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Temperature induced internal stress in Carrara marble

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Abstract. Stone physical weathering, deterioration and damage (e.g. bowing, cracking, microfracturing) represent a serious problem for preservation of sculptural and architectural heritage objects. Although different mechanisms of such degradation might be responsible (e.g. chemical or biogenic), there is an understanding in the geological community that physical reasons for stone degradation and role of stress are of primary importance. In this work Carrara marble was a chosen for investigation: a calcitic type with ~20% of dolomite. Neutron diffraction was used to investigate the phase composition, the texture, and the strain/stress in calcite and dolomite phases in a bulk marble sample. Evolution of the stress state was studied by measuring strains in calcite and dolomite at two temperatures with clear evidence of thermally induced microstresses. Results are discussed in connection to the theory of composite materials and a micro-mechanical explanation of the general problem of marble deterioration is suggested.

Introduction

Durability is an important issue to consider when specifying stones as a cladding material for exterior exposure or using stone in sculpture or other artworks. The spectacular bowing behaviour of marble slabs has given a negative image to this material. The complete replacement of facade panels of some prestigious buildings like the Amoco building in Chicago [1], the Finlandia Hall in Helsinki, the Grand Arche de la Defense in Paris or the University Library in Göttingen [2], all made of marble coming from the Carrara area, are often cited as examples of the concerns for the durability of this material.

Detailed knowledge of the mechanisms and rates of decay for weathering and deterioration of marbles is of greatest interest for the protection and conservation of historical monuments [3]. Suffice it to say that Michelangelo's statue of David is carved from Carrara marble, the Pantheon and Trajan's Column are also made of this stone. One of the most extreme examples of marble damage is shown in Fig. 1.The numerous cases of damage to sculptures, architectural heritage objects or facade marble stones indicate that the deterioration of building stones depends mainly on climate conditions.

Different calcitic marble types, which are often used as cladding material, have been studied by other means than non-destructive stress analysis to elucidate possible mechanisms of marble deterioration. The lattice preferred orientation (crystallographic texture), grain shape preferred orientation, grain size distribution and grain interlocking were investigated (on-site analysis from building facades and laboratory tests) to study the combined effect of gravity, daily thermal cycles and moisture on the decay of marble properties, and particularly on the bowing phenomenon. All applied approaches reveal that the texture, in combination with the grain shape preferred orientation, control the intensity and anisotropy of marble deteriorationweathering behaviour [4, 5].

(a)  (b) 

Fig. 1. Sculpture in the Orangerie of Potsdam-Sanssouci (a) in its original shape and (b) its total damage after 110 years of exposure.

The role of thermal cycling in the deterioration of marbles and its connection to the stress state and micro-cracking was demonstrated in several studies. Kessler (1919) found that repeated heating may lead to permanent dilatation owing to micro-fracturing. Based on laboratory testing, Logan et al. [1] explained the bowing of marble slabs on the Amoco building as a result of anomalous expansion-contraction behaviour of calcite together with the release of locked residual stresses. It has been shown that weathering behaviour is influenced by anisotropic thermal expansion and existing cracks [3]. In [6] it was shown that stress generated during the geological history of the rock could be responsible for the bowing intensity.

Neutron diffraction, although much rarer, has also been a useful tool and a non-destructive method to investigate the texture, and the spatial and orientation dependence of strain in a bulk marble sample. It was demonstrated in earlier investigations [7] of texture and residual strain by neutron time-of-flight (TOF) diffraction using the neutron TOF texture diffractometer SKAT [8] and the strain- stress diffractometer EPSILON-MDS [9] at JINR, Dubna (Russia).

This study focuses on a more detailed investigation of a Carrara marble in different environmental conditions with deeper research of the important factors influencing marble deterioration. The purpose of the research is to reproduce closely different environmental factors which are known to be important in the process of deterioration of marble and study them in-situ in a non-destructive neutron diffraction stress experiment. The analysis of the thermally induced stresses is reported in this paper.

