Neutron diffraction study of the contribution of grain contacts to nonlinear stress-strain behavior

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[1] Repeatable, hysteretic loops in quasi-static loading measurements on rocks are well known; the fundamental processes responsible for them are not. The grain contact region is usually treated as the site of these processes, but there is little supporting experimental evidence. We have performed simultaneous neutron diffraction and quasi-static loading experiments on a selection of rocks to experimentally isolate the response of these contact regions. Neutron diffraction measures strain in the lattice planes of the bulk of the grain material, so differences between this strain and the macroscopic response yield information about grain contact behavior. We find the lattice responds linearly to stress in all cases, oblivious to the macroscopic unrecoverable strains, curvature, and hysteresis, localizing these effects to the contacts. Neutron diffraction shows that the more granular rocks appear to distribute stresses so that the same strain appears in all the grains, independent of crystallographic orientation. INDEX TERMS: 3909 Mineral Physics: Elasticity and anelasticity; 3902 Mineral Physics: Creep and deformation; 3954 Mineral Physics: X ray, neutron, and electron spectroscopy and diffraction; 3994 Mineral Physics: Instruments and techniques; 3694 Mineralogy and Petrology: Instruments and techniques. Citation: Darling, T. W., J. A. TenCate, D. W. Brown, B. Clausen, and S. C. Vogel (2004), Neutron diffraction study of the contribution of grain contacts to nonlinear stress-strain behavior, Geophys. Res. Lett., 31, L16604, doi:10.1029/2004GL020463.

1. Introduction

[2] Brought to a "state of ease" (conditioning) by application of high stresses, most rocks display a repeatable, often curved, stress-strain loop under cyclic loading [Adams and Coker, 1906; Boitnott, 1993; Hilbert et al., 1994]. Recoverable hysteretic and nonlinear elastic processes produce multiple values of strain for stresses between the cycle end values. The details of these processes, which produce similar effects in many different kinds of rocks, are usually ascribed to grain-contact effects. The literature reports a number of models that can qualitatively describe this behavior, such as the Hertz-Mindlin model [Nihei et al., 2000] and the P-M space model [McCall and Guyer, 1994; Guyer et al., 1997], but the assignment of model elements to real physical processes is difficult, limiting the predictive power of the models. Part of this difficulty lies in examining the interior of the rock – surface grains and contacts are not in the same strain state as interior grains. The aim of our experiments is to separate the contribution of the grain contacts and the small volume in the immediate vicinity of the contact from the contribution of the bulk of the crystal grain volume.

[3] Neutrons are ideal probes for atomic-scale studies of the strain in the interior of rock samples. Neutron diffraction has been used to examine strain distributions in polyphase rocks [Schofield et al., 2003], textures [Wenk et al., 2003], and also the effects of monotonic uniaxial stress in bedded sandstone [Frischbutter et al., 2000]. Unlike x-rays, low-energy neutrons penetrate deeply into matter, and scatter from light elements. Bragg diffraction of neutrons provides information on crystal lattice spacings, averaged over a large sample volume. Changes occurring in small fractions of this volume (less than 2%) in general will not produce significant effects in the measured diffraction spectrum. This spectrum only provides data on the large fraction of material *not* involved in contacts or bonds. We examine the average lattice strain of the crystals to establish the contribution of the grain average volume to the nonlinear effects. Differences between this average lattice-level response and the macroscopic strain response are attributable to effects occurring in small regions at or near the contact points.

