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Using neutron diffraction to examine the onset of mechanical twinning in calcite rocks

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Abstract

Experimental calibration of the calcite twin piezometer is complicated by the difficulty of establishing the stresses at which the twins observed in the final deformation microstructures actually formed. In principle, this difficulty may be circumvented if the deformation experiments are performed in a polychromatic neutron beam-line because this allows the elastic strain (and hence stress) in differently oriented grains to be simultaneously monitored from diffraction patterns collected as the experiment is proceeding. To test this idea small strain ($<0.3\%$), uniaxial compression experiments have been performed on Carrara marble (grain size $150\ \mu\text{m}$) and Solnhofen limestone ($5\ \mu\text{m}$) at temperatures of 20° - 600°C using the ENGIN-X instrument at the ISIS neutron facility, UK. At the lowest temperatures (25°C Carrara; 200°C Solnhofen) the deformation response was purely elastic up to the greatest stresses applied ($60\ \text{MPa}$ Carrara; $175\ \text{MPa}$ Solnhofen). The sign of the calcite elastic stiffness component c_{14} is confirmed to be positive when the obverse setting of the calcite rhombohedral lattice in hexagonal axes is used. In the Carrara marble samples deformed at higher temperatures, elastic twinning was initiated at small stresses ($<15\ \text{MPa}$) in grains oriented such that the Schmid factor for

twinning was positive on more than one *e*-twin system. At greater stresses (65 MPa at 200°C decreasing to 41 MPa at 500°C) there was an abrupt onset of permanent twinning in grains with large Schmid factors for twinning on any one *e*-twin system. No twinning was observed in the Solnhofen limestone samples deformed at 200° or 400°C at applied stresses of < 180 MPa. These results highlight the potential of this approach for detecting the onset of twinning and provide, through experiments on samples with different microstructures, a strategy for systematically investigating the effects of microstructural variables on crystallographically-controlled inelastic processes.

Keywords: mechanical twinning, palaeostress, calcite, Carrara marble, Solnhofen limestone, neutron diffraction

1. Introduction

The orientation and abundance of mechanical *e*-twins in naturally deformed calcite-bearing rocks are widely used to evaluate palaeostresses and strains (for several case studies, see Lacombe, 2010). From a consideration of the crystallography of twinning on calcite *e*-planes (e.g. Handin and Griggs, 1951), techniques have been developed that allow calcite twinning microstructures to be used to infer the orientations of the principal stresses (Turner, 1953; Dietrich and Song, 1984; Shelley, 1992), to apply constraints on the relative magnitude of these stresses (Spang, 1972; Pfiffner and Burkhard, 1987), and to obtain the orientations and magnitudes of the principal strains (Groshong, 1972; 1974; Groshong et al., 1984). The magnitude of the difference between the greatest and the least principal stresses (the differential stress) may be evaluated from experimental calibrations of twin abundance as a function of differential stress (Rowe and Rutter, 1990). Alternatively, by assuming that mechanical twinning occurs once some critical shear stress resolved on the twin plane along the twin displacement vector has been attained, the magnitude of the differential stress experienced by a calcite rock with randomly oriented grains may be estimated from the relative number of twinned and untwinned grains (Jamison and Spang, 1976). When combined with twin orientation measurements, this last approach

55 may be re-developed to evaluate the complete deviatoric stress tensor (e.g. Laurent et al., 1981; 2000;
 56 Lacombe and Laurent, 1992; Nemcock et al., 1999; Lacombe, 2007; Gagala, 2009; Yamaji, 2015a;
 57 2015b).

58 Each of these techniques involves several approximations which restrict their applicability and
 59 introduce significant uncertainties into the results (for informative commentaries, see Burkhard, 1993;
 60 Ferrill, 1998; Rybacki et al., 2013). Among these we draw particular attention to the following. Firstly,
 61 the value of the critical resolved shear stress for twinning, and its dependence on deformation variables
 62 such as temperature, strain-rate and strain, is not tightly constrained by experiments. There is even
 63 doubt about whether or not a critical resolved shear stress for mechanical twinning exists at all
 64 (Christian and Mahajan, 1995; De Bresser and Spiers, 1997). Secondly, mechanical twinning is widely
 65 recognized to be sensitive to microstructural variables such as grain size and crystallographic preferred
 66 orientation (e.g. Rowe and Rutter, 1990; Meyers et al, 2001; Beyerlein et al., 2010). However, the
 67 nature of this effect remains poorly characterized. Thirdly, the application of several of these
 68 techniques to polycrystalline rocks and/or the interpretation of the findings usually involves an
 69 approximation that stress is homogeneous at the grain scale so that the magnitude and orientation of
 70 the grain scale stresses can be taken to be the same as those applied to the rock as a whole. Yet in a
 71 polycrystal comprising differently oriented grains of a mechanically anisotropic material, this cannot
 72 be precisely true. These matters all touch upon the strongly felt intuition that whether or not a grain
 73 twins is likely to be sensitive to factors that influence the local stress state within the microstructure,
 74 and is not simply determined by the macroscopically applied stress.

