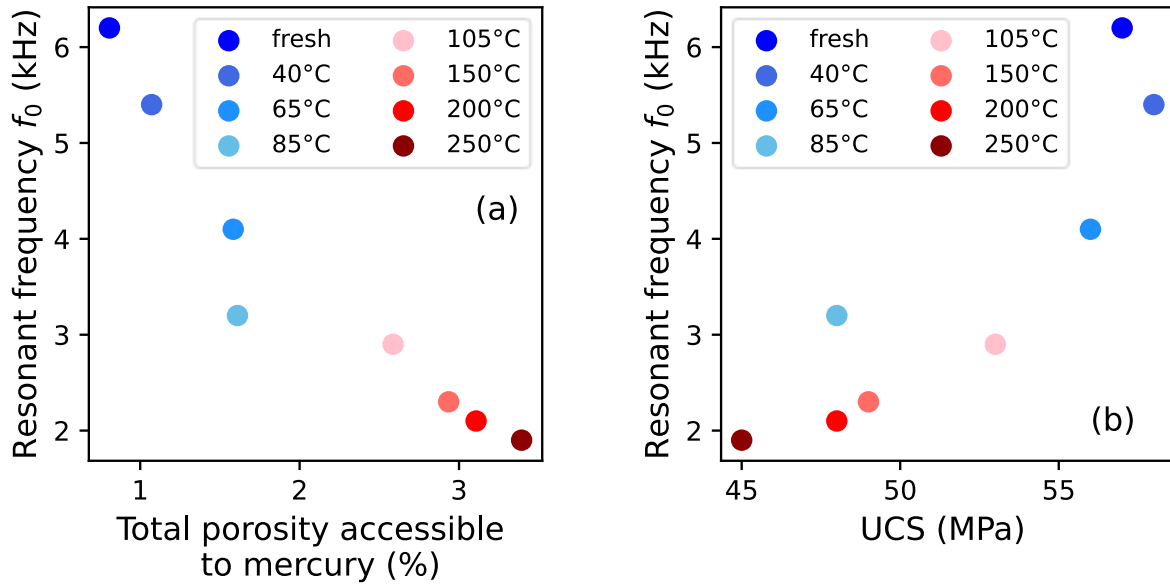


**Fig. 10** (Color online) Values of the two UCS measurements (empty circles) made on Carrara marble samples heated at different temperatures, and their linear trend (dashed line)

## 4 Discussion

Calcite crystals have a strongly anisotropic thermal dilation coefficient:  $26 \times 10^{-6} \text{ K}^{-1}$  parallel to the crystallographic c-axis and  $-6 \times 10^{-6} \text{ K}^{-1}$  perpendicular to c-axis (Siegesmund et al. 2000b; Grell et al. 2004). This anisotropy of the thermal dilation coefficient has long been shown to result in the development of intergranular decohesion when calcitic marble is subjected to temperature variations (Siegesmund et al. 2000a; Grell et al. 2004; Malaga-Starzec et al. 2006). This mechanism could well explain the progressive decrease of resonant frequency  $f_0$  found along this study (Fig. 5), as this parameter is linked to the material stiffness. Indeed, Fig. 11 (a) shows that the resonant frequency  $f_0$  decreases with increasing porosity which reflects the widening of intergranular spaces. This widening is also noticeable in Fig. 7 as the proportion of pores with access radius between 0.01 and 1  $\mu\text{m}$  decreases with heating temperature for the benefit of pores with access radius between 1 and 10  $\mu\text{m}$ . Waragai (2023) found a similar shift in pore access radius of Carrara marble between untreated samples and samples subjected to five thermal cycles between 4 and 84  $^{\circ}\text{C}$ . The progressive loss of cohesion in marble samples as heating temperature increases is also supported by UCS measurements: Fig. 11 (b) shows that the resonant frequency  $f_0$  decreases as the mechanical strength of marble samples diminishes. SEM observations also show that the intergranular spaces widen as heating temperature increases, and that they affect the sample more and more homogeneously. Fig. 8 illustrates this phenomenon on a fracture plan for the unheated sample and the sample heated at 85  $^{\circ}\text{C}$ . In addition to microcracks, areas with localized microcracking is visible along some grain edges, as it is shown on Fig. 9. This may be explained by the fact that, during the heating of marble, calcite grains expand parallel to c-axis and thus neighbor grains could enter in contact and undergo friction from shear stress as they do not have the same orientations. Such friction could be responsible for the localized microcracking on the grain edges. Conversely, during the cooling, calcite grains contract parallel to c-

axis and intergranular spaces are created. They result in a loss of cohesion between grains, leading to a loss of stiffness at the macroscopic scale.