Marble: thermal and mechanical characterization

The temperature effects on the stress state of marble are at the focus of the current study. Several important factors must be taken into account: (i) as much as 20 vol.% of dolomite can be present in the selected samples; (ii) calcite has extreme thermal expansion anisotropy, linear expansion coefficient in the c-axis direction is $\alpha_c = 26\times10^{-6}$ K^{-1} while in perpendicular direction it is negative, $\alpha_a = -5\times10^{-6}$ K^{-1}; (iii) dolomite's thermal expansion coefficient in the c-axis direction is the same as for calcite, $\alpha_c = 26\times10^{-6}$ K^{-1}, but in the perpendicular direction it is of the opposite sign to calcite, $\alpha_a = +5\times10^{-6}$ K^{-1} [10]; (iv) orientation anisotropy (crystallographic texture) is usually present in marbles since it is plastically soft material, thus the properties are modulated by texture; and (v)

although close, the elastic properties of calcite and dolomite are somewhat different: the quasi-isotropic value of Young's modulus for calcite is 84 GPa vs. 118 GPa in dolomite [11]. All these factors are important for the micromechanical interaction of phases and result in a specific microstress state under temperature changes, heating/cooling, and can be investigated quantitatively and non-destructively using neutron diffraction.

Samples: Carrara marble

For the present project Carrara marble was chosen because it is not only a popular material, but also it is the most well studied in many physical aspects such as texture, microstructure etc. Freshly cut material from a marble quarry in Carrara (Italy) was used for testing. The samples were cut and marked correspondingly in regards to the geologically fixed coordinate system shown in Fig. 2. For the neutron strain experiments three types of samples were cut: (a) 100×100×100 mm^3 (b) 30×40×100 mm^3 (c) 20×20×20 mm^3 (two samples).

Fig. 2. (a) Samples of Carrara marble and (b) their geological framework. The larger cube-like marble samples measure100 mm on side.

Neutron diffraction study: phase, texture and strain analysis

Three kinds of characterization were conducted by means of neutron diffraction using instruments at the Australian research reactor OPAL.

(i) Quantitative phase analysis was done using the neutron high-resolution powder diffractometer ECHIDNA. Neutron diffraction patterns were collected in the range of 4° to 163° using wavelength of 1.62 Å with sample spinning to reduce effects of texture and obtain better grain statistics. The patterns were treated using the Rietveld refinement technique to yield volume fractions of the calcite and dolomite phases. Two marble samples, 20×20×20 mm^3, were measured in order to study sample-to-sample variation in the analysis.

(ii) Measurements of texture with neutron diffraction were carried out using the KOWARI diffractometer at wavelength 2.84 Å using the 20×20×20 mm^3 cube samples. Diffraction patterns were measured by 2D PSD at detector angles of 60° and 74°. Due to the relatively large angular coverage of 15°, it was possible to resolve (104) and (006) pole figures of calcite and dolomite in one detector position and (110) and (113) pole figures in the other position. In the measurements, an approximately 5°×5° equiangular mesh of complete pole figures was achieved.

(iii) Neutron stress experiments on the strain scanner KOWARI involved a specially designed sample environment unit (a temperature chamber) in order to control temperature (from room temperature to 100˚C). A sample with dimensions 30×40×100 mm^3 was used in measurements with

a gauge volume 10×10×10 mm^3. Two phases, calcite and dolomite, were measured in the same experimental setup twice, at room temperature and elevated temperature of 100˚C, therefore the temperature rise was 80˚C. Measurements were done in the main plane of the sample, 40×100 mm resulting in a 2D mesh with 3×9 points. Due to poor grain statistics, known from earlier trials, the experiment involved not just the standard 3 perpedicular (normal) directions but many more. For calcite as many as 282 directions were tested, each measured for 10 sec. For dolomite, due to its smaller volume fraction and weak diffraction signal, the number of directions was cut to 65 while measurement time incresed to 80 sec.