75 Nevertheless, despite these limitations, it is undeniable that analyses of calcite twinning have made
 76 a significant contribution to regional reconstructions of tectonic stresses and strains, and are able to
 77 place informative constraints on the kinematic evolution of sedimentary basins (e.g. the case studies
 78 described by Lacombe, 2010). This, together with the potential that exists for extending these twin-
 79 based techniques to other minerals such as dolomite, pyroxene and quartz (Carter and Raleigh, 1969;
 80 Tullis, 1980; Wenk et al., 2006), provides a strong motivation for seeking the kind of improved
 81 understanding of the factors influencing mechanical twinning that also increases confidence in twin-

82 based palaeostress and strain estimates.

83 Attempts to use rock deformation experiments to reduce the uncertainty in twin-based palaeostress
 84 and strain techniques are hampered by the fact that it is difficult to monitor the onset and progress of
 85 mechanical twinning within polycrystalline samples during the experiments. The extent of twinning is
 86 instead obtained by examining the microstructures of the deformed samples after the experiment. This
 87 only provides information about the end-result of the deformation and does not indicate when during
 88 the deformation the twinning occurred. Nor does it provide information about precursory elastic
 89 twinning, a phenomenon that is well-documented in calcite single crystals (e.g. Klassen-Neklyudova,
 90 1964; Kaga and Gilman, 1969; Boyko et al., 1994; Clayton and Knap, 2011).

91 The penetrating nature of neutrons offers a potential solution to these difficulties. By performing the
 92 deformation experiment within a polychromatic beam of neutrons and collecting diffraction data
 93 (effectively powder diffraction patterns) at different applied loads, changes in lattice spacing in several
 94 sub-sets of differently oriented grains may be simultaneously monitored as a function of the applied
 95 load. These changes in lattice spacing may be converted into the elastic strains. By comparing how
 96 these elastic strains change with increasing applied load in each of these sub-sets of grains, the onset
 97 and progress of crystallographically-controlled processes such as twinning in grains that are favourably
 98 oriented for them to occur may be tracked. In principle, polychromatic synchrotron X-rays may be
 99 used in the same way (e.g. Withers, 2013), but whereas the small gauge volumes accessed by
 100 synchrotron X-rays are ideal for high spatial resolution (sub-mm to micron) strain mapping (e.g. Chen
 101 et al., 2011), the larger gauge volumes accessed by neutrons provide a more convenient route to
 102 evaluating strain within a volume of sample that is large compared with the grain size.

103 In this study we report the results of some neutron diffraction experiments of this kind performed
 104 on two calcite rocks with different grain sizes. We show that the onset of mechanical twinning at small
 105 strains ($<0.3\%$) in calcite can be monitored in this way.

106

107 **2. Background to the adopted experimental strategy**

108 Being able to monitor the onset and progress of mechanical twinning during a deformation

109 experiment provides a method for establishing whether or not a macroscopic critical resolved shear
 110 stress can be defined, and if it does, then also the magnitude and sensitivity of that stress to
 111 deformation variables such as temperature and strain-rate. By performing experiments on samples with
 112 different microstructures, the influence of microstructural variables may be quantified.

113

114 *2.1. Critical resolved shear stress for twinning*

115 Experiments on a wide range of engineering materials show that mechanical twins nucleate at an
 116 externally applied stress that is much smaller in magnitude than theoretically predicted, and that when
 117 they do nucleate, they do so in regions of highly localized strain, that is, at localized stress
 118 concentrations on grain boundaries or other lattice defects (Christian and Mahajan, 1995). Two
 119 perspectives on twin nucleation then logically follow. Firstly, by analogy with dislocation glide, one
 120 might envisage that the magnitude of the local stress required to nucleate twins is approximately the
 121 same throughout the sample but also note that within the sample there is a wide range in the magnitude
 122 of local stress concentrations. Twinning occurs as the externally applied stress is increased and
 123 increasing numbers of the stress concentrators attain the critical activation stress. Alternatively, one
 124 might envisage that there is an array of potential twin nucleation sites, each with a different critical
 125 activation stress that reflects the specific local lattice structure at that site. In this case, as the externally
 126 applied stress is increased, more of these sites activate. In the former perspective it makes sense to
 127 refer to a critical resolved shear stress for twinning; in the latter perspective it does not. Most
 128 commentaries on twinning favour the latter perspective (e.g. Reed-Hill and Abbaschian, 1992;
 129 Christian and Mahajan, 1995; Tomé et al., 2011), and accordingly probabilistic models of twin
 130 nucleation have been developed that accommodate local lattice structure variability and a range of
 131 activation stresses (e.g. Beyerlein and Tomé, 2010; Beyerlein et al., 2011; Niezgoda et al., 2013).
 132 Nevertheless, if widespread twin nucleation is initiated over a small stress interval, it may be possible
 133 to define an apparent critical resolved shear stress that could be used in palaeostress analysis. A
 134 mechanism for rapid bursts of twin nucleation is provided by the observation that a twin propagating
 135 across one grain may nucleate a twin in the adjacent grain when the local stress concentration