**Fig. 11** (Color online) Evolution of resonant frequency  $f_0$  with (a) total porosity accessible to mercury and with (b) UCS in marble samples heated at different temperatures

Even before its heating, the fresh quarried block of Carrara Gioia marble was already exhibiting relatively high levels of nonlinearity. Indeed, the nonlinear parameter  $\alpha$  of core samples ranged between  $(4.4 \pm 0.7) \times 10^3$  and  $(10 \pm 4) \times 10^3$  before heating (see section 3.1 and Fig. 4). Values of the same order are found for Asian white marble in Johnson et al. (2004) ( $\alpha = 27,006$  for ambient conditions). However in other studies, values can be significantly lower, e.g.  $149 \pm 45$  for Carrara marble in Johnson and Sutin (2005). Values measured on this fresh marble block correspond to relatively high levels of nonlinearity and lead to think that numerous features of nonclassical nonlinearity (linked to the quality of grain contacts) are present in the fresh marble block even before thermal weathering.

The nonlinear parameter  $\alpha$  is sensitive to deterioration at the mesoscopic scale, i.e., between the size of the grain contacts and the grain assemblage. It is sensitive to very local phenomena occurring at grain contacts such as opening/closing of microcracks or friction (Van Den Abeele et al. 2000; Ostrovsky and Johnson 2001a; Johnson 2005; Johnson and Sutin 2005; Payan et al. 2014). For some granular materials, the nonlinear parameter  $\alpha$  exhibits an increase with thermal damage. That is the case for concrete (Payan et al. 2012, 2014), mortar (Genovés et al. 2019) and sandstone (Johnson et al. 2004) for instance. Unlike other granular materials, marble is composed of only one mineral (calcite) and has no cemented material in between grains, which can result in a different nonlinear behavior.

In this study, the nonlinear parameter  $\alpha$  increases for heating temperatures between 23 and 85 °C (mild temperature range), and then keeps diminishing for heating temperatures between 85 and 250 °C (Fig. 5 (b)). The initial increase could be explained by the phenomena occurring at intergranular contacts between calcite grains such as the closing/opening of the intergranular spaces created by heating (Fig. 8) and the friction between adjacent grains (Fig. 9). A hypothesis for the subsequent diminution of the nonlinear parameter  $\alpha$  is the loss of these intergranular contacts. Indeed, intergranular spaces between calcite grains widen as heating temperature increases, and contacts between adjacent grains are thus gradually lost and with them the local nonlinear phenomena occurring at grain contacts. The porosimetry data support this hypothesis as the total porosity jumps from 1.6% to 2.6% between 85 and 105 °C, and as the radius of pore access is shifted from between 0.01 and 1  $\mu\text{m}$  to between 1 and 10  $\mu\text{m}$  with increasing heating temperature (Fig. 6 and Fig. 7). This hypothesis

thus allows decoupling the thermal degradation affecting Carrara Gioia marble at the mesoscopic scale for the mild heating temperatures (40 – 85 °C), and at progressively higher scale (macroscopic) above 85 °C. Above 85 °C, granular decohesion caused by thermal weathering is so large that nonlinear phenomena at grain contacts are lost. The nonclassical nonlinearity thus provides a helpful alert tool for the detection of the damage initiation.

The transition point between 85 and 105 °C for the change in the nonlinear parameter behavior could also suggest that water content plays a role in the nonlinear parameter variations since it corresponds to water phase change. Indeed, water saturation level influences the nonlinear parameter measurements (Van Den Abeele 2002; Gao et al. 2022, 2023). Nevertheless, we do not think that change in water content linked to evaporation above 100 °C is responsible for the transition point between 85 and 105 °C since months after heating the nonlinear parameter  $\alpha$  is still greater for the sample heated at 85 °C than for other samples.