2. Experiments

[4] We have used the SMARTS (Spectrometer for MAterials Research at Temperature and Stress) [Bourke et al., 2002] beamline at the Los Alamos Neutron Science Center (LANSCE) to examine the lattice strain response of rock samples to both conditioning and cyclic stresses while simultaneously measuring the macroscopic strain response. SMARTS is a time-of-flight (TOF) spectrometer, which enables all diffraction data from a polycrystal sample to be collected at fixed angles. In SMARTS a cylindrical sample held at 45° to the incident beam is compressed along its axis. Detectors at ±90° to the beam count diffracted neutrons. This geometry and general TOF spectroscopy principles are discussed in the article by Schofield et al. [2003]. The neutron spectra used in our analysis correspond to diffraction from all lattice planes with normals collinear with the applied stress. The distance between these atomic planes (d-spacing) is reduced under applied compressive stress. Lattice strains are determined from changes in the lattice spacings relative to an initial value. The sample is subject to a holding stress of around 4 MPa, at which we zero the strain gauge and measure the initial d-spacings. The macroscopic strain is measured by a 12.5 mm or 25 mm jaw-width extensometer strain gauge. Initial destructive experiments determined breaking stresses: our cycles were limited to 70% of these values. Measurements were carried out at ambient temperature (24°C–28°C) and humidity
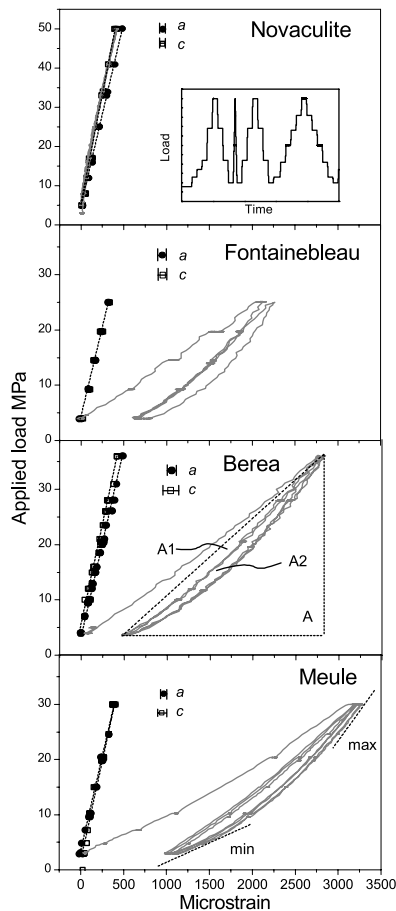
Figure 1. Stress-strain curves for SiO_2-based samples, and strain in the a and c lattice parameters. The inset shows the novaculite loading sequence. Maximum and minimum loop gradients are indicated on the meule data. On the Berea data, the dotted triangle is the reference area, A. A1 is the area between the hypotenuse and the upper path of the loop. A2 is the area within the loop.

$(24\% < RH < 32\%)$. The samples spent two weeks after being cored and polished stabilizing in these conditions.

[5] Macroscopic stress and strain values were recorded every 10s throughout the experiment for each sample. The applied stress was changed at 3 MPa/min between the fixed values of stress where neutron data was collected for 15 minutes. The inset in Figure 1 shows an example of the load variation.

[6] Two perpendicularly directed lattice parameters (a, c) are needed to describe the trigonal unit cells of both quartz and calcite. Rietveld analysis of the diffraction spectra provide the spacing, and more accurately, the *changes* in spacing (strain) of the lattice planes, and also the changes in the lattice parameters. In this letter we discuss only the neutron data for the response of the a and c lattice parameters under compression for comparison with the macroscopic compression data.

[7] Two sets of sandstones and limestones, each set having nearly identical mineral components but different porosities and grain interfaces, were selected: (1) Arkansas novaculite with Fontainebleau, Berea, and Meule (green Vosges) sandstones are entirely or mostly quartz, SiO_2, and

(2) Carrara marble and Lavoux limestone are both nearly pure calcite, $CaCO_3$. The novaculite is a fine grained (grains $\approx 5~\mu$) polycrystal quartzite that is $>99.5\%$ SiO_2 and is within $\pm 2\%$ of the density of single crystal quartz. The material is hard and strong. Fontainebleau sandstone (France) is also almost pure quartz ($>99\%$, trace amounts of other minerals) with grains $\approx 150~\mu$ and porosity of 24%. Contacts between the grains occur at points so light abrasion dislodges them. The other sandstone samples, Berea (quartz $85 \pm 8\%$, feldspar $8 \pm 1\%$, kaolinite $5 \pm 1\%$ other 2%)and meule (quartz ($74 \pm 8\%$, feldspar $21 \pm 4\%$ other 4%) are not pure minerals and are included for reference. The sandstones are of particular interest because, as *Adams and Coker* [1906] complained, they display extraordinary hysteresis. Carrara marble (Italy, calcite $> 99\%$) is a dense white marble of compacted calcite grains with a grain size centered around 250 microns and a density almost equal to that of calcite. Contacts between calcite grains are areal due to its metamorphic origin, but they are not strongly bonded; individual grains can be removed. The Lavoux limestone (France, calcite $> 99\%$, trace amount of kaolinite) has very fine ($<10~\mu$), well bonded calcite grains, forming a porous structure with some oolites of $100-120~\mu$ size, and inclusions of calcite grains. All samples were cylinders of 13.4 mm diameter and 26.0 mm length, with flat, parallel ends ground perpendicular to the axis. XRD was used to identify the mineral components of the porous rocks, and the porosity was determined by the ratio of rock to mineral density.