136 associated with its tip reaches the grain boundary, that is, twin nucleation may be autocatalytic (Ecob
137 and Ralph, 1983).

138 In palaeostress analyses based on calcite twinning, a critical resolved shear stress of 10 MPa is
139 widely used (Lacombe, 2010). This value is consistent with the stresses obtained from the twin
140 microstructures of coarse-grained calcite marbles that have been experimentally deformed in axial
141 compression to known differential stress (Lacombe and Laurent, 1996; Laurent et al., 2000). It is also
142 consistent with the results of axial compression and axial extension experiments on calcite single
143 crystals favourably oriented for *e*-twinning. These show that the critical resolved shear stress for
144 twinning decreases from ~12 MPa at 20°C to ~6 MPa at 400°C, although the precise values are
145 sensitive to how the yield point of the samples is defined (Turner et al., 1954; Turner and Heard, 1965;
146 Laurent et al., 2000, Fig. 9). These experiments show negligible changes in critical resolved shear
147 stress with strain-rate over the range 10^{-1} to 10^{-7} s⁻¹ (Turner and Heard, 1965), although significant
148 strain-rate sensitivity is implied at much faster strain-rates by calcite twinning microstructures formed
149 at meteorite impact sites (Lindgren et al., 2013).

150 The observation that an apparent critical resolved shear stress for the onset of mechanical twinning
151 in calcite can be plausibly defined and that this exhibits only a small decrease with increasing
152 temperature and decreasing strain-rate, matches findings from deformation experiments on engineering
153 materials (Christian and Mahajan, 1995). In engineering materials some attention has been given to
154 obtaining the precise form of the temperature, strain-rate and also pre-strain sensitivities but these
155 remain poorly constrained (Meyers et al., 2001).

156

157 2.2. *The effect of microstructure on twinning*

158 The observation that mechanical twins nucleate at grain boundaries and other defects implies that
159 twinning is sensitive to microstructural variables. Particular attention has been given to the effect of
160 grain size, both in calcite (Rowe and Rutter, 1990; Newman, 1994; Rocher et al., 2004) and in
161 engineering materials (e.g. Meyers et al., 2001; Beyerlein et al., 2010; Ghaderi and Barnett, 2011).
162 Mechanical twinning is inhibited by decreasing grain size. This has been rationalized by noting that

grain boundaries limit the size of twins, and hence with decreasing grain size greater stresses are required to ensure that the energy cost of creating new twin boundaries does not outweigh the mechanical work done by the twin (Hosford, 1993, p.183). Alternatively, finer grained polycrystals require a greater twin number density to achieve given strain, and this requires greater stress (Barnett, 2008). Several studies on engineering materials report that the stress required for twinning follows a Hall-Petch type grain size dependence ($\sigma = \sigma_0 + kd^{-1/2}$, where σ_0 and k are material parameters and d is grain size) in which the slope, k , of the dependence is much greater than that observed for dislocation creep (Meyers et al., 2001). Nevertheless, there remains considerable uncertainty about how this grain size effect is achieved, and whether it is really captured by a Hall-Petch type relation.

To obtain greater insight into the influence of microstructure on mechanical twinning, grain by grain characterizations of twin microstructures have been performed on 2D sections through experimentally deformed polycrystalline samples (e.g. Spiers, 1979; Capolungo et al., 2009, Beyerlein et al., 2010; Ghaderi and Barnett, 2011). In these studies twinning activity is considered with reference to how well oriented an individual grain is for twinning as defined by the magnitude of its twin Schmid factor, m . For axisymmetric loading this is given by

$$m = \cos \phi \cos \lambda \quad (1)$$

where ϕ is the angle between the loading direction and the normal to the twin plane, and λ is the angle between the loading direction and the twin displacement vector (e.g. Dieter, 1988, p.124-125). Various measures of twinning activity have been used including, (a) the percentage of grains containing a twin (twinning incidence), (b) the volume fraction of a grain that is in twinning orientation (twin volume fraction), and (c) the number of twins per grain per unit length (twin density). These show different correlations with microstructural variables (e.g. Rowe and Rutter, 1990; Ghaderi and Barnett, 2011).