Overall, the results presented here are not consistent with an ability of marble to heal itself during the heating process. This hypothesis, presented by Johnson et al. (2004) to explain a diminution of the nonlinear parameter  $\alpha$  between measurements at ambient temperature and after heating at 200 °C for Asian white marble, fall short to explain the decrease of the resonant frequency  $f_0$  (Fig. 5), the microstructural evolution (Fig. 6), mechanical tests (Fig. 10) and observations made previously. Specifically, more porosity is created (Fig. 6) in the form of microcracks visible in SEM (Fig. 8 and Fig. 9) when heating temperature increases, which invalidates the idea of a healing of the grain contacts during the heating process. On the contrary, this study evidences a progressive decohesion of marble until complete disintegration occurring at 500 °C with sample breakage.

Along this trend, the nonlinear parameter  $\alpha$  exhibits a significant increase for temperatures ranging between 40 and 85 °C. This illustrates that weathering already appears in Carrara marble in the mild temperature range. This is consistent with the studies of Malaga et al. (2002) and Schouenborg et al. (2007). The evolution of the nonlinear parameter  $\alpha$  with heating temperature confirms from laboratory testing that exposure to temperatures as low as 40 °C can initiate damage at marble microscopic scale. In situ monitoring on buildings and stones shows that this temperature range can be reached on marble exposed outdoors (Viles 2005; Schouenborg et al. 2007). This extreme sensitivity of marble to thermal alteration could therefore easily affect marble heritage subjected to climatic variations.

## 5 Conclusions

The application of NRUS on Carrara Gioia marble samples heated at various temperatures allows monitoring thermal degradation at macroscopic (resonant frequency) and mesoscopic (nonlinear parameter) scales. In brief, the results clearly show that the resonant frequency gradually decreases with thermal damage. The evolution of porosity and pore access as the heating temperature rises could well explain this progressive loss of stiffness. The nonlinear parameter which increases up to 85 °C as it could be expected, decreases onward. This could result from the progressive loss of intergranular contacts as decohesion between marble grains increases.

The evolution of both parameters (resonant frequency and nonlinear parameter) indicates that thermal damage of Carrara Gioia marble already starts at temperatures as low as 40 °C. Such temperatures are often reached on facades or objects exposed outdoors even in the temperate climatic area. The induced increasing porosity and loss of stiffness make this originally non-porous, compact and hard material much more sensitive to any degradation processes which are responsible for stone degradation: chemical dissolution, sulphation, soluble salt crystallizations, freezing-thaw cycles, etc. Only an efficient protection against insolation or even an indoor exposure could be able to preserve Carrara Gioia marble artworks of the first stages of intergranular decohesion.

After this introductory work dealing with thermal damage, future works will be focused on simulating outdoor exposure conditions to study their effects on Carrara marble: samples will undergo thermo-hygic cycles at mild temperatures. Such cycling will allow investigating the fatigue effects on marble. NRUS that has proved to be an appropriate and accurate non-destructive technique, will be used for the long-term monitoring of marble samples ageing. Supplemental studies would also be necessary to see whether results presented here can be extended to other marble varieties and other rock types.

