Experimental report

07/12/2015

Proposal: **1-02-149**

Council: 4/2014

Title: Residual stress change resulting from stress corrosion in Carrara marble

Research area: Other...

This proposal is a new proposal

Main proposer: **Kerry LEITH**

Experimental team: Kerry LEITH
Jens WALTER
Anne VOIGTLAENDER

Local contacts: Thilo PIRLING
Emmanuelle SUARD

Samples: $CaCO_3$

Instrument	Requested days	Allocated days	From	To
D2B	3	0		
SALSA	3	5	18/11/2014	23/11/2014

Abstract:

This investigation will contribute to a sparse dataset of measured type II and III residual stresses in natural rock, and provide first data on their relationship to material damage resulting from stress corrosion under constant or cyclic tensile loading. Although these residual stresses have been shown to play a fundamental role in determining the elastic behavior of engineering materials, their effect on brittle and elastic rock materials remains unclear. We will undertake standard notched 3-point bending tests on samples of Carrara marble over a 1 - 2 month preparatory testing period. During this period weak HCl solution will be applied to artificial cracks created at the center of five samples subjected to high bending stresses overprinted by low-magnitude cyclic loading. Induced stress corrosion is expected to interact with type II and III residual stresses as tensile bonds enhance the kinetics of chemical reactions. Resulting material degradation will preferentially relax local lattice stresses, and therefore maximum residual stress magnitudes. We expect this effect will be evident in a narrowing of calcite diffraction peaks observed using the D2B or SALSA beam lines.

ILL Experimental report SALSA, *Proposal Nr. 1-02-149*

Residual stress change resulting from stress corrosion in Carrara marble

Voigtländer, A. & K. Leith

Introduction

The proposal "Residual stress change resulting from stress corrosion in Carrara marble" (1-02-149) was granted five days beam time at the SALSA instrument at the ILL 18.-23. November 2014.

Residual stresses and strains have been shown to play a fundamental role in determining the elastic behavior of engineering materials [*Withers*, 2007], yet the effect of these stresses on brittle and elastic rock material behavior remains unclear [*Engelder*, 1993]. Moreover, the alteration of these residual strains due to environmental stresses (chemical and physical) has not so far been investigated. An improved understanding of residual strain will provide a foundation for new research into micro-mechanical controls on macroscopic rock behavior, and contribute to diverse aspects of Earth science. Our investigation adds to a sparse dataset of measured residual stress magnitudes in natural rock, and provides first data on the relationship between residual strains and material damage resulting from stress corrosion under constant tensile loading.

Carrara Marble was chosen as an exemplary rock for its high purity (>98% $CaCO_3$) as well as its homogeneity in grain size (~200 µm), microstructure and minor texture. Complementary texture measurements conducted using the x-ray goniometer at the Geologisches Zentrum Göttingen, Germany (GZG) show no preferred texture. Previous measurements on Carrara Marble indicate residual stress magnitudes of up to 75 MPa resulting from it's formation and exhumation [*Scheffzük et al.*, 2006]. We hypothesize these residual stresses will both affect, and be affected by, the process of stress corrosion as tensile type I and II residual stresses are likely to enhance the kinetics of chemical reactions, and resulting material degradation will allow preferential relaxation of local lattice stresses. Intragranular strain (type II) relaxation is indicated by a narrowing of the diffraction peaks, while intergranular strains (type I) can be assessed by the relation of the peak position to an unstrained reference peak position.

Our neutron diffraction measurements indicate no clear reduction of intragranular residual stresses (type II), as a result of stress corrosion, rather a broadening of the peak width at the fracture tip. Shifts in the peak position and thus residual elastic strains (type I) are evident in all samples.

Method

In a four-month-long preparatory three-point bending test on three large 1100 x 100 x 100 mm Carrara Marble samples, we induced stable low stress conditions in which strains were concentrated at the tip of a saw cut and pre-cracked notch. A corrosive environment was created at the tip of the notch on two samples (M2 and M4) by dripping calcite saturated water (pH ~ 7.5-8). Sample M5 was loaded in the same way, but kept dry. Following the three-week bedding period with loads of 55% of the instant wet fracture toughness (Kic, ~2.5kN), loads on the samples were increased to 77% of the Kic in M2 and M5, and 85% of the Kic in M4. The samples were then unloaded prior to failure, and cored shortly before they were tested for changes in residual elastic strains at the SALSA diffractometer.