Studies of this kind have confirmed that statistically there is a strong correlation between whether or not a grain twins and the magnitude of its twin Schmid factor but that there are well oriented grains that do not twin and poorly oriented grains that do (Capolungo et al., 2009; Beyerlein et al., 2010). Both twin volume fraction and twin thickness are, however, observed to increase with twin Schmid factor (Spiers, 1979; Capolungo et al., 2009; Beyerlein et al., 2010). This suggests that while twin

190 nucleation may be a probabilistic process controlled by local lattice structure and stress concentrations,
 191 twin growth is controlled by longer range stresses and is governed by a Schmid-type criterion (Tomé et
 192 al., 2011).

193 Elastic and plastic anisotropy mean that stress gradients are generated at grain boundaries by the
 194 misorientation of the lattices across them. Hence it is expected that twinning is sensitive to
 195 misorientation and therefore to texture (crystallographic preferred orientation). In the 2D
 196 microstructural analyses the influence of texture on twin nucleation and twin growth has been
 197 examined by correlating misorientation with the number of twins per segment of grain boundary and
 198 with twin thickness respectively. Results from strongly textured magnesium and zirconium imply that
 199 both twin nucleation and twin growth are favoured by small misorientations (Capolungo et al., 2009;
 200 Beyerlein et al., 2010).

201 In these studies the influence of grain size on twinning has been examined, (a) by subdividing the
 202 distribution of grain sizes in the 2D microstructure into several grain size classes and by then carrying
 203 out the microstructural analysis on each size class, (b) by carrying out the microstructural analysis on
 204 samples with different mean grain size, or (c) by a combination of (a) and (b). The different
 205 approaches have produced conflicting results. Results from strongly textured magnesium and
 206 zirconium using method (a) show that the number of twins increases with grain size but that twinning
 207 incidence and twin volume fraction are independent of grain size (Capolungo et al., 2009; Beyerlein et
 208 al., 2010). Results from a strongly textured titanium and magnesium alloy using method (b) show that
 209 twin volume fraction increases with grain size, and that moreover, it does so in such a way that the
 210 stresses at given strain when the deformation is dominated by twinning are consistent with a Hall-
 211 Petch type grain size dependence (Ghaderi and Barnett, 2011). Results from calcite with a near random
 212 texture using method (c) show that twinning incidence and twin volume fraction increase with grain
 213 size but that twin density is independent of grain size (Rowe and Rutter, 1990). These different results
 214 perhaps arise in part from the fact that method (a) and method (b) are not examining the same grain
 215 size effect (Ghaderi and Barnett, 2011). In method (a) the grain size is apparent (a small grain may be
 216 a section through the tip of a large grain) while in method (b) the grain size is the mean of a grain size

distribution. Moreover, if twinning is sensitive to grain size and twin nucleation is an autocatalytic phenomenon, twinning is probably also sensitive to grain size distribution because the number of grains in which twin nucleation can be easily stimulated will be influenced by the proportion of grains that are relatively small.

Analysis of twin microstructures on 2D sections encounters the problem that the local orientation and magnitude of the stresses in each grain are unknown. In the absence of information, an approximation of homogeneous stress is used allowing the twin Schmid factor for any grain to be defined with reference to the externally applied stresses. However, elastic anisotropy and the requirements of strain compatibility mean that this cannot be strictly true (e.g. Burnley, 2013), and this is probably significant for twin nucleation. Assessing the grain by grain variation of principal stress directions within a twin microstructure is challenging because the method for obtaining these directions using twin orientation assumes that the twinned grain has the maximum possible twin Schmid factor (0.5); twinning at sub-optimal twin Schmid factors introduces a spread in calculated principal stress directions. Nevertheless, using this assumption, stress orientation measurements obtained from sparsely twinned Solnhofen limestone samples that had been experimentally deformed in axial compression to strains of ~15% show a deviation away from the externally applied loading direction of up to 40° (Cline, 2014). In assessing grain by grain variations of stress magnitude within calcite polycrystals during twinning dominated deformation, it is frequently noted that the smooth rather than discontinuous variation of twin volume fraction with twin Schmid factor (defined with reference to the externally applied stress) implies that the grains do not all experience the same strain (Spiers, 1979). However, even if the deformation is not one of homogeneous strain, it does not then follow that it is one of homogeneous stress.