## Declarations

**Conflict of Interest** The authors have no relevant financial or non-financial interests to disclose.

## References

- Åkesson U, Lindqvist JE, Schouenborg B, Grelk B (2006) Relationship between microstructure and bowing properties of calcite marble claddings. *Bull Eng Geol Environ* 65:73–79. <https://doi.org/10.1007/s10064-005-0026-x>
- Averbakh VS, Bredikhin VV, Lebedev AV, Manakov SA (2017) Nonlinear acoustic spectroscopy of carbonate rocks. *Acoust Phys* 63:346–358. <https://doi.org/10.1134/S1063771017030022>
- Ferrero AM, Marini P (2001) Experimental Studies on the Mechanical Behaviour of two Thermal Cracked Marbles. *Rock Mechanics and Rock Engineering* 34:57–66. <https://doi.org/10.1007/s006030170026>
- Gao L, Shokouhi P, Rivière J (2023) Effect of Grain Shape and Relative Humidity on the Nonlinear Elastic Properties of Granular Media. *Geophysical Research Letters* 50:e2023GL103245. <https://doi.org/10.1029/2023GL103245>
- Gao L, Shokouhi P, Rivière J (2022) Effect of relative humidity on the nonlinear elastic response of granular media. *Journal of Applied Physics* 131:055101. <https://doi.org/10.1063/5.0073967>
- Genovés V, Carrión A, Escobar D, et al (2019) Nonlinear Acoustic Spectroscopy and Frequency Sweep Ultrasonics: Case on Thermal Damage Assessment in Mortar. *J Nondestruct Eval* 38:61. <https://doi.org/10.1007/s10921-019-0599-0>
- Gherardi F, Kapridaki C, Roveri M, et al (2019) The deterioration of Apuan white marble in contemporary architectural context. *Journal of Cultural Heritage* 35:297–306. <https://doi.org/10.1016/j.culher.2018.06.008>
- Grelk B, Goltermann P, Schouenborg B, et al (2004) The laboratory testing of potential bowing and expansion of marble. In: *Proceedings of the international conference on dimension stone*. Taylor & Francis Group plc, A.A. Balkema Publische, Prague, Czech Republic, pp 253–259
- Guyer RA, Johnson PA (1999) Nonlinear Mesoscopic Elasticity: Evidence for a New Class of Materials. *Physics Today* 52:30–36. <https://doi.org/10.1063/1.882648>

- Johnson P, Sutin A (2005) Slow dynamics and anomalous nonlinear fast dynamics in diverse solids. *The Journal of the Acoustical Society of America* 117:124–130. <https://doi.org/10.1121/1.1823351>
- Johnson PA (2005) Nonlinear Elastic Wave NDE I. Nonlinear Resonant Ultrasound Spectroscopy and Slow Dynamics Diagnostics. In: *AIP Conference Proceedings*. AIP, Golden, Colorado (USA), pp 377–384
- Johnson PA, Zinszner B, Rasolofosaon P, et al (2004) Dynamic measurements of the nonlinear elastic parameter  $\alpha$  in rock under varying conditions: NONLINEAR ELASTIC PARAMETER IN ROCK. *J Geophys Res* 109:. <https://doi.org/10.1029/2002JB002038>
- Kessler DW (1919) Physical and chemical tests on the commercial marbles of the United States. Department of Commerce
- Koch A, Siegesmund S (2004) The combined effect of moisture and temperature on the anomalous expansion behaviour of marble. *Env Geol* 46:. <https://doi.org/10.1007/s00254-004-1037-9>
- Köhler W (1991) Untersuchungen zu Verwitterungsvorgängen an Carrara-Marmor in Potsdam-Sanssouci. *Berichte zu Forschung und Praxis der Denkmalpflege in Deutschland, Steinschäden-Steinkonservierung* 2:50–53
- Lord Rayleigh (1934) The Bending of Marble. *Proceedings of the Royal Society of London Series A, Containing Papers of a Mathematical and Physical Character* 144:266–279
- Mahmutoglu Y (1998) Mechanical Behaviour of Cyclically Heated Fine Grained Rock. *Rock Mechanics and Rock Engineering* 31:169–179. <https://doi.org/10.1007/s006030050017>
- Malaga K, Lindqvist JE, Schouenborg B (2002) Experimental study on the variation in porosity of marble as a function of temperature. *Geological Society, London, Special Publications* 205:81–88. <https://doi.org/10.1144/GSL.SP.2002.205.01.07>
- Malaga-Starzec K, Åkesson U, Lindqvist JE, Schouenborg B (2006) Microscopic and macroscopic characterization of the porosity of marble as a function of temperature and impregnation. *Construction and Building Materials* 20:939–947. <https://doi.org/10.1016/j.conbuildmat.2005.06.016>
- Malaga-Starzec K, Panas I, Lindqvist JE, Lindqvist O (2003) Efflorescence on thin sections of calcareous stones. *Journal of Cultural Heritage* 4:313–318. <https://doi.org/10.1016/j.culher.2003.09.002>
- Marini P, Bellopede R (2009) Bowing of marble slabs: Evolution and correlation with mechanical decay. *Construction and Building Materials* 23:2599–2605. <https://doi.org/10.1016/j.conbuildmat.2009.02.010>
- Marini P, Bellopede R (2007) The Influence of the Climatic Factors on the Decay of Marbles: an Experimental Study. *American J of Environmental Sciences* 3:143–150. <https://doi.org/10.3844/ajessp.2007.143.150>
- Mechri C, Scalerandi M, Bentahar M (2019) Separation of Damping and Velocity Strain Dependencies using an Ultrasonic Monochromatic Excitation. *Phys Rev Applied* 11:054050. <https://doi.org/10.1103/PhysRevApplied.11.054050>
- Menningen J, Sassoni E, Sobott R, Siegesmund S (2021) Constraints of the durability of inorganic and organic consolidants for marble. *Environ Earth Sci* 80:370. <https://doi.org/10.1007/s12665-021-09664-w>
- Menningen RJ (2020) Ultrasonic tomography for the characterization of the weathering state of marble: A systematic study about influencing parameters. Georg-August-Universität Göttingen