3. Results and Discussion

[8] Figures 1 and 2 show results for all the rock samples. All figures show the macroscopic stress-strain response (continuous line) for the initial compression and subsequent cycles, and the strains in the a and c lattice parameters (legend shows typical errors). The plateaus which appear in some of the plots are at the holding stresses for neutron measurements, indicating creep. The lattice strain data are shown as points with a line of best fit through them. The
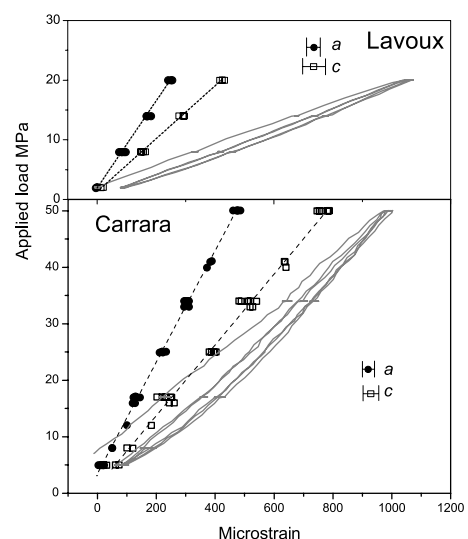
Figure 2. Stress-strain curves and strain in the a and c lattice parameters for $CaCO_3$-based samples.

Table 1. Parameters Describing the Macroscopic Loops

Sample Rock	Porosity %	A1/A[a] %	A2/A[a] %	Max[a] GPa	Min[a] GPa
Novaculite	0.2 ± 0.2	–	–	–	96
Fontainebleau	24 ± 0.5	12	24.6	23	8
Meule	21 ± 2	7	18.6	20	7
Berea	20 ± 2	15	12.2	23	8
Carrara	0.4 ± 0.2	11	9.4	62	30
Lavoux	22 ± 0.5	2	6.1	21	14

[a]Curvature, hysteresis, and gradient measures. See Figure 1.

scatter apparent in some of the groups of points is random scatter - there is no correlation with the looping behavior of the macro curve.

[9] We have characterized the macroscopic loops with several parameters that are defined in Figure 1 and listed in Table 1. The steepest and shallowest tangent gradients on the loop, (max, min, Figure 1) bound the static moduli, and, although the dynamic moduli are generally larger than the static moduli, they also appear to bound the dynamic moduli. For the looping plots, we define the areas A1, between the upper path and the straight line joining the endpoints (a measure of the curvature), and A2, contained within a closed loop (energy lost per cycle). Both are normalized to the area, A, of a triangle representing the energy for an elastic compression. Table 2 contains parameters describing the lattice behavior from Rietveld refinement of the neutron data. We compare the maximum lattice strain, averaged over both a and c parameters, $\langle\epsilon_{\mathrm{latt}}\rangle$ with the strain width of the loops, ϵ_{loop}, as an indicator of the strain defect which must be absorbed by deformation of unobservable small regions (contacts). The slope, $\Delta\sigma/\Delta\epsilon_{a,c}$, of the best fit lines through the lattice strain data is not a true modulus measurement because the actual stress at each grain is unknown. For the porous rocks, the true material cross-section is reduced from the sample cross-section, increasing the real stress in the material. To compensate for this, we also tabulate "stress corrected" slopes, $\Delta\sigma/\Delta\epsilon_{a,c}^*$, which are the measured values divided by the factor (1-porosity). This correction assumes an homogenous distribution of the porosity. While our sampling is not sufficient to state whether these assigned values are characteristic for each kind of rock, they provide our basis for comparison between samples.

[10] The Novaculite (Figure 1) stands out in this data set. It displays negligible conditioning or hysteresis and after an initial softening shows the only linear macroscopic response. Young's modulus for this linear section is 95.7 ± 2 GPa, which falls within the tight Hashin-Shtrikman (H-S) bounds for a quartz polycrystal aggregate calculated by *Watt and Peselnick* [1980], consistent with the appearance of completely bonded grains and no porosity. The stiff initial modulus is anomalous and is probably due to contact area effects creating inhomogeneous stress near the ends. The gradients of the lattice data (also anomalously large by 5–10%), are clearly separated, and consistent with the size and ratio of the anisotropic constants for quartz (c_{11} = 87 GPa, c_{33} = 106 GPa). The ratio of average lattice to macro strain (close to 100%) tells us the strain is entirely absorbed in the grains.