Four cylindrical subsamples (ø = 50 mm, h = 100 mm) were cored vertically through the notch area of M2, M4 and M5 as well as a reference non-loaded sample M0 (Figure 1). We measured three diffraction peaks corresponding to crystallographic planes (110), (104) and (006)) in all three directions (tangential to the notch - x, radial – y and vertically - z), sampling with a high resolution below the notch (0.5mm steps), a lower resolution (10-20mm) at the middle of the sample, and again a higher resolution at the bottom of the sample, resulting in a total measuring points of at least 25 per sample, direction, and hkℓ-plane (Figure 1). The measurement volume was about 2mm x 2mm x 10mm and the sample stage was used in oscillating mode to enhance reflection intensity. Each measurement comprised of *n=4000* counts.

The results at each interval were compared to M0, our 'unstrained' sample, allowing us to isolate the effects of external loading and water

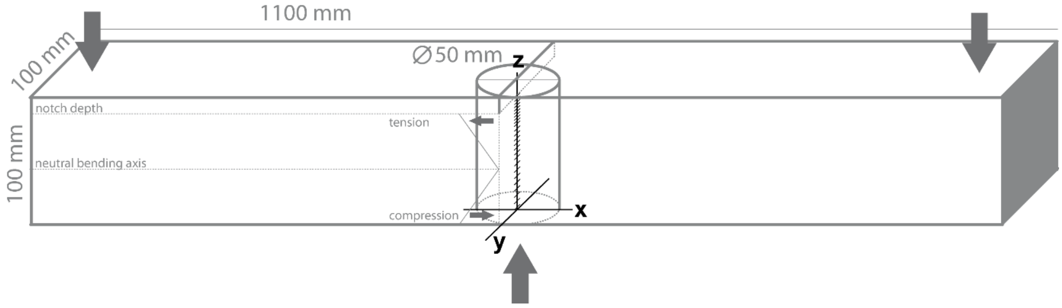

Figure 1 Three-point-bending preparatory test, sample dimension and orientation

availability on residual strains. Absolute strain values were not obtained as no strain-free sample was available. Estimations on a strain-free reference state are theoretically derived based on Rao et al., 1967.

The SALSA beam line provided continuous flux neutrons at 1.64 Å. Marble samples were placed on the hexapod stage which allowed automatic rotation and measurement in two spatial directions (x and y). Sample orientations were then manually adjusted to allow measurement in the third spatial direction (z). As this was the first measurement of a geomaterial conducted on SALSA, an initial scan was conducted to evaluate the chosen peak positions and check intensities of the diffracted beam. The measurement procedure was programmed for all measurements to ensure consistent workflow for all samples. Diffraction data was fitted using a single Gaussian peak fit using LAMP, the standard diffraction fitting software provided by the ILL. The hkℓ (006) and (104) were fitted together with the same background, (110) was fitted separately. Both fits have an individual background fit clearing instrumental errors. Fluorescence thin sections of the notch-crack area were prepared to check against the neutron diffraction data (Figure 2).

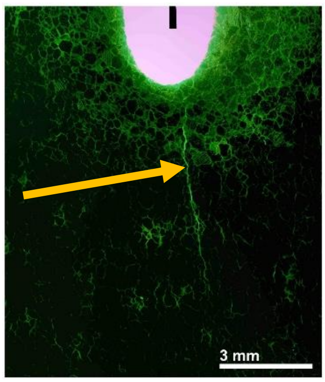

Figure 2 Fluorescene thin section of M4 sample area below the notch, traces of fractures and lamellas glow in green. A continuous fracture is evident along grain boundaries (arrow)

Preliminary results

The narrowing of the diffraction peaks was assessed by the comparing the full-width at half maximum (FWHM, 2θ°), a good metric to evaluate type II residual strain. A pronounced shift in the peak position and thus the d-spacing, upon residual strain type I (macrostress) change, was also expected, due to non-recoverable strains induced during the pretest. Texture measurements at the GZG allowed us to exclude directional influences on the elastic strain as no preferred orientations of crystallite planes could be resolved, the planes are essentially randomly distributed (Figure 3).

Elastic and plastic strains were induced in the sample during our preparatory three-point bending test. These were superimposed on pre-existing residual strains resulting from the geological origin of the marble. Unloading of the specimens following the preparatory bending tests should result in a reversal of the induced strain field where (non-recoverable) creep has occurred. This will, for example, result in an increase in compressive intergrain strains in regions that have undergone extensional deformation. Recoverable strains (in this case associated with brittle damage) should, however, result in very little change to the intergranular strain field.