2.3. Neutron diffraction experiments in engineering materials

Over the last thirty years neutron diffraction techniques have been widely used on engineering materials both to measure residual elastic strains in samples subjected to different thermomechanical pre-treatments and to monitor elastic strains within samples during deformation experiments (e.g.

244 Fitzpatrick and Lodini, 2003; Hutchings et al., 2005; Schajer, 2013). Neutron diffraction has also been
 245 used specifically to monitor the onset and progress of mechanical twinning during deformation testing
 246 of several metals (e.g. Gharghouri et al., 1999; Brown et al., 2005; Oliver et al., 2005; Clausen et al.,
 247 2008; Muránsky et al., 2009; 2010; Máthis et al., 2012). This has led to significant improvements in
 248 identifying the onset of twinning and the mechanism of twin growth in these materials (reviewed by
 249 Preuss et al., 2010).

250 In these mechanical twinning studies on metals, axial compression or axial extension experiments
 251 are performed at atmospheric pressure within a neutron beam. The ductility of the metals investigated
 252 means that they can be deformed without fracturing to strains well beyond their yield point. The
 253 incident beam of neutrons comprises neutrons with a range of energies (wavelengths). The diffracted
 254 neutrons are collected in detector banks set at a fixed angle to the loading direction. Because the
 255 incident neutron beam is polychromatic, a diffraction pattern spanning a range of lattice d -spacings is
 256 collected in each detector bank. The peak at given d -spacing in the diffraction pattern collected in
 257 given detector bank represents diffraction from those grains within the sample which are oriented such
 258 that they satisfy the Bragg condition for that d -spacing. Each peak therefore corresponds to a
 259 differently oriented sub-set of grains within the sample. The onset and progress of twinning is
 260 monitored from the changing diffraction peak intensities as the lattice is reoriented by twinning. In
 261 most studies to date, this effect has been amplified by using strongly textured materials and by then
 262 applying the load in a direction with respect to this texture that favours twinning. This also ensures that
 263 twinning rather than slip on other systems dominates the mechanical response.

264 In these studies sharp changes in diffraction peak intensity are observed at the onset of twinning
 265 (e.g. Brown et al., 2005; Oliver et al., 2005). As the applied load is increased further, the rate of
 266 change of intensity decreases implying that the twinning saturates as twin nucleation sites are used up
 267 (Brown et al., 2005). At the onset of twinning in some materials, abrupt off-loading is observed in sub-
 268 sets of grains that are well oriented for twinning (Clausen et al., 2008; Preuss et al., 2010). In some
 269 experiments twinning and de-twinning have been monitored over several loading-unloading cycles
 270 (Gharghouri et al., 1999; Wu et al., 2008). The changing relative contribution of twinning and

271 dislocation slip has also been evaluated by comparing observations made on textured samples in
 272 compression and extension (where twinning is favoured in one but not the other), and by performing
 273 tests at different temperatures (Oliver et al., 2005).

274

275 *2.4. Aims of this study*

276 The neutron diffraction techniques developed using engineering materials have been extended to
 277 geological materials to evaluate residual elastic strains (e.g. Scheffzük et al., 1998; 2004; Luzin et al.,
 278 2014) and to monitor elastic strains and textural changes during loading (e.g. Frischbutter et al., 2000;
 279 Covey-Crump et al., 2001; 2003; 2013; Wenk et al., 2007; Piazzolo et al., 2013; Wilson et al., 2015).

280 The primary aim of the present study was to determine if the onset of twinning during axial
 281 compression of calcite rocks can be observed using neutron diffraction, and if so, to determine the
 282 applied stress at which this occurs. The experiments were performed on a coarse-grained marble
 283 (Carrara marble) and a fine-grained limestone (Solnhofen limestone) so that observations from
 284 samples in which twinning was expected to occur at the deformation conditions could be compared
 285 with observations from samples in which it was not.

286 Since accurate measurement of the applied stress was as important to the aims of the study as
 287 simply detecting the onset of twinning, a key requirement was that the observations could be made on
 288 samples of similar size and shape to those generally used in axial compression tests on rocks (typically
 289 circular cylinders of at least 1 cm diameter and with a length:diameter aspect ratio of ~2.5). Axial
 290 compression tests on samples of this size may be performed within a neutron beam-line at elevated
 291 temperature ($<700^{\circ}\text{C}$) or, by using a pressure vessel manufactured from a relatively neutron
 292 transparent material (e.g. an aluminium alloy), at elevated confining pressure ($<400\text{ MPa}$) (Covey-
 293 Crump et al., 2006; Schofield et al., 2006; Hall et al., 2010). However, a pressure vessel that combines
 294 neutron transparency with sufficient strength at high temperatures to permit experiments at
 295 simultaneously elevated temperature and confining pressure has yet to be designed. The permanent
 296 deformation response of polycrystalline calcite at atmospheric pressure is dominated by brittle
 297 processes, and these are not easily suppressed either at high temperature even at moderate confining