[11] The Fontainebleau sandstone shows several remarkable differences: there is considerable macroscopic hyster-

esis and nonlinearity; the strain apparent in the lattice is only one-fifth of the strain in the loop, and it is always linear with applied stress; the elastic anisotropy of the quartz crystals is gone – the strains in the a and c lattice parameters are identical. The excess strain is absorbed in the contacts partially by compression of a small area contact, and partially in shear strain as rotation and motion of grains reduces the pore volume. This strain does not break most of the contacts so the rock remains intact. The initial conditioning path has done permanent damage by breaking many grains loose: these may still contribute to the compressive stiffness, and may also be major effects in the hysteresis, since they do have boundaries which are able to engage in frictional sliding. This accommodation of grains and contacts occurs so that the strain appears uniformly in all grains despite crystallographic orientation.

[12] The meule and Berea sandstones show very similar behavior to the Fontainebleau, particularly in the lattice strains, indicating that the mechanism for accommodating the compressive strain is similar. They are linear, nonhysteretic and make no distinction between the conditioning or looping portions of the macroscopic behavior. In these sandstones, the diffraction is dominated by the quartz grains, even though other components comprise up to 25% of the material volume in the Berea and Meule (T. Proffen, unpublished high statistics data, 2003). The added clays and feldspars probably produce the slight separation of the a and c lattice slopes, tending to the direction expected from single crystal moduli, but have a greater effect on the macroscopic nonlinear and hysteretic parameters, giving Berea only 50% of the apparent hysteresis of Fontainebleau.

[13] The Lavoux (Figure 2) has a porosity very like the sandstones, but has much lower nonlinearity and hysteresis than any of them, and in fact, significantly lower than the Carrara. The "corrected" slopes are close to the Carrara values, suggesting that the intergranular bonds are similar, so deformation into the pore space and inhomogeneous strain may account for the low fraction of strain apparent in the lattice average. The Carrara marble shows a curved loop like the sandstones, despite zero porosity like the novaculite. The loop never shows a modulus as high as the H-S *lower* bound for calcite (77.2 GPa), indicating it is not as well-bonded as the novaculite, although the major part (66%) of the strain does appear in the grain volume average. The a and c lattice gradients are well separated in the expected direction for calcite (c_{11} = 149 GPa, c_{33} = 85 GPa) but are low by 25%–50%.

[14] Our initial studies of the peak amplitudes indicate no significant initial texture in the samples. The peak widths broaden by about 3%, linearly with stress, but recover on

Table 2. Parameters Describing the Lattice Data

Sample Rock	$\frac{\langle\epsilon_{\mathrm{latt}}\rangle}{\epsilon_{\mathrm{loop}}}$ %	$\left(\frac{\Delta\sigma}{\Delta\epsilon}\right)_a$ GPa	$\left(\frac{\Delta\sigma}{\Delta\epsilon}\right)_c$ GPa	$\left(\frac{\Delta\sigma}{\Delta\epsilon}\right)_a^*$ GPa	$\left(\frac{\Delta\sigma}{\Delta\epsilon}\right)_c^*$ GPa
Novaculite	106	98 ± 1	115 ± 2	98 ± 1	115 ± 2
Fontainebleau	21	65 ± 2	67 ± 2	86 ± 2	88 ± 2
Meule	18	68 ± 1	75 ± 2	86 ± 1	95 ± 2
Berea	20	65 ± 1	73 ± 2	81 ± 1	91 ± 2
Carrara	66	99 ± 1	62 ± 1	99 ± 1	62 ± 1
Lavoux	35	73 ± 2	45 ± 1	94 ± 2	58 ± 1

Single-crystal moduli, quartz: c_{11} = 87 GPa, c_{33} = 106 GPa.
Single-crystal moduli, calcite: c_{11} = 149 GPa, c_{33} = 85 GPa.

unloading. This would not as expected for irreversible processes such as dislocation production.

4. Summary

[15] We demonstrate that the remarkable stress-strain characteristics of most rocks are produced by a few percent of the material volume at the grain contacts. This volume deforms reversibly without destroying the bonds which provide the shear and tensile strength of the rock. The volume-average lattice response in the grains in all samples shows a Hooke's Law behavior for both conditioning and cyclic applied stress. The significant nonlinearity and hysteresis in the macroscopic behavior is dominated by the deformation of small material volumes near bonds and contacts, inhomogeneous stress in the grains and the pore space available for grain motion. In the sandstones these effects conspire to produce identical compressive strains in the grains despite different crystallographic orientations. The novaculite shows the limit of a dense, well bonded linear elastic material where the expected elastic anisotropy is apparent in the grains, and the lattice behavior closely matches the macroscopic response. The marble and limestone behaviors fall between these cases. This combined analysis seems able to distinguish grain contact properties in rocks, independent of porosity, although the fundamental source of nonlinearity will require further detailed microscopic examination.

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