

Texture, spatial and orientation dependence of internal strains in marble: a key to understanding the bowing of marble panels?

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Abstract: A Carrara marble sample was measured using neutron time-of-flight diffraction on its crystallographic preferred orientation (texture), a strain scan through the sample and strain pole figures to explain the effect of deformation of marble plates. Strong compressional residual strain values of up to $\epsilon = -1.3 \times 10^{-3}$ measured with residual strain pole figures in a virgin bulk sample have been found. Obviously, the magnitude of residual strain depends on the sample size. Features of the observed texture pole figures and internal strain pole figures are related to each other by their sample orientations. Texture and residual strain measurements were combined with investigations of thermal expansions under dry and wet conditions in different directions to the main stress direction.

Numerous cases of damage to sculptures, architectural heritage or façade marble stones indicate that the deterioration of building stones depends mainly on climate. The clear morphological alteration of marble even within a short exposure time (e.g. Grimm 1999) is well known. Recently, it has also been proposed that physical weathering is the initial stage of deterioration of marble (see Siegesmund *et al.* 2000).

Durability is an important issue to consider when specifying stones as a cladding material for exterior exposure. But the spectacular bowing behaviour of marble slabs has given a negative image to this material. The complete replacement of façade panels of some prestigious buildings like the Amoco building in Chicago (Logan *et al.* 1993), the Finlandia Hall in Helsinki, the Grand Arche de la Defense in Paris or the University Library in Göttingen (see Fig. 1), all made of marble coming from the Carrara area, are often cited as examples of the concerns for the durability of these materials. However, bowing was frequently reported from ancient gravestones (e.g. Grimm 1999). Detailed knowledge of the mechanisms and rates of decay is important in order to protect historical monuments, as well as to reduce loss of marble during reconstruction. Kessler (1919) found that repeated heating may lead to permanent dilatation owing to microfracturing. Based on laboratory testing, Logan *et al.* (1993) 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. Hypotheses proposed by other researchers have assumed the presence of moisture or gravity variation in the material (e.g. Winkler 1994). The reasons for the observed deformation are still under discussion. It turns out, for example, that natural marble also shows complex anisotropic weathering behaviour. It has been shown (Siegesmund *et al.* 2000; Koch & Siegesmund 2002) that weathering behaviour is influenced by thermal expansion, existing cracks (Siegesmund *et al.* 2000) and preferred crystallographic orientation (here referred to as texture) of calcite and/or dolomite (Ruedrich *et al.* 2001; Zeisig *et al.* 2002).

The present paper focuses on the effects of internal stresses. To verify the theory that locked-in stress – that is, stress generated during the geological history of the rock – could be responsible for the bowing intensity, fresh material from a marble quarry in Carrara (Italy) was used for testing. Neutron diffraction was used as a non-destructive method to investigate the texture, and the spatial and orientation dependence of strain in a bulk marble sample. Based on earlier investigations (ScheffzüK *et al.* 2004) of texture and residual strain by neutron time-of-flight (TOF) diffraction, this study will focus on a more detailed investigation of a Carrara marble sample. To do this, the neutron TOF texture diffractometer SKAT (Ullemeyer *et al.* 1998) and the strain–stress diffractometer EPSILON-MDS (Frischbutter *et al.* 2000; Walther *et al.* 2000) at JINR, Dubna

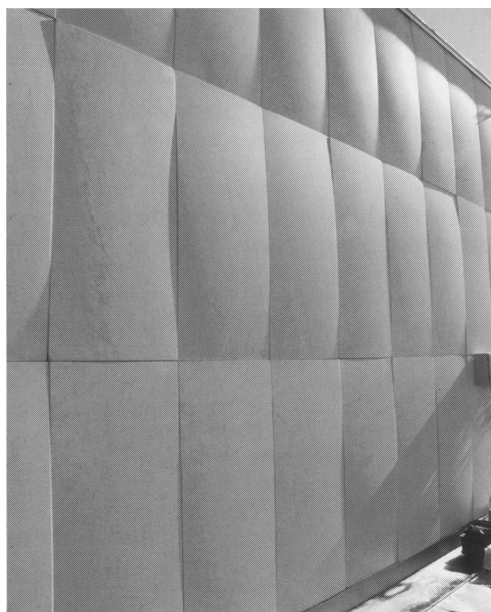


Fig. 1. Typical bowing behaviour of façade panels at the University Library in Göttingen.

(Russia) have been employed. The measured spectra were processed with a program developed recently to extract detailed Bragg diffraction lines by fitting the peak parameters. Such an approach allows one to demonstrate the crystallographic texture as well as the internal strain. Much attention was paid to accuracy and methodology, and the SKAT texture instrument was used to determine strain pole figures in relation to the residual strain determined by strain scans with higher resolution than the EPSILON-MDS strain diffractometer.

To constrain the bowing to internal strain relationship, the sample was also investigated with respect to the rock fabric, *in situ* stresses and thermal expansion behaviour under dry and wet conditions.

Rock sample and microfabrics

An oriented block of around 1 m³ was taken from the Carrara area (Fig. 2). The sample was oriented with respect to the foliation plane ([xy] plane while [z] is perpendicular to the foliation) and the principal stress directions σ_1 , σ_2 and σ_3 . The stress directions were measured by the over-coring method and revealed to be: $\sigma_1 = (5.13 \pm 1.07)$ MPa, $\sigma_2 = (3.72 \pm 0.61)$ MPa and $\sigma_3 = (1.89 \pm 1.32)$ MPa (Alnaes pers. comm.).