pressures (e.g. Fischer and Paterson, 1989) or at room-temperature even at large confining pressures (e.g. Fredrich et al., 1990; Wong et al., 1996; Renner and Rummel, 1996; Baud et al., 2000; Schubnel et al., 2005). Given these realities, we decided to perform atmospheric pressure experiments at elevated temperature and to focus on deformation at small strains ($<0.3\%$), and hence at applied stresses (<70 MPa for Carrara marble and <180 MPa for Solnhofen limestone) smaller than those required for the onset of intragranular fracturing. Compared with similar experiments on metals, these small strains restrict the opportunity for using texture development to monitor the onset of twinning, and instead place emphasis on monitoring changes in elastic strain within differently oriented sub-sets of grains.

The principal experiments were performed at 200°C . Calcite twinning piezometry is most frequently applied to rocks deformed at 50° to 150°C and so the choice of 200°C was partly motivated by the desire to use a similar temperature. However, the primary motivation was to maximize ductility while minimizing the number of twins and intragranular fractures that might be induced by the large thermal expansion anisotropy of calcite during heating to the test conditions. On the basis that any observed temperature dependence might help to constrain the interpretation of the observations made at 200°C , the main datasets were supplemented by additional uniaxial compression experiments on Carrara marble at temperatures in the range 20° - 600°C and an experiment on Solnhofen limestone at 400°C .

316

3. Experimental methods

The practicalities of collecting neutron diffraction data from engineering materials during the type of deformation tests used in this study are described elsewhere (e.g. Daymond, 2006; Holden, 2013). Matters arising from the use of geological rather than engineering materials are discussed by Schofield et al. (2003).

322

3.1. Starting materials

The Carrara marble samples were obtained from the same block of Lorano Bianco marble that was

324

characterized in detail by Pieri et al. (2001). This is a white, granoblastic, pure calcite marble with mean grain size of $\sim 150 \mu\text{m}$, and a near random crystallographic preferred orientation. It has a porosity of 0.4% (Delle Piane et al., 2015). The Solnhofen limestone samples were obtained from the same block that was described by Llana-Fúnez and Rutter (2005). This is a fine-grained ($\sim 5 \mu\text{m}$) limestone with a porosity of 5% and which comprises 97% calcite and 3% impurity phases (primarily organic matter and clay minerals along the grain boundaries). It has a weak crystallographic preferred orientation characterized by a broad girdle of c -axes (maximum intensity 1.9 times uniform) parallel to the bedding plane. Cylindrical samples, 10 mm in diameter and approximately 25 mm long, were cored from each block. The long axis of the Solnhofen limestone samples was normal to bedding.

334

3.2. *Deformation experiments and collection of neutron data*

The neutron measurements were collected as time-of-flight, powder diffraction data on the ENGINE-X beam-line at the ISIS neutron spallation source, Rutherford Appleton Laboratory, U.K. (Johnson and Daymond, 2002; Daymond and Edwards, 2004). On this beam-line polychromatic pulses of neutrons are directed at the sample, and the diffracted neutrons are recorded in two banks of detectors fixed at $\pm 90^\circ$ to the incident beam. The samples were loaded in axial compression in an Instron load frame positioned such that the load axis was horizontal and at 45° to the incident beam. In this geometry the detector bank on one side of the sample records neutrons diffracted from lattice planes with scattering vectors parallel to the loading direction (axial direction), while the detector bank on the other side of the sample records neutrons diffracted from lattice planes with scattering vectors normal to the loading direction (radial direction). Thus the diffraction patterns collected at different loads in the axial detector bank provide information about how the lattice parameters and d -spacings change parallel to the loading direction, while the diffraction patterns collected in the radial detector bank provide this information in a direction normal to the applied load (Fig. 1). The angular coverage of each detector bank is $\pm 14^\circ$ and hence ‘parallel’ and ‘normal’ are to be understood as lying within this angular range in each case.

Neutron data were collected from a gauge volume $4 \times 4 \times 7 \text{ mm}^3$ located at the centre of the sample.

352 The sample was assembled between two alumina rams. The whole assembly was heated in air by four
353 radiant furnaces, two located above the sample and two below it. To maintain a stable temperature
354 profile along the length of the sample assembly, each end of the assembly was water-cooled. From
355 thermal profile calibrations it is estimated that the temperature variation within the measured sample
356 volume was less than 2°C. During neutron diffraction data collection temperature was measured by a
357 thermocouple with its tip held in contact with the surface of the sample ~3 mm from one end.