- Migliori A, Sarrao JL (1997) Resonant ultrasound spectroscopy: applications to physics, materials measurements, and nondestructive evaluation. Wiley, New York
- Ostrovsky LA, Johnson PA (2001a) Dynamic nonlinear elasticity in geomaterials. *Riv Nuovo Cim* 24:1–46. <https://doi.org/10.1007/BF03548898>
- Ostrovsky LA, Johnson PA (2001b) Nonlinear dynamics of rock: Hysteretic behavior. *Radiophysics and Quantum Electronics* 44:450–464. <https://doi.org/10.1023/A:1017953331645>
- Payan C, Ulrich TJ, Le Bas PY, et al (2014) Quantitative linear and nonlinear resonance inspection techniques and analysis for material characterization: Application to concrete thermal damage. *The Journal of the Acoustical Society of America* 136:537–546. <https://doi.org/10.1121/1.4887451>
- Payan C, Ulrich TJ, Le Bas PY, Guimaraes M (2012) Quantitative linear and nonlinear resonant inspection techniques for characterizing thermal damage in concrete. In: *Proceedings of the Acoustics 2012 Nantes Conference*. Nantes, France, pp 2587–2592
- Peng J, Rong G, Tang Z, Sha S (2019) Microscopic characterization of microcrack development in marble after cyclic treatment with high temperature. *Bull Eng Geol Environ* 78:5965–5976. <https://doi.org/10.1007/s10064-019-01494-2>
- Primavori P (2015) Carrara Marble: a nomination for ‘Global Heritage Stone Resource’ from Italy. *Geological Society, London, Special Publications* 407:137–154. <https://doi.org/10.1144/SP407.21>
- Rasolofosaon P, Zinszner B, Johnson PA (1997) Propagation des ondes élastiques dans les matériaux non linéaires Aperçu des résultats de laboratoire obtenus sur les roches et des applications possibles en géophysique. *Rev Inst Fr Pét* 52:585–608. <https://doi.org/10.2516/ogst:1997061>
- Remillieux MC, Guyer RA, Payan C, Ulrich TJ (2016) Decoupling Nonclassical Nonlinear Behavior of Elastic Wave Types. *Phys Rev Lett* 116:115501. <https://doi.org/10.1103/PhysRevLett.116.115501>
- Remillieux MC, Ulrich TJ, Payan C, et al (2015) Resonant ultrasound spectroscopy for materials with high damping and samples of arbitrary geometry: RUS FOR ARBITRARY SHAPE AND HIGH DAMPING. *J Geophys Res Solid Earth* 120:4898–4916. <https://doi.org/10.1002/2015JB011932>
- Rivière J, Shokouhi P, Guyer RA, Johnson PA (2015) A set of measures for the systematic classification of the nonlinear elastic behavior of disparate rocks. *J Geophys Res Solid Earth* 120:1587–1604. <https://doi.org/10.1002/2014JB011718>
- Royer-Carfagni GF (1999) On the thermal degradation of marble. *International Journal of Rock Mechanics and Mining Sciences* 36:119–126. [https://doi.org/10.1016/S0148-9062\(98\)00169-7](https://doi.org/10.1016/S0148-9062(98)00169-7)
- Sáez-Pérez MP, Durán-Suárez JA, Castro-Gomes J (2024) Study of the correlation of the mechanical resistance properties of Macael white marble using destructive and non-destructive techniques. *Construction and Building Materials* 418:135400. <https://doi.org/10.1016/j.conbuildmat.2024.135400>
- Sassoni E, Graziani G, Ridolfi G, et al (2017) Thermal behavior of Carrara marble after consolidation by ammonium phosphate, ammonium oxalate and ethyl silicate. *Materials & Design* 120:345–353. <https://doi.org/10.1016/j.matdes.2017.02.040>
- Schouenborg B, Grell B, Malaga K, et al (2007) Testing and Assessment of Marble and Limestone (TEAM)—Important Results from a Large European Research Project on Cladding Panels. *J ASTM Int* 4:100855. <https://doi.org/10.1520/JAI100855>