The investigated Carrara marble sample was bright white and contained locally different

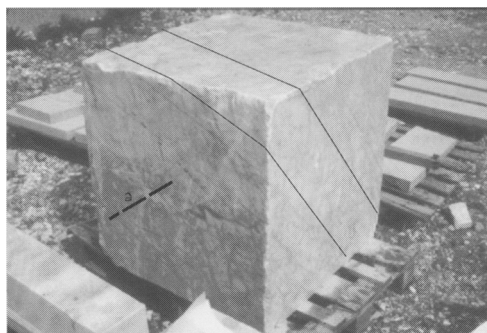


Fig. 2. Fresh marble block that was used to obtain the sample material for the present investigations. Black lines reflect the foliation. Note that the block is in a situation in which the platform represents the upper surface in nature. For a nature-like orientation, the block must be rotated 180° around the $\langle a \rangle$ -axis.

concentrations of typically grey veins. The veins were folded and showed a streak-like distortion, and usually varied in thickness from 1 to 10 mm. Locally, at a decimetre-scale, a preferred orientation of the grey veins could be observed. The microfabrics were homogeneous and fine grained. The sample showed a nearly perfectly recovered grain fabric with straight grain boundaries and frequent 120° triple junctions (Fig. 3). The grain size varied from 140 to 500 μm , the averaged grain size was about 250 μm . Only a very few grains were twinned. A detailed description of the twinning mechanisms and the application for palaeostress estimation is described by Rowe & Rutter (1990). The macroscopically visible grey veins

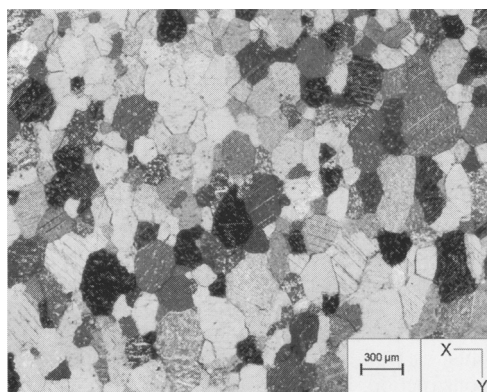


Fig. 3. Microscope observations of Carrara marble microstructure: homogeneous nearly perfect recovered microfabrics and fine-grained material, grain size 140–500 μm , grain fabric with straight grain boundaries and frequent 120° triple point junctions.

were more fine grained, but showed very strong undulose extinction. The undulose extinction and the formation of subgrains occurred to such an extent that individual grains were difficult to detect. Grain boundaries were interlobate and a great number of fluid inclusions or graphite are probably responsible for the grey colour of the veins.

Experiment

In general, crystalline materials can be investigated by diffraction methods, so that by fulfilling the Bragg law

$$2d \sin \Theta = n\lambda \quad (1)$$

(with d the lattice spacing, Θ the diffraction angle and λ the wavelength), Bragg diffraction lines corresponding to their Miller indices are detectable. Based on the high penetration depth of neutrons in matter, neutron diffraction enables one to investigate samples in the centimetre range. In particular, the neutron TOF technique carries out the simultaneous detection of all Bragg reflections in a given range of wavelengths. This technique is well suited to investigating minerals because the peak separation of lines in a line-rich diffraction pattern is possible as a result of the high resolution common for minerals with lower crystal symmetry.

At the pulsed research reactor IBR-2 in Dubna, the diffractometers EPSILON-MDS for strain-stress analysis and SKAT for texture analysis have a neutron flight path of about 101.3 (EPSILON-MDS) and 103.8 m (SKAT) respectively, and makes it possible to investigate Bragg diffraction lines with lattice spacing of up to $d = 5.5 \text{ \AA}$ simultaneously.

The spherical sample method of Tobisch & Bunge (1972) is used to place the sample completely into the neutron beam. Consequently, a spherical bulk sample with a gauge volume of up to 100 cm^3 can be investigated without geometrical corrections.

Figure 4 demonstrates the sum of all 1368 spectra (for $\varphi = 0^\circ - 90^\circ$, $\vartheta = 0^\circ - 360^\circ$ with $\Delta\varphi = \Delta\vartheta = 5^\circ$) of the SKAT diffractometer for the calcite powder sample; lattice spacings and their corresponding Bragg reflections are also indicated. The mineral content of other phases, such as graphite, quartz and dolomite, is lower than 5%. The background (Bkg) of the Bragg diffraction peak (see Fig. 5) has been approximated by a linear relationship with the background parameters b and k :

$$\text{Bkg} = kt + b. \quad (2)$$

The non-symmetrical Bragg peak was fitted by the bell-shaped asymmetrical Gaussian function of the

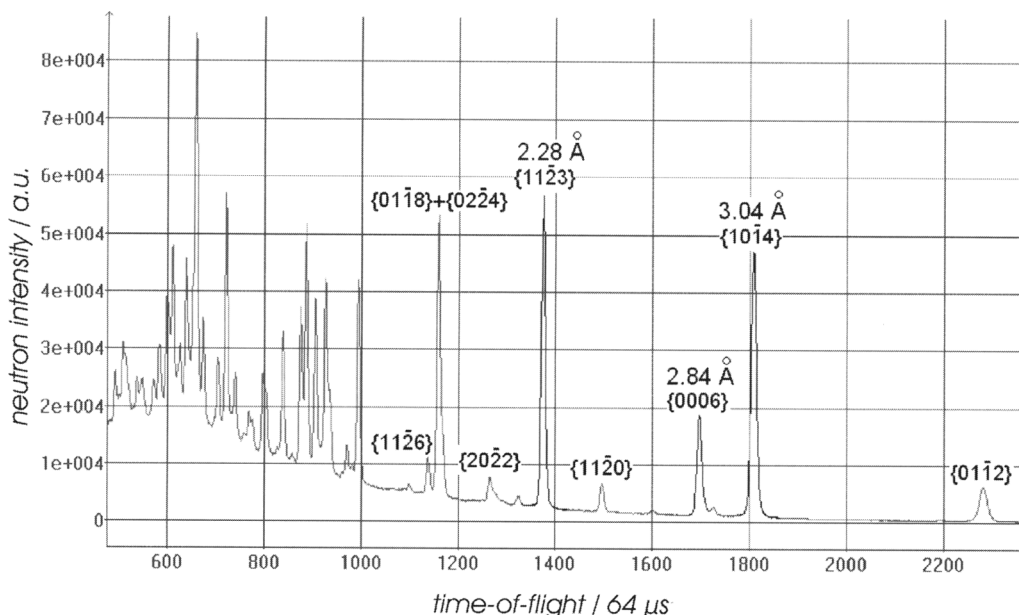


Fig. 4. Sum of all the 1368 spectra for calcite powder (SKAT). Bragg reflections indicated by their Miller indices and the corresponding d -values are presented.