Results suggest we induced strains in all samples (with respect to the M0-unstressed reference). Distinct patterns in residual and differential strains (Figure 4) can be observed throughout the vertical section in hkℓ (104) and (006), while (110) is strained in compression around 200 µstrain in all samples; between the dry M5 and wet sample (M2 and M4) indicating a change in the deformation mechanism due to the presence of water. M5 shows a higher differential strain immediately below the notch, extensional strain in the x-direction as well compressional strains in the y-direction are preserved and an ideal s-shape pattern of strain distribution along the measured vertical in the x-direction [*Holzhausen and Johnson*, 1979]. We suggest water present at the crack tip increased the rate of corrosion, allowing a greater relaxation of extensional strains during the preparatory test, leading to a subsequent increase in compression when the samples were returned to the neutral position prior to our measurement. Plastic deformation in M5, the dry sample, induced extensional intergranular strain near the notch upon unloading. Even though sample M5 shows the highest extensional strains of up to 400 µstrain in the intergranular strains, the intragranular strains, as evident in the FWHM, don't show an alteration due to the loading and unloading. This indicates the deformational process is restricted to the grain boundaries. Grain boundary sliding, a common process in fine grained calcite, is therefore likely the dominant process. No fracturing is evident in the thin sections of M5.

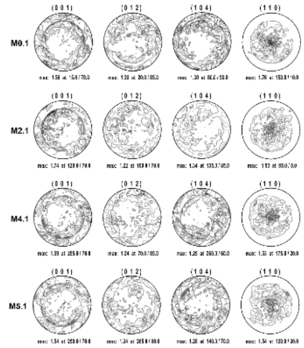

Figure 3 ODF plots of the tested Carrara Marble samples

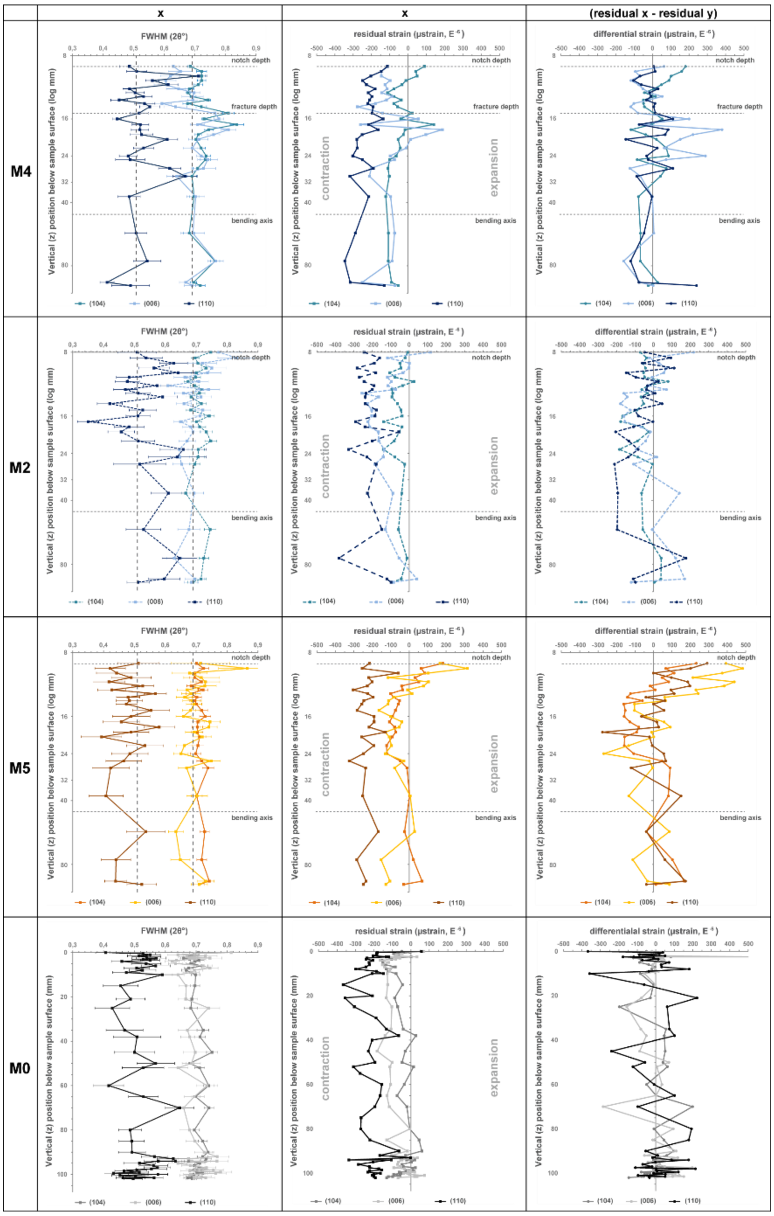

Figure 4 FWHM and residual strain in x-direction for all samples and hkℓ (104), (006) und (110) along the measured gradient. Dashed vertical lines in FWHM indicate mean FWHM of M0 (110) respectively (104) and (006). Differential strain of x- and y-directional measurements.