Two small samples, 20×20×20 mm^3 cubes, were used as a reference, "d_0" sample, measured in 360 directions for 60 sec exposure time each and then averaged. The measured d-spacing data sets from two different temperatures were treated using this d_0 value obtained at room temperature to calculate strains and then stress tensor components were evaluated from the $\sin^2$psi-fit of many strain values. The example in Fig. 3 demonstrates such data analysis. Over 27 measurement positions the average χ^2-value of 1.5 for calcite and 1.0 for dolomites suggests that grain statistics and neutron counting statistics were sufficiently equilibrated in the measurements.

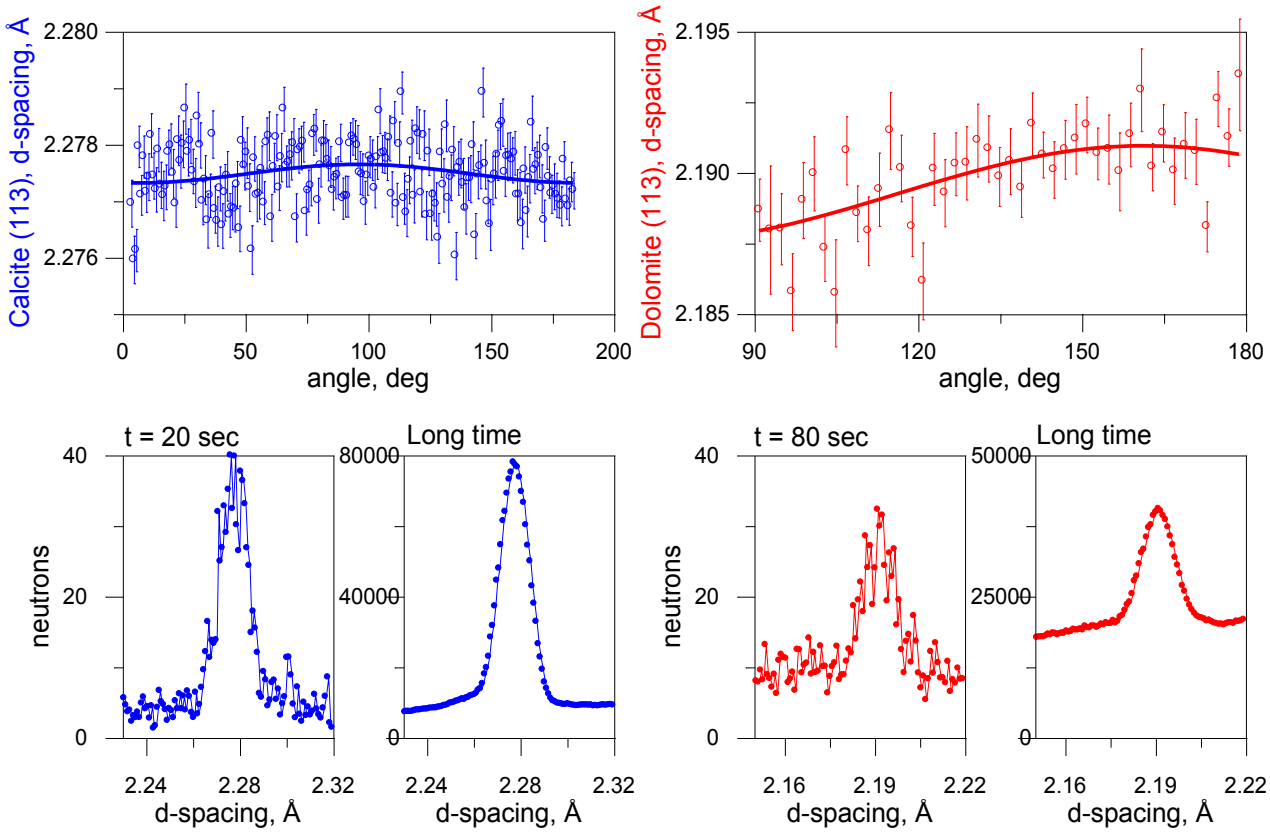

Fig. 3. Examples of multiple direction stress fitting for calcite and dolomite. Symbols are experimental points, solid line is a $\sin^2\psi$ -fit (only the part of the data points that belong to the same plane is shown).