358 The following procedure was adopted in each experiment. First the sample was held at a small load
359 (corresponding to an axial stress of 1 MPa) and heated at 20°C/min to the desired test temperature.
360 After a thermal equilibration period of 30-45 min, diffraction data were collected. Once a diffraction
361 pattern of sufficient quality had been obtained (~20 min), the sample was taken to a greater load and
362 then held there while further diffraction data were collected. This process was repeated until
363 diffraction patterns from a large number of loads had been collected. During the experiments the
364 shortening of the sample was not monitored directly because of the risk of damage to the capacitance
365 extensometer that is normally used for this purpose should the sample undergo rapid brittle failure.
366 However, no shortening of the sample while the sample was held at constant load was detected by the
367 Instron crosshead position sensor during any of the intervals of neutron counting. In most cases the
368 experiment was terminated when the sample underwent sudden macroscopic brittle failure during
369 loading but the 200°C experiments and the 400°C Solnhofen limestone experiment were ended well
370 before macroscopic failure so that the final length of the sample could be measured. This allowed the
371 permanent axial strain that accumulated during loading (between intervals of neutron counting) to be
372 evaluated in those experiments. The applied load was converted into an applied axial stress by dividing
373 by the initial cross-sectional area of the sample. All strains are stated as logarithmic strains.

374 In the 200°C experiments diffraction data were collected from 57 different loads within the applied
375 stress range of 1-70.5 MPa for Carrara marble and from 36 different loads in the range 1-175 MPa for
376 Solnhofen limestone. Smaller datasets (mostly 10-15 different loads) were acquired in the experiments
377 performed at other temperatures.

378

3.3. Diffraction data analysis

A compilation of calcite crystallographic information relevant to this study is given in Supplementary document 1. Throughout the Miller-Bravais indices $hkil$ of calcite are specified with reference to the hexagonal structural cell ($a = 4.9896 \text{ \AA}$, $c = 17.0610 \text{ \AA}$ at 25°C). The obverse setting of the rhombohedral lattice in the hexagonal axes is used, and the convention of replacing $i = -(h+k)$ by a dot in the Miller-Bravais indices is used to avoid confusion when $l > 9$.

The diffraction data were collected as time-of-flight data that were focused, background subtracted, normalized to the incident flux distribution, and then binned as $\Delta t/t = 0.0002$. Example diffraction patterns collected at 200°C are shown in Fig. 2, with time-of-flight converted to d -spacing by combining de Broglie's equation with Bragg's equation (e.g. Schofield et al., 2003).

The diffraction data obtained at given applied load may be analysed by using Rietveld refinement to fit the whole diffraction pattern and thereby to obtain values of the lattice parameters (e.g. Young, 1993). Alternatively, the peaks may be fitted individually to obtain the d -spacing of each peak at given applied load. Whole pattern fitting generally requires that the symmetry of the calcite crystal structure be rigorously maintained and so takes no account of any elastic anisotropy-induced distortions in the shape of the unit cell that may occur with increasing applied load. Hence the strains within the sub-set of grains that contribute to any given reflection are more precisely described by the single peak approach. In this study we used whole pattern Rietveld refinements to evaluate volume-average strains, and single peak analysis to evaluate the strains experienced by grains in different orientations with respect to the loading direction. In order to maintain consistency, both the Rietveld refinements and the single peak analyses were performed using the General Structure Analysis System (GSAS) software package (Larson and Von Dreele, 2004).

In the Rietveld analysis initial calcite crystal structure parameters for the first refinement were taken from Maslen et al. (1993). For each sample the first refinement was performed on data collected at the least applied load, with scale, background, absorption coefficient, lattice parameters, fractional coordinates, and isotropic atomic displacement factors all refined from the source data to produce a sample-specific seed-file for subsequent refinements. GSAS allows a spherical harmonic description of

texture to be included within the Rietveld refinement (Von Dreele, 1997), and so to account for the effects of the small crystallographic preferred orientation within the Solnhofen limestone samples, this option was enabled during the preparation of the seed-file for those samples. The resulting value of Bunge's texture index, J , was 1.27 and 1.07 for the axial and radial diffraction patterns respectively (1 = random; ∞ = single crystal).