The results for the stress corrosion samples M4 and M2 show a reduction in local intergranular extensional strain below the notch in the upper part of the sample (in hkℓ (104) and (006)), indicating no strain was built up upon the loading. At the fracture tip of M4 (approximately at 14-15mm) there are extensional intragranular strain (50 to 200 µstrain) present. We suggest this is due to loading in the preparatory test, which concentrated stress near the fracture tip, causing a plastic deformation zone, which shifted downwards as the fracture propagated. Thin sections of the notch area support the diffraction data, as a narrow but continuous fracture following grain boundaries is evident in M4 (Figure 2), suggesting the fracture relaxed stresses on grain boundaries as it propagated.

An overall narrowing of the peak width in the stress corrosion samples M4 and M2 is not observed (ref. unaltered sample M0, Figure 4). The FWHM data of M4 shows a decrease in width in the region below the notch in the tangential direction (x) in hkℓ-plane (006). A second narrowing of the (006) peak is observed in M2 and M4 (stress corrosion samples) 3 – 4 mm below the notch. In the vicinity of the fracture tip, below 15mm in sample M4, hkℓ (006) and (110) show a peak broadening, indicating induced strains on the intragrain scale. At ambient temperature and low applied stresses such intragranular strains can be accommodated by dislocation (glide and slip) along defects. As the strongest broadening in the peak width is observed below the notch in the wet samples, it can be suggested that due to the presence of water the density of dislocation increased close to the fracture. Diffraction peak (104) is little affected in either sample (Figure 4).

Thin section microscopy of the notch area reveals a clear fracture along grain boundaries in the wet samples (Figure 2), while the sample kept dry, did not show any prominent fracture. These results suggest stress corrosion and subcritical fracture preferentially acts along local grain boundaries, causing local relaxation. The neutron diffraction technique applied here samples a relatively large gauge volume, and does not necessarily capture effects of stress corrosion at the fracture tip. This may explain why a relaxation of the grain boundaries and resulting bulk shift in the peak position due to stress corrosion is thus not visible in the bulk measurement. Loading can also increase dislocation density near the crack tip, and may, in fact, induce a broadening of the diffraction peaks rather than a narrowing as opening or extensional strains areconcentrated, while already broken grain boundary bonds are relaxed.

Overall the diffraction measurement results show a) that constant low stress affects the strain state of a rock especially if altered by the presence of water, b) residual strains in the Carrara Marble exist and are superimposed by low applied loads, and c) to investigate the very local process of stress corrosion, it needs further investigation at higher resolution, e.g. synchrotron-tomography.

Publication of the results

The preliminary results have been presented at the General Assembly of the European Geoscience Union (EGU) in Vienna, Austria in April 2015 *("Induced damage in Carrara Marble as a result of long-term low-magnitude environmental stresses"* by Voigtländer, Leith, Krautblatter, Walter). A research paper comprising the neutron diffraction measurements at SALSA is in preparation [Voigtlaender et al. in prep.] we aim for publication in the "Journal of Geophysical Research".

Testing facilities

The testing atmosphere at the ILL was very favorable for our proposal. Thanks to the guidance of Dr. Thilo Pirling it was possible to conduct all measurements in the presumed time slot, assigned. Furthermore, we were able to measure an additional set of two directions in a naturally weathered Carrara Marble. The powdered marble sample, proposed as a strain-free reference in the proposal, has not been measured after a discussion of whether it would really display a strain-free reference. The milling of the rock induces further strains (mechanically as well as thermal), which cannot be resolved.

The SALSA allows measurements at low angles single peaks, which could be shown is also suitable for mono-phase geomaterials e.g. calcite marble. For only one reflection is measured at a time, measurements are also restricted to a few directions, which limit the applicability to no-cubic and polyphase materials, such as rocks. The data was processed and fitted directly at the ILL, making it possible to work with the data right away, enriching further experiments and discussion of the results.

During the measurements errors in the work flow occurred as the hexapod of SALSA could not move. The errors could be solved by cleaning actions, but the measurements were interrupted and had to be restarted or even redone. This significantly affected our available sampling time, and the unplanned maintenance required an 'all-hours' service from the instrument scientist – for which we are extremely grateful.

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