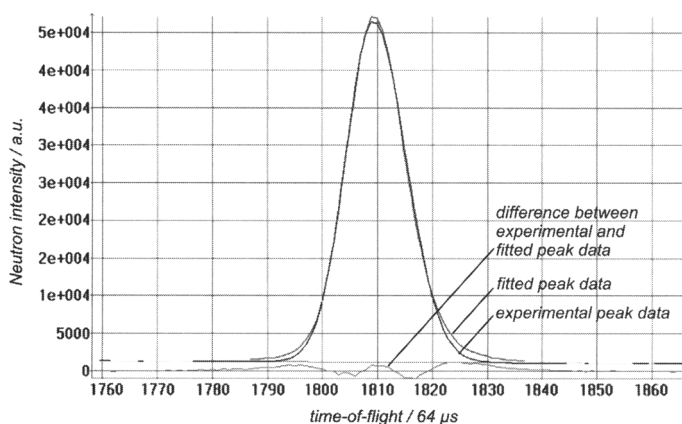


Fig. 5. Individual peak $\{10\bar{1}4\}$ approximation: experimentally measured peak, fitted peak, and the difference between measured and fitted curves are plotted.

following form:

$$I(t) = \begin{cases} A_0 \exp\left(-\frac{(t-t_0)^2}{2\sigma_1^2}\right) & t \leq t_0 \\ A_0 \exp\left(-\frac{(t-t_0)^2}{2\sigma_2^2}\right) & t \geq t_0 \end{cases} \quad (3)$$

Here, $A_0(\varphi, \vartheta)$ describes the amplitude, $t_0(\varphi, \vartheta)$ the position and $\sigma_i(\varphi, \vartheta)$ are different half-widths at the half maximum of the Bragg peak. Four parameters with their uncertainties ΔA_0 , Δt_0 , $\Delta \sigma_1$, $\Delta \sigma_2$ can be determined for each individual Bragg reflection peak by processing all of the 1368 diffraction pattern. Not only the amount of data has to be processed, but also a large quantity of numerical operations has to be fulfilled. Using the parameters $A_0(\varphi, \vartheta)$, $\sigma_1(\varphi, \vartheta)$, $\sigma_2(\varphi, \vartheta)$, one can produce texture pole figures, the parameter $t_0(\varphi, \vartheta)$ is used to produce the internal strain pole figures.

Figure 5 illustrates the approximated function and the quality of the fit of an individual Bragg peak. One can see that the difference between the experimental and fitted curves is even smaller than the peak background. This is the criteria for high accuracy of the peak fit on one side and of the reasonable choice of the peak shape on the other side.

Texture

The physical properties of calcite, such as thermal expansion and elastic modulus, are highly anisotropic. Consequently, it is necessary to know whether a sample has a crystallographic preferred orientation (texture) to predict the material behaviour. Although, a strong texture is usually formed during plastic deformation, a weak one does not usually demonstrate primary plastic deformation to any high degree.

A cubic sample (edge length 80 mm) was investigated with the SKAT diffractometer. The powder, prepared from the sample with a grain size of 50 μm , was used as the texture- and strain-free reference of the sample. The Bragg diffraction lines of the trigonal calcite shown in Figure 4 were used to investigate texture and strain. Only those Bragg diffraction lines that do not overlap and have the best peak/background ratio were chosen to analyse the peak parameters. The (0006) Bragg reflection peak was used because the pole figure for this crystallographic index corresponds to the distribution of the c -axis, which is the most informative. The accuracy of the peak position estimation obtained for the calcite powder sample is illustrated in Figure 6. Because of the non-spherical sample geometry, the texture data have been corrected by their integral peak-background relation (see Nikolayev *et al.* 2005).

The measured texture of sample g4 shows a low texture strength (cf. Fig. 7). The texture could be characterized as an incomplete fibre texture or the one with very elongated components. The small circle distribution on the $\{10\bar{1}4\}$ pole figure demonstrates evidence for the incomplete fibre texture. The minimum value on all pole figures is larger than 0.69 m.r.d. (multiple of random distribution) and the maximum value is less than 1.25 m.r.d. The smallest minimum value among all pole figures gives an estimate of the volume part of the grains that does not have a preferred orientation. That means that more than 70% of the grain volume fracture is distributed uniformly and only a small volume fracture has a weak preferred orientation. Thus, the measured sample has a very weak texture. The marble block from which the sample was cut possesses an homogeneous texture.

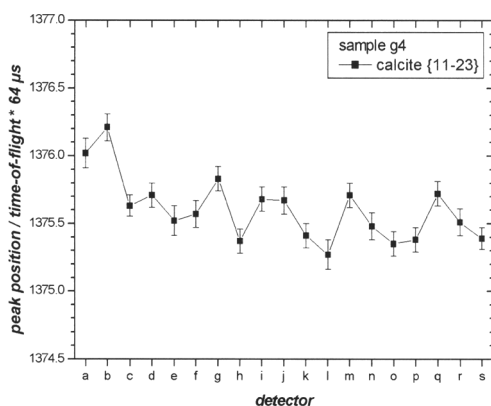


Fig. 6. Dependence of the peak position from the detector at the SKAT diffractometer, the error bars demonstrate the quality of peak position reconstruction for the powder sample.

Residual strain

In mechanics the definition of a strain is derived from a displacement between 'loaded' and

'unloaded' states. In general, the medium is considered contiguous. However, at the scale of the crystallographic lattice the medium could not be considered as a contiguous one. Nevertheless, elastic stress modifies the lattice distances that can be observed by diffraction experiments. So, internal or macroscopic strain can be detected by diffraction methods.

The macroscopic intracrystalline strain is defined as:

$$\epsilon^{hkl} = \frac{d^{hkl} - d_0^{hkl}}{d_0^{hkl}}. \quad (4)$$

Using the neutron TOF technique the d -values correspond with the detected time channels, as seen in Figure 4. Bragg diffraction peaks $(10\bar{1}4)$ and $(11\bar{2}3)$ were analysed using the measured spectra for sample g4. Utilizing powder measurements to estimate the stress-free state, macroscopic internal strain was obtained for this sample. Figure 7 displays the corresponding texture and strain pole figures. Qualitatively, strain pole figures are very similar despite the fact that their corresponding texture pole

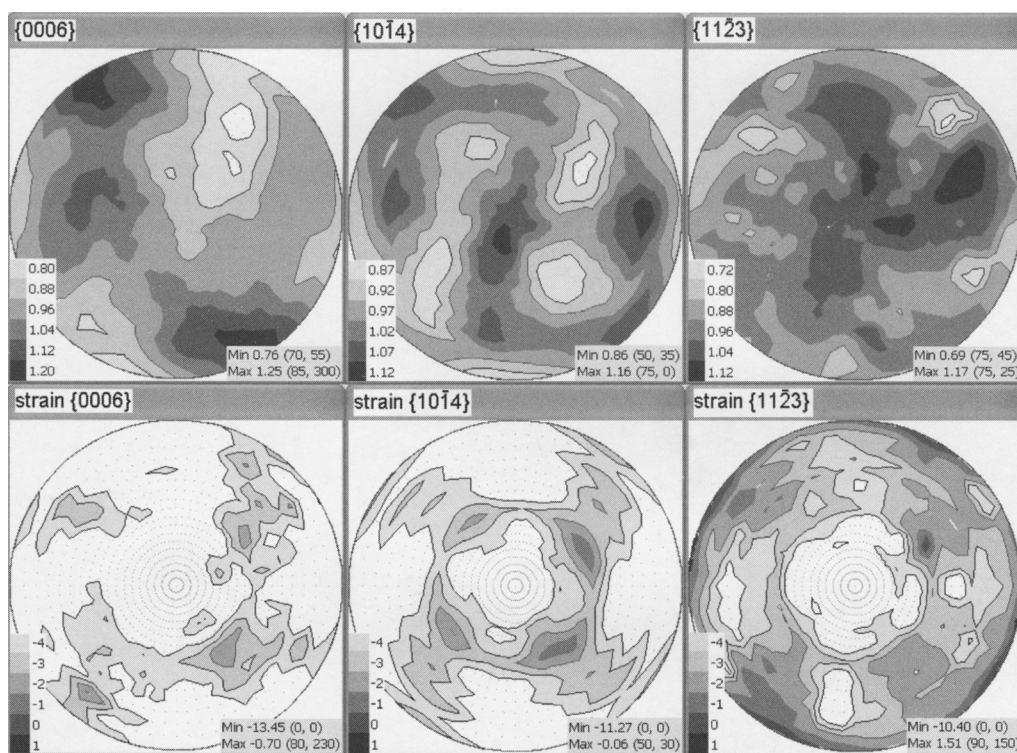


Fig. 7. Experimental pole figures (equal area projection; upper row) and internal strain pole figures (ϵ in 10^{-4} , lower row) for sample g4.

figures are different. It means that the microscopic strain, calculated by using different diffraction lines, gives similar magnitudes and features. If the internal strain tensor has constant values then the index surface is ellipsoidal. As one can see from the strain pole figures, they are not ellipsoidal, i.e. the strain field in the studied sample has a much more complicated character. Consequently, the internal strain in the studied sample is not uniform. The strain maxima in Figure 7 are bent over the foliation plane by about 45° .

Next to measurements of sample g4 on SKAT, detailed studies of the sample were carried out on the EPSILON-MDS diffractometer. Figure 8 displays the specific directions for which neutron diffraction patterns were collected by a gauge volume of $5 \times 5 \times 5 \text{ mm}^3$. The sample was translated on the goniometer table by steps of 9 mm to carry out strain scans. Strain values are plotted at various sections. Figures 9 and 10 display the strain values for the Bragg diffraction lines $(10\bar{1}4)$ and $(11\bar{2}3)$. Position points of the sample were measured with an exposition time of 2 h at each position and marked by $\varepsilon_2, \dots, \varepsilon_8$. Afterwards, the sample was rotated about the $[z]$ -axis by 175°

counter-clockwise and a further scan was carried out. The corresponding positions are marked by $\varepsilon'_2, \dots, \varepsilon'_8$. Figure 10 demonstrates in the upper row (Fig. 10a, b) the strain data of scan 1 and in the lower row (Fig. 10c, d) the strain data of another scan (scan 2). The figures reflect the strain inhomogeneities. Furthermore, the upper row shows the strain of two different peaks $(10\bar{1}4)$ and $(11\bar{2}3)$ for the collimators 7 and 8, whereas the lower row shows these reflections $(10\bar{1}4)$ (Fig. 10c) and $(11\bar{2}3)$ (Fig. 10d) for two directions $[x]$ and $[z]$, perpendicular each to other.

The main stress directions determined by mechanical testing with the over-coring method (Alnaes pers. comm.) lies in the foliation plane. They were used as initial data, with the following values in the polar coordinate system:

$$\sigma_1 = (5.13 \pm 1.07) \text{ MPa} \quad (\varphi = 61.7^\circ, \vartheta = 218^\circ)$$

$$\sigma_2 = (3.72 \pm 0.61) \text{ MPa} \quad (\varphi = 77.3^\circ, \vartheta = 121.2^\circ)$$

$$\sigma_3 = (1.89 \pm 1.32) \text{ MPa} \quad (\varphi = 31.5^\circ, \vartheta = 10.9^\circ).$$

Figures 9 and 10 demonstrate that strain values obtained on different crystallographic diffraction

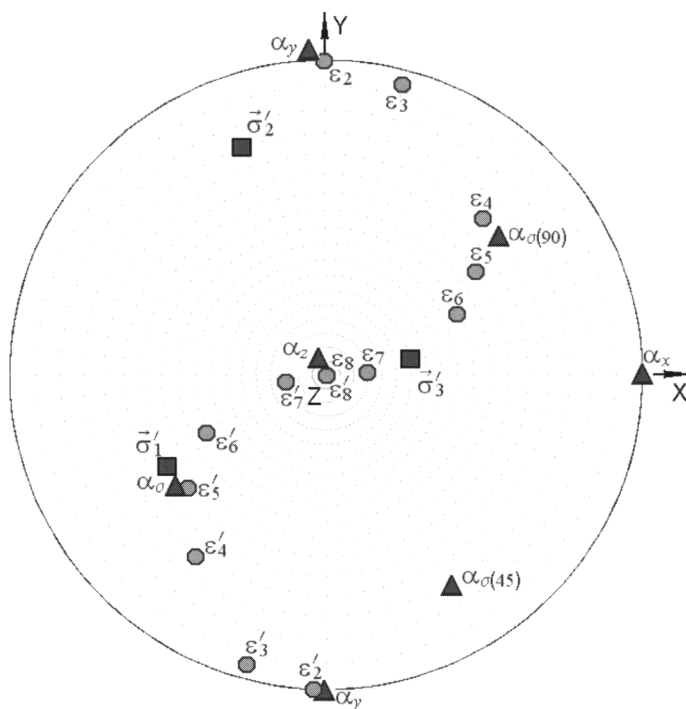


Fig. 8. Directions measured with the EPSILON-MDS diffractometer, stress main axes σ_1 , σ_2 and σ_3 , were obtained by an over-coring technique and orientations of samples used for thermal expansions studies (■, directions determined by mechanical test data; ▲, directions determined by bowing studies; ●, directions determined with neutron diffraction at EPSILON-MDS).

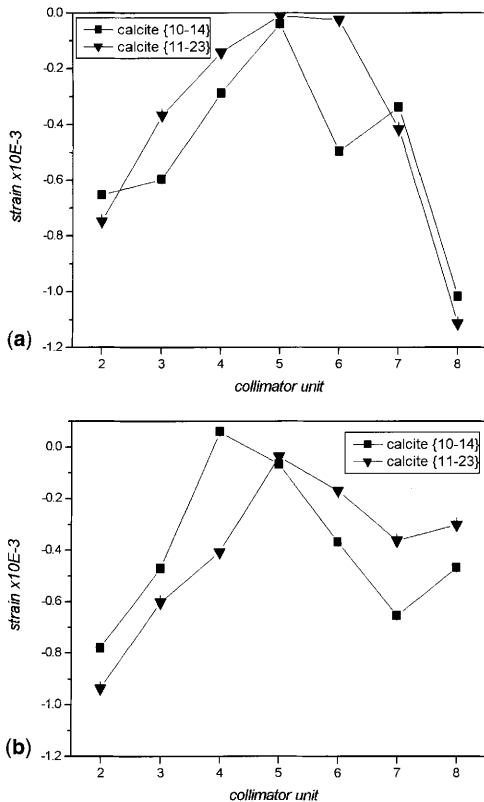


Fig. 9. Strain values measured at EPSILON-MDS at neighbouring scan positions in the sample g4 with seven collimator units.

lines are very similar and confirm the reliability of the extracted values. One can also see that the internal strain within the sample has a complicated distribution along the studied strain scan that is far from the uniform values accepted by many models. As shown in equation (5), strain values are dimensionless and express the relative change of lattice spacing. A negative value of strain corresponds to compression and the positive one corresponds to tension. Tables 1 and 2 illustrate the summarized maximum and minimum strain values for directions for which the thermal expansion was studied. The maximum values for different directions have shown qualitatively similar tendencies by measurements on both instruments.

To conclude, internal strain was measured on the investigated sample g4. The internal strains are distributed in a complicated way that does not correspond to a constant value of the strain field. Strain maxima are bent over the foliation plane by about 45° . A careful cross-check of the results has confirmed the reliability of the obtained strain values.

Thermal expansion and bowing behaviour

Thermal expansion expresses the relative length change of a sample. The relationship with the temperature is non-linear, i.e. the thermal expansion coefficient, α , which describes the specific length change (10^{-6} K^{-1}) depends on the considered temperature interval. In sum, up to now all experimentally determined data of marbles as a function of the heating and subsequent cooling cycle can be classified into four overall categories: (a) isotropic thermal expansion without residual strain; (b) anisotropic thermal expansion without residual strain; (c) isotropic thermal expansion with residual strain; and (d) anisotropic thermal expansion with residual strain (Siegesmund *et al.* 2004). The residual strain may be observed even as a result of very small temperature changes, as shown for the temperature range $20\text{--}50^\circ \text{C}$ by Battaglia *et al.* (1993).

Owing to their anisotropic behaviour, many samples have shown a large difference in residual strain after subsequent cooling down to room temperature. The thermal dilatation as a function of temperature basically had the following characteristics (Figs 11 & 12): during the heating–cooling cycle ($20\text{--}90\text{--}20^\circ \text{C}$) the slope increased successively until the destination temperature was reached. All samples generally exhibited a pronounced increase of residual strain after cooling down. In detail, the thermal expansion experiment found a weak directional dependence where the highest residual stresses were observed parallel to the $[x]$, $[z]$ and σ_1 directions (around $0.3\text{--}0.4 \text{ mm m}^{-1}$), while parallel to the $[y]$ -direction and 90° to σ_1 somewhat lower values ($0.1\text{--}0.2 \text{ mm m}^{-1}$) are evident. During the first cycle the residual strain increased significantly for almost all directions. After the second temperature cycle the residual strain did not increase while heating. Koch & Siegesmund (2004) have reported that the increase in the residual strain is limited and may end after the fifth cycle. Under wet conditions the marble showed very different expansion behaviour. They started to expand continuously. This increase in water-enhanced residual strain after five further temperature cycles was relatively high and could reach maximum values of around 0.8 mm m^{-1} (see Figs 11 & 12). The moisture content after heating cycles apparently influences the intensity of marble degradation. Surprisingly, the weak directional dependence under wet conditions was less pronounced and more or less uniform in all directions.

To record the bowing potential of the samples (slabs of $400 \times 100 \times 30 \text{ mm}$), test-specimens were fixed in an apparatus in which they were

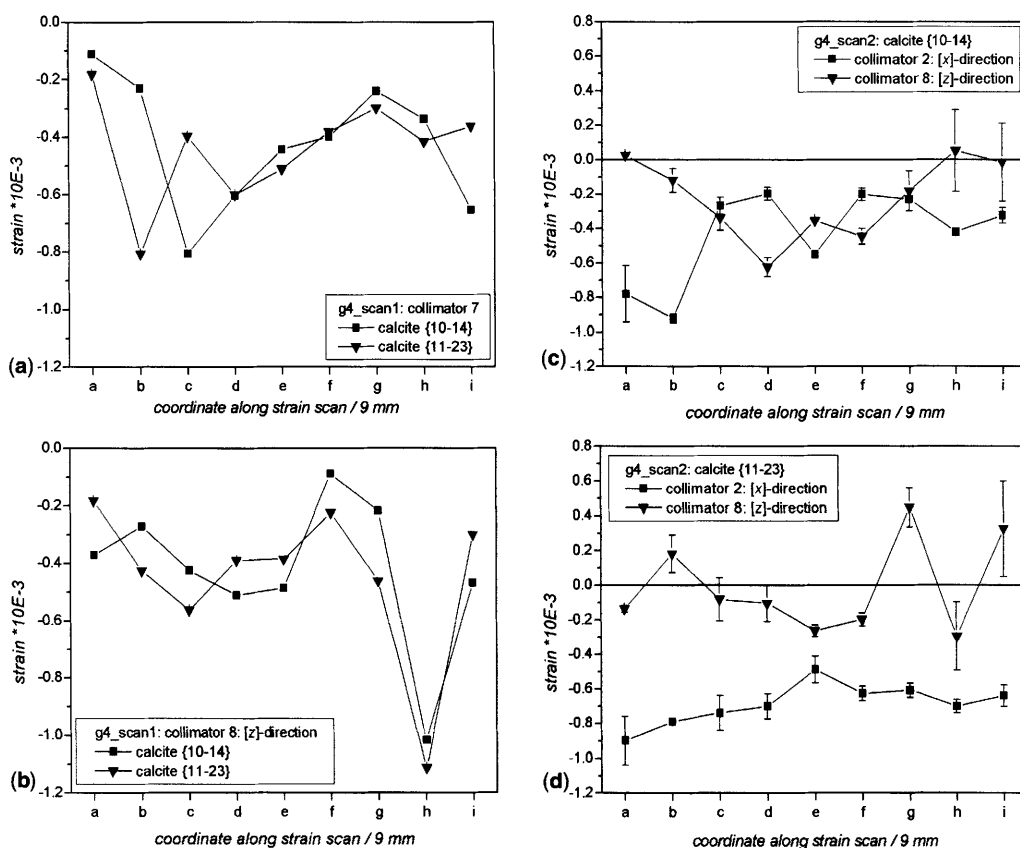


Fig. 10. Strain values measured at EPSILON-MDS with one collimator unit for different positions in the g4 sample: (a) and (b) strain scan 1; (c) $\{10\bar{1}4\}$ and (d) $\{11\bar{2}3\}$ strain scan 2 reflects two sample directions, $[x]$ and $[z]$, oriented perpendicular to each other.

exposed to varying temperatures on their upper side, and exposed to varying moisture on their underneath side. Both parameters, temperature and moisture, influenced bowing and change within a testing cycle of 24 h. The temperature interval on the upper side of the sample ran from 20 to 80 °C, and maximum values were obtained

approximately 1–3 h after the onset of heating. Subsequently, the maximum value is preserved for another 3 h. During all the heating cycle, the test specimens were bedded into coarse-grained sand, which steadily reduced its moisture content in response to the temperature rise. Cooling of the specimens took over 16 h.

Table 1. Residual strain values: the sample main axes and three directions in relation to the main stress direction, σ_1 , measured on the EPSILON-MDS diffractometer

Direction	$\epsilon(10^{-4})$ max. g4 edge	$\epsilon(10^{-4})$ min. g4 edge	$\epsilon(10^{-4})$ max. g4 middle	$\epsilon(10^{-4})$ min. g4 middle	$\epsilon(10^{-4})$ max. g4 rotated	$\epsilon(10^{-4})$ min. g4 rotated
$[x]$						
$[y]$	0.24	−7.77	1.86	−5.57	−5.17	−8.45
$[z]$	−2.64	−5.58	−1.17	−6.56	−1.56	−10.65
parallel to σ_1					5.68	−1.89
45° to σ_1						
90° to σ_1						

Table 2. Residual strain values at (0006), ($10\bar{1}4$) and ($11\bar{2}3$) for the sample main axes and three directions in relation to the main stress direction, σ_1 , measured on the SKAT diffractometer

Direction	$\epsilon(10^{-4})$ {0006}	$\epsilon(10^{-4})$ { $10\bar{1}4$ }	$\epsilon(10^{-4})$ { $11\bar{2}3$ }	$\epsilon_{\text{average}}(10^{-4})$
[x]	-4.35	-5.21	-0.07	-3.21
[y]	-5.76	-4.44	-0.17	-3.46
[z]	-13.45	-11.27	-10.4	-11.7
parallel to σ_1	-3.22	-2.71	-2.18	-2.7
45° to σ_1	-2.32	-2.04	-1.24	-1.87
90° to σ_1	-4.04	-3.31	-1.91	-3.09

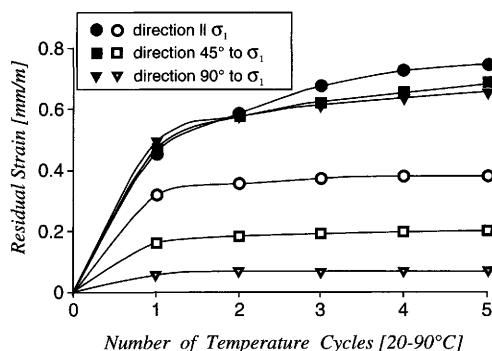


Fig. 11. Residual strain represents the permanent length change after heating and cooling cycles (five cycles in total). The thermal expansion was measured in different directions with respect to the *in situ* stress field, i.e. parallel to σ_1 , 90° to σ_1 and 45° to σ_1 . Filled symbols characterize samples measured under wet conditions, and open symbols under dry conditions.

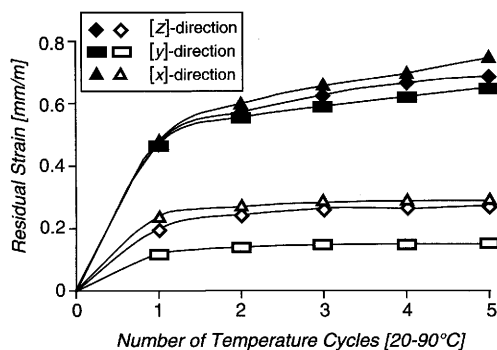


Fig. 12. Residual strain represents the permanent length change after heating and cooling cycles (five cycles in total). The thermal expansion was measured in different directions with respect to the rock fabrics (directions [x], [y] and [z]). Filled symbols characterize samples measured under wet conditions, and open symbols under dry conditions.

The results have shown rapid bowing of all specimens during the first five to eight heating cycles (Fig. 13). After 10 cycles, trends can be observed that allow a separation into three groups. Pieces with a relatively low bowing potential at this time (directions [x], [y] and 90° to σ_1) demonstrated deformation of approximately 0.75–1.00 mm m⁻¹. Other slabs (directions [z], parallel to σ_1 and 45° to σ_1) have shown bowing rates of 1.2–1.5 mm m⁻¹ after 10 heating cycles, whereas at the same time even stronger bowing of approximately 1.7 (direction parallel to σ_1) and 1.9 mm m⁻¹ (direction [z]) can be observed. During the following cycles, a decrease of the bowing intensity can be recognized for some plates, especially the one prepared from the [z] direction. After 45 cycles, two pieces that were prepared with respect to the general orientation (directions [x], [y]) showed the lowest values, whereas the direction parallel to σ_1 as well as the [z] direction displays the highest values. In contrast to the thermal expansion the bowing has shown much greater directional dependence, which is significant if the [z] and [y] direction are compared.

Discussion and conclusion

Thermal expansion behaviour and the residual strain, i.e. progressive microcracking, may be easily explained by the texture and single crystal coefficients of calcite. The coefficient, α , of calcite is extremely anisotropic (Kleber 1990): $\alpha_{11} = 26 \times 10^{-6} \text{ K}^{-1}$ parallel and $\alpha_{22} = -6 \times 10^{-6} \text{ K}^{-1}$ perpendicular to the crystallographic c -axis, i.e. calcite contracts normal to the c -axis and expands parallel to the c -axis while heating. For a marble sample with the texture given in Figure 14 a variation in thermal dilatation of between 4.47×10^{-6} and $4.77 \times 10^{-6} \text{ K}^{-1}$ because of the girdle-like and weak c -axis distribution was calculated. It is clearly documented that texture-based thermal expansion is more or less isotropic. Thermally induced microcracking

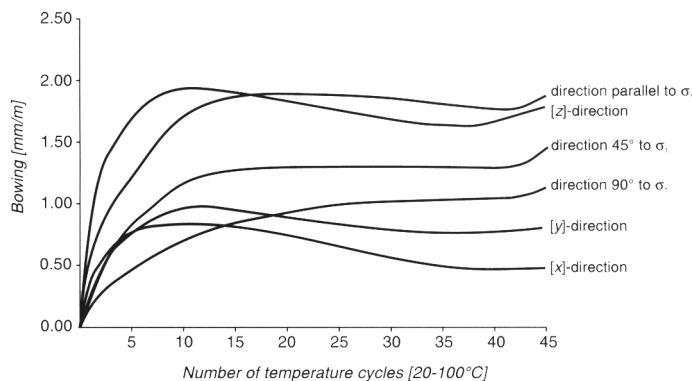


Fig. 13. Potential bowing behaviour of samples, which were prepared with respect to σ_1 and the rock fabrics (directions [x], [y] and [z]).

leads to a residual strain after heating due to tensile, compressive or shear stresses along grain boundaries and thus to deterioration of the rocks' quality. Microstructure-based finite-element simulations reported by Weiss *et al.* (2002, 2003) confirm the experimental results with respect to the magnitude and mechanisms of thermal degradation. Variations in texture may significantly affect the distribution of thermal stresses within marble. There is a strong inverse correlation between thermal stresses and degree of texture, as higher elastic strain energies are associated with

weakly textured marbles and vice versa. Moreover, grain-to-grain orientation relationships, frequently called misorientations, and their distributions are also important parameters. Different misorientations lead to variations in the elastic energy density that are of the same order of magnitude to those related to the texture itself (Weiss *et al.* 2003). However, many authors (e.g. Sage 1988 or Koch & Siegesmund 2004) demonstrate that the increase in residual strain stops after a few heating cycles if moisture is absent. Therefore, Bucher (1956) and Winkler (1994) pointed out the

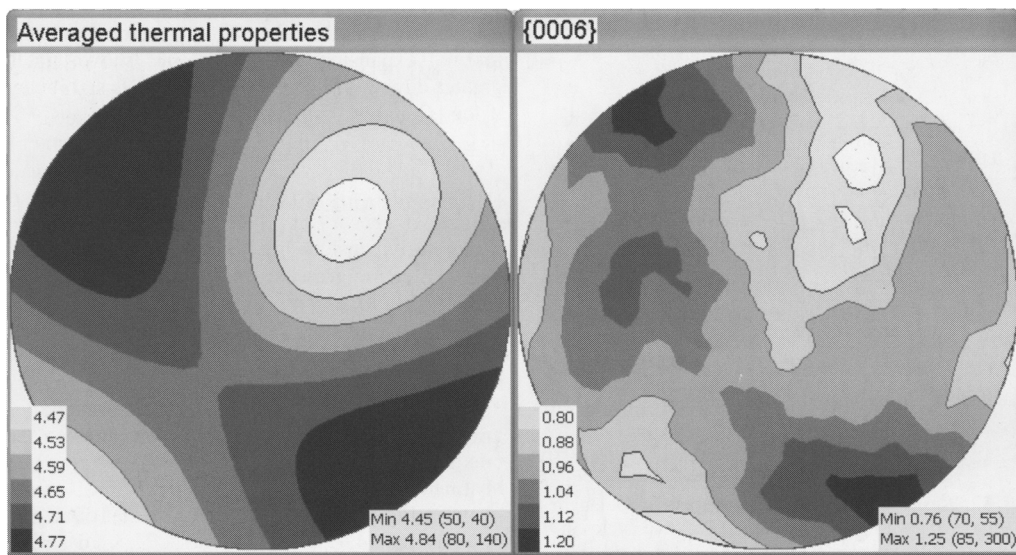


Fig. 14. Left: averaged thermal properties: the thermal coefficients for calcite single crystals $\alpha_{\parallel c} = 26 \times 10^{-6} \text{ K}^{-1}$, $\alpha_{\perp c} = -6 \times 10^{-6} \text{ K}^{-1}$ were used for calculations: thermal expansion in $[10^{-6} \text{ K}^{-1}]$. For the isotropic case the thermal coefficient is $\alpha_i = 2/3\alpha_{\perp c} + 1/3\alpha_{\parallel c} = 4.67 \times 10^{-6} \text{ K}^{-1}$. Right: experimental {0006} pole figure of sample g4.

importance of moisture in the degradation. In the presence of moisture a residual strain increase may be observed causing progressive marble decay. Winkler (1996) explained this behaviour in terms of oriented molecular layers (thickness of 2–3 nm) in capillaries of less than 0.1 μm that could be responsible for swelling by elongation and stone disruption. Poschlod (1990) argued that capillary condensation cannot be responsible for the decay process because the STERN-layer and GOUY–CHAPMANN-layer are not active under normal climatic conditions (below 100 °C). However, although the process of moisture-driven deterioration is not yet understood, the residual strain is much higher (2–3 times higher) if compared with the dry conditions. In addition, the bowing potential of the same marble is unexpectedly high and strongly directional dependent.

Owing to the above-mentioned single crystal thermal properties and the c -axis maximum, the maximum thermal degradation is closely linked to this direction that may roughly coincide with the area enclosed by the $[z]$ and σ_1 directions, i.e. the maximum concentration of the c -axes within the broad girdle-like arrangement. The weak texture is also clearly documented in the residual stresses, although the misorientation of individual grain-to-grain orientation may produce internal stresses leading to microcracking. Owing to the observed texture and thermal expansion data, the bowing behaviour was unusually high parallel to the $[z]$ and σ_1 directions, with maximum values of 2 mm m^{-1} . This cannot be explained solely by either rock fabric or by thermal expansion behaviour.

The methods of neutron diffraction for the investigation of crystallographic preferred orientation, intracrystalline strain by strain scans and residual strain pole figures are suitable for the acquisition of high-quality data based on properties and dimensions of the crystallographic lattice. Combined data from crystallographic texture and strain pole figures give unique data sets that provide an improved understanding of marble deformation behaviour.

In general, the investigated sample is characterized by a very weak crystallographic texture, on the one hand, and large bowing anisotropy, on the other. Macroscopic strain also reveals a high degree of anisotropy. This means that the bowing behaviour of the studied sample could be strongly related to internal stresses. In particular, the observed texture of the cubic sample g4 can be characterized as weak, and all pole figures show low intensities. The $\{0006\}$ basal plane pole figure is characterized by a girdle-like distribution and low intensities under 1.0 m.r.d., maxima were found in the $\{0006\}$ pole figure with intensities up to 1.25 m.r.d. Furthermore, features of orthorhombic sample symmetry have been observed in the

$\{10\bar{1}4\}$ pole figure. The data sets for texture pole figures could be also used for the analysis of strain by generation of strain pole figures. Mainly compression strain states were observed in the strain pole figures. Mean strain values were found for all crystallographic directions in the range of ϵ from -2×10^{-4} to -4×10^{-4} , but minimum compressional strain values are of about $\epsilon = -1.3 \times 10^{-3}$. This orthorhombic sample symmetry was also found in all three strain pole figures $\{0006\}$, $\{10\bar{1}4\}$ and $\{11\bar{2}3\}$. So, the relationship between the crystallographic preferred orientation and the strain distribution in the pole figures is obvious because the texture pole figures are also characterized by orthorhombic sample symmetry. The measured compressional residual strain values in the large sample with dimensions of 80 × 80 × 80 mm were up to -1.3×10^{-3} higher than in marble plates with dimensions of 100 × 100 × 30 mm, similar to previous investigations by Scheffzük *et al.* (2004) where compressional residual strains were found to be -7×10^{-4} . Residual strain values, measured on quartz (Frischbutter *et al.* 2000), were also in the range of $\pm 4 \times 10^{-4}$. So, it is assumed that the magnitude of the compressional residual strain depends on the dimension of the sample.

Logan (2004) carried out cyclical marble experiments and reported that stored residual strain contributes to a loss of strength within the marble, but, more importantly, it is a critical factor in the development of the bow. This elastic strain may be the result of the geological history of the material, or may be developed as a result of the differential thermal expansion of calcite, because he found that thermal cycles at 36 °C after 30 days produced an increase in the residual strain of up to 10^{-4} . In contrast, this study has shown that the residual strain in a bulk natural sample has a magnitude of 10^{-3} , which can be seen to be a result of geological history, taking into account the stress redistribution and/or stress relaxation by sample extraction. In addition, Logan (2004) reported that the loss of tensile strength by accumulation of damage, regardless of the size of thermal cycles, is one factor leading to bowing. This means that strongly bowed panels are characterized by a loss of their mechanical properties and that intracrystalline residual stress could be the driving force.

Based on the observed homogeneous microstructure and its texture, the marble sample can be seen as nearly isotropic. Although the strain–stress behaviour is influenced by grain boundaries and pores, a linear relation between strain and stress, described by Hooke's law ($\epsilon_{ij} = S_{ijkl}\sigma_{kl}$, with ϵ_{ij} the local elastic strain, S_{ijkl} the elastic compliances and σ_{kl} the local stresses), can be applied. Using the elastic constants for the trigonal

calcite $E_{\alpha\text{-axis}} = 87.8$ GPa and $E_{c\text{-axis}} = 57.6$ GPa, one can estimate the maximum stress value. The observed minimum strain value of $\varepsilon = -1.34 \times 10^{-3}$ in the {0006} strain pole figure corresponds with a residual stress magnitude of about $\sigma_{c\text{-axis}} = 77.5$ MPa. At the present time, no work has been reported in which strain pole figures have been converted to stress pole figures because the local stress σ_{kl} and the local strain ε_{ij} vary from one crystallite to another. Moreover, they vary within the individual crystallites, even if submicroscopic defects, like point defects or dislocations, are ignored. Thus, different lattice orientations in each crystallite in polycrystalline materials imply that the compliances S_{ijkl} are in principle different in each crystallite. Thus, heterogeneous strain and stress distribution occur not only from one crystallite to another, but even inside each crystallite. The transition from strain to stress has been described in several respects by Brakman (1987a).

Two directions [y] and [z], each perpendicular to the other, have been investigated by strain scans across the sample cross-section with a higher resolution. It is obvious that mainly contraction was observed. In general, and in comparison to the [z] direction, the [y] direction shows strain values with a stronger compression for (10 $\bar{1}$ 4) as well as for (11 $\bar{2}$ 3).

The influence of crystallographic texture on diffraction measurements of residual stress provides several approaches for a better understanding of material behaviour in the future. Up to now, the relationship has been discussed mainly for cubic materials (Brakman 1987b; van Houtte & de Buyser 1993). The interaction between strain and texture for materials with lower symmetrical crystals is more difficult to establish. Nevertheless, further investigations of structural geological features, rock fabric, weathering, thermal effects, crystallographic preferred orientation, and residual stresses and their interactions are necessary to improve our understanding of the bowing effects observed in marble panels. Results from thermal expansion, together with the observed different intensities of bowing in comparison with neutron diffraction data of residual strain and texture, underline the suggestion that so-called locked-in stress should have an important impact on the bowing of marbles. To detect this locked-in stress, the neutron TOF diffraction measurements can be regarded as a suitable method, but ongoing investigation is necessary to establish this approach as a measure of the bowing behaviour.

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