- Sena Da Fonseca B, Ferreira Pinto AP, Piçarra S, et al (2021) Consolidating efficacy of diammonium hydrogen phosphate on artificially aged and naturally weathered coarse-grained marble. *Journal of Cultural Heritage* 51:145–156. <https://doi.org/10.1016/j.culher.2021.08.003>
- Siegesmund S, Menningen J, Shushakova V (2021) Marble decay: towards a measure of marble degradation based on ultrasonic wave velocities and thermal expansion data. *Environ Earth Sci* 80:395. <https://doi.org/10.1007/s12665-021-09654-y>
- Siegesmund S, Ruedrich J, Koch A (2008) Marble bowing: comparative studies of three different public building facades. *Environ Geol* 56:473–494. <https://doi.org/10.1007/s00254-008-1307-z>
- Siegesmund S, Ullemeyer K, Weiss T, Tschegg EK (2000a) Physical weathering of marbles caused by anisotropic thermal expansion. *International Journal of Earth Sciences* 89:170–182. <https://doi.org/10.1007/s005310050324>
- Siegesmund S, Weiss T, Tschegg EK (2000b) Control of marble weathering by thermal expansion and rock fabrics. In: *Proceedings of the 9th International Congress on Deterioration and Conservation of Stone*. Venice, pp 205–213
- Ten Cate JA, Shankland TJ (1996) Slow dynamics in the nonlinear elastic response of Berea sandstone. *Geophys Res Lett* 23:3019–3022. <https://doi.org/10.1029/96GL02884>
- Ulrich T, McCall KR, Guyer RA (2002) Determination of elastic moduli of rock samples using resonant ultrasound spectroscopy. *The Journal of the Acoustical Society of America* 111:1667–1674. <https://doi.org/10.1121/1.1463447>
- Van Den Abeele KE-A (2002) Influence of water saturation on the nonlinear elastic mesoscopic response in Earth materials and the implications to the mechanism of nonlinearity. *J Geophys Res* 107:2121. <https://doi.org/10.1029/2001JB000368>
- Van Den Abeele KE-A, Carmeliet J, Ten Cate JA, Johnson PA (2000) Nonlinear Elastic Wave Spectroscopy (NEWS) Techniques to Discern Material Damage, Part II: Single-Mode Nonlinear Resonance Acoustic Spectroscopy. *Research in Nondestructive Evaluation* 12:31–42. <https://doi.org/10.1080/09349840009409647>
- Viles HA (2005) Microclimate and weathering in the central Namib Desert, Namibia. *Geomorphology* 67:189–209. <https://doi.org/10.1016/j.geomorph.2004.04.006>
- Waragai T (2023) Influence of thermal cycling in the mild temperature range on the physical properties of cultural stones. *Journal of Cultural Heritage* 59:171–180. <https://doi.org/10.1016/j.culher.2022.12.001>
- Weiss T, Rasolofosaon PNJ, Siegesmund S (2002) Ultrasonic wave velocities as a diagnostic tool for the quality assessment of marble. *Geological Society, London, Special Publications* 205:149–164. <https://doi.org/10.1144/GSL.SP.2002.205.01.12>
- Wu Q, Li B, Jiang X (2023) Triaxial Test Study on Energy Evolution of Marble after Thermal Cycle. *Minerals* 13:428. <https://doi.org/10.3390/min13030428>
- Zhang Y, Ta X, Qin S (2022) Effect of heat treatment on physico-mechanical behaviour of a natural building stone: Laizhou dolomite marble. *Journal of Building Engineering* 47:103885. <https://doi.org/10.1016/j.jobe.2021.103885>