Peak Profile function 1 in GSAS was used to fit the diffraction data (Larson and Von Dreele, 2004, p.141-154). This describes peak profiles as a convolution of two back-to-back exponentials with a Gaussian line shape. The variance (s^2) of the Gaussian profile is a function of d -spacing and is described by

$$s^2 = (\text{sig-0})^2 + (\text{sig-1})^2 d^2 + (\text{sig-2})^2 d^4 \quad (2)$$

In our refinements sig-0 and sig-2 were set to pre-defined values in the instrument parameter file to model the instrument peak shape and so only sig-1 was allowed to vary. The value of sig-1 obtained applies to the whole pattern and is not specific to any individual peak. Changes in sig-1 with applied load reflect changes in strain-broadening, that is, changes in the distribution of local strains induced by lattice defects (e.g. dislocations, twin boundaries) within the grains that contribute to the diffraction peaks. Hence changes in sig-1 are potentially an indication of the onset of a defect generating process.

The final parameters from the data refinement at the least applied load were used as the initial values for the subsequent refinements for all remaining loads. Each refinement was performed in an identical fashion, with 8 variables (4 background, 1 scale factor, 2 calcite lattice parameters, and the sig-1 parameter). Various measures of the quality of the fits are tabulated in Supplementary document 2 (Table S2.1). Typical calculated patterns from the Rietveld analysis, together with the difference between the observed and calculated pattern, are shown in Fig. 2.

Several diffraction peaks were available for single peak analysis. The choice of peaks that were actually analysed was based on the desire to include a wide range of differently oriented grains so that we sampled grains with a wide-range of elastic stiffness and susceptibility to e -twinning. However, to minimize uncertainties in the calculated lattice strains, the peaks that were analysed were also restricted, with one exception, to those that remain tightly defined in terms of position, intensity, and

shape at all applied loads and temperatures. The peaks that best satisfy these constraints (in approximate order of increasing uncertainty on the calculated lattice strains) are 10.4, 11.3, 00.6, 10.8, 10.2, 21.1, 30.0, 21.5, 31.4 and 11.0. The one exception was 30.0 which could not be used at temperatures above 200°C because it becomes too close to 00.12 to be separately resolvable. The analysis of the single peaks was undertaken using the RAWPLOT routine within GSAS. All peaks within a predefined d -spacing range were analysed simultaneously and were fitted without any crystallographic constraint. In all cases the position, intensity, and peak-broadening parameter were refined. The final parameters from the refinement of the data obtained at the least applied load were used as the initial parameters for the peak fitting at all remaining loads.

The diffraction data for the primary datasets at 200°C were collected over a d -spacing range of 0.1 - 3.95 Å. However, to reduce data acquisition times and thereby to allow data to be collected at a greater number of loads and temperatures, in some of the experiments the diffraction data were collected over a narrower d -spacing range (0.4 - 3.2 Å). Details of which datasets are affected in this way are given in Supplementary document 2 (Table S2.1). The smaller d -spacing range excludes the mechanically significant 10.2 peak at 3.868 Å. At temperatures below 200°C information for this direction was obtained using the small 20.4 peak but at higher temperatures this peak is too close to the large 10.8 peak to be separately resolvable.

3.4. Mechanical data analysis

The elastic strain parallel to the scattering vector at a given load is

$$\varepsilon_{hk,l} = -\ln(d_{hk,l}/d_{0,hk,l}) \quad (3)$$

where $d_{hk,l}$ is the d -spacing of the hk,l peak of interest, and $d_{0,hk,l}$ is that d -spacing at zero load. The experiment set up does not allow zero load measurements and so $d_{0,hk,l}$ was obtained for each hk,l peak in each experiment by least squares fitting a linear or quadratic polynomial to the $d_{hk,l}$ versus applied load data obtained over the smallest few loads and by then extrapolating back to zero load. Volume-average elastic strains, ε_a and ε_c , parallel to the scattering vector may be obtained from the whole pattern Rietveld refinements by using the lattice parameters a and a_0 or c and c_0 respectively in Eq. (3).

460 A volumetric elastic strain parallel to the scattering vector is conveniently defined for comparison with
 461 the linear elastic strains as

$$462 \quad \varepsilon_V = - (1/3) \ln (V / V_0) \quad (4)$$

463 where $V (= a^2 c \sin 60^\circ)$ is the apparent unit cell volume obtained using the lattice parameters from the
 464 whole pattern Rietveld refinement at given load, and V_0 is that volume at zero load. Values of a_0 , c_0
 465 and V_0 were obtained in the same way as $d_{0,hk,l}$.

466 As noted above, the lattice distortions induced by elastic anisotropy are not accommodated in
 467 Rietveld analyses when peak positions are determined only by varying lattice parameters. However, in
 468 practice, since some peak positions are overestimated and others underestimated, it is observed that
 469 Rietveld refinement does provide a good estimate of the volumetric elastic strain in a polycrystal of
 470 randomly oriented grains (Daymond, 2004). In the experiments at 200°C the uncertainties on the
 471 lattice spacings and instrument calibrations lead