(iv) The Young's modulus was measured with the Impulse Excitation Techniques for two samples, one that was intended for in-situ neutron measurements and another being a control sample. The two samples were measured twice, before and after thermal in-situ cycling. Because of method accuracy better than 1 GPa, an accurate measure of potentially accumulated damage was available.

Results and discussion

(i) Phase analysis of just two cube samples showed large local variation of the dolomite amount in the selected marble pieces, 28% and 18% of volume fraction. It is not entirely surprising taking into account the grain size and very non-uniform distribution of dolomite that can be seen in Fig. 2 as darker areas in comparison with white calcite. Since such a big difference was obtained for samples with dimensions 20×20×20 mm^3, even bigger variation in the volume fraction is expected in the stress experiment when the gauge volume is only 10×10×10 mm^3.

(ii) To demonstrate the strength of the texture of calcite and dolomite (006) pole figures are shown in Fig. 4. Even though the dolomite seems to have a sharper texture it might be due to the fact that it is a minor phase and statistical uncertainties might lead to larger min/max variations. Results of the texture analysis (ODF reconstruction by MTEX [12]) were used to evaluate anisotropy of the physical properties which are also shown in Fig. 4 to illustrate their correlations with the pole figures. Although clear anisotropy is evident and correlate with the basal pole figure, the small numerical variation between min and max values make the assumption of isotropy a good approximation. In the same way, the thermal expansion coefficient can be evaluated from texture

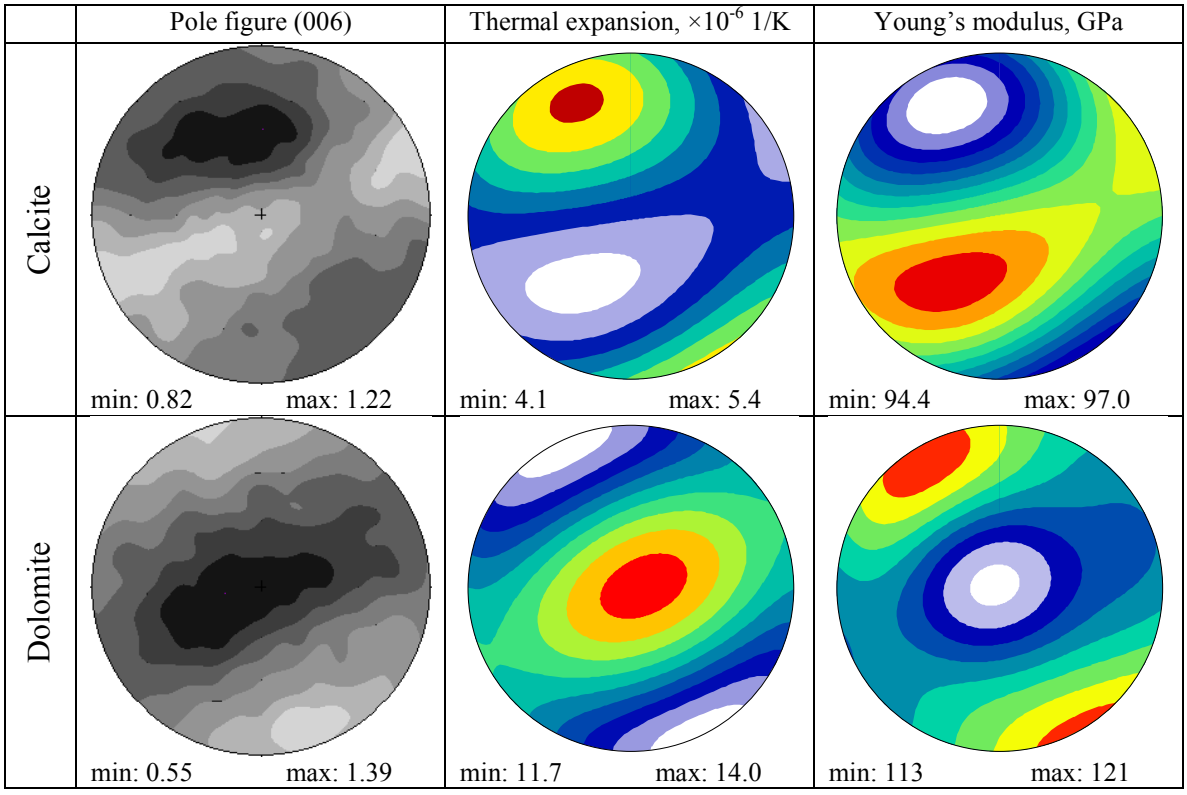

Fig. 4. Experimental textures and physical properties computed therefrom.

(Fig. 4) and the isotropic approximation seems to be also reasonable. The marble properties when averaged over two phases are expected to have even less anisotropy judged by positions of max/min values on the properties diagrams.

(iii) Using a constant d_0 approximation and the assumption of constant phase composition (77% calcite – 23% dolomite, average of the experimental data) stresses were calculated and separated into macro- and micro-stresses using the standard procedure for multi-phase materials [13]. In the initial stress state, some variation of stress was noticed with microstresses being lower on the edges of the sample indicating, most likely, damage during sample cutting out of a bigger block. This variation of some 20-30 MPa has not influenced the differential thermally induced stress that has

demonstrated uniformity and isotropy. Because of that all 27 measured points and 3 normal stress components were treated statistically, as an ensemble of 81 measurements of the same thermal hydrostatic microstress, and results of such treatment are shown in Fig. 5a. Following this approach, the whole data set was reduced to only two stress values characterising thermally induced hydrostatic micro-stress in calcite, 9 ± 3 MPa, and dolomite, -31 ± 9 MPa.

Although interpretation of the experimental results is unambiguous and the observed effects are thermally induced, it is useful to evaluate the microstresses based on a simple quasi-isotropic model, since little anisotropy exists in the samples and it can be described well enough in the isotropic approximation. The Hashin-Shtrikman bounds [14] were calculated assuming isotropic and particulate microstructure that provided a certain range of matrix-inclusion interaction scenarios (from dolomite inclusion in calcite matrix to calcite inclusion in dolomite matrix). The calculated elastic response for the both phases is presented in Fig. 5b to the nominal temperature change of $\Delta T = 60°C$ (rather than experimentally set $\Delta T = 80°C$) to achieve an agreement with the experimental data. This discrepancy might be a result of possible biases (e.g. setpoint bias of temperature control), statistical variations (e.g. local variations of phase composition), inaccuracy of the approximations used and change in microstructure (e.g. selective microcracking), but most probably this is the sum of all of the above.

(iv) Young's modulus measurements demonstrated beyond doubt that the sample acquired a certain amount of damage due to a single thermal cycling: Young's modulus of the test sample degraded from 56.8 ± 0.6 GPa to 44.6 ± 0.6 GPa, while the control sample has not shown any change within the error bars, 57.3 ± 0.6 GPa and 58.3 ± 0.6 GPa. Since no phase transformations can be involved in the studied temperature range and plasticity also can be excluded for there was with no external loading, the stress relief can be unambiguously attributed to microcracking.

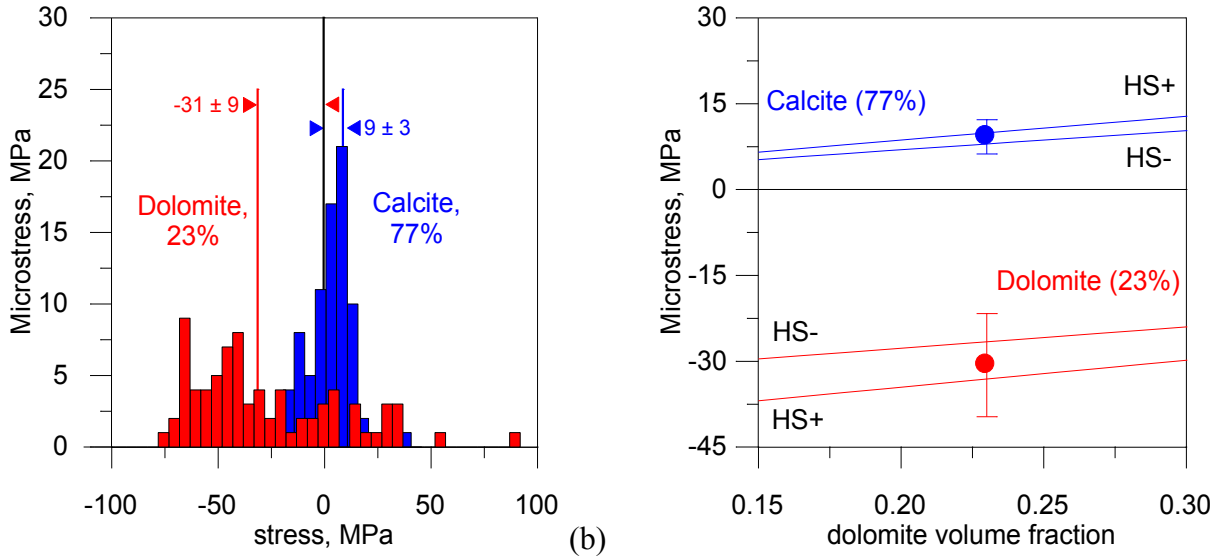

Fig. 5. (a) The histogram of the thermal stress values for calcite (blue) and dolomite (red) shown with their averages (blue and red lines). Microstress values for calcite and dolomite measured from their average (black line). (b) The experimental stress values (symbols) judged against Hashin-Shtrikman bounds (lines) calculated using a quasi-isotropic approximation.

Conclusions

Although not easy, stress measurements in geological materials, such as marble, are feasible and valuable characterization can be provided. The major difficulties are (i) the necessity to measure several phases, in the case of marble calcite and dolomite; (ii) due to the usually coarse grain microstructure, stress measurements require relatively large gauge volume and therefore (iii) up to

several hundred directions might be required to get a statistically significant result. Other technical difficulties include (iv) necessity to work with rather large wavelength of ~3 Å that does not usually lie within the optimum conditions for a residual stress diffractometer, (v) relatively low intensity of the diffraction peaks due to low crystal symmetry as well as (vi) complicated diffraction pattern due to multiple phases and the low crystal symmetries of many minerals.

For our material of choice, Carrara marble, it was shown that thermally induced stress can be responsible for weathering and deterioration of the marble. It was shown experimentally that one-time thermal cycling gave rise to thermally induced microstress. This stress was also predicted within a model approach in the conditions of weak crystallographic texture in both phases that was also confirmed in a neutron diffraction texture experiment. A relatively simple quasi-isotropic micromechanical model was assumed and used for evaluation of microstresses in the two-phase system that was in reasonable agreement with experimental results. Based on results of the neutron diffraction stress experiment and Young's modulus tests, no macro-damage was detected due to thermal straining, but a significant change in micro-stress state caused micro-cracking in the test sample. Although the intentionally exaggerated temperature change might not be exactly relevant to the real daily and seasonal temperature variation experienced by marble, the principal mechanism of microcracking occurrence was experimentally confirmed. On the other hand, smaller natural temperature variations but in much greater numbers during long periods of time might result in even greater accumulated damage, as shown by some historical examples (for example, see Fig. 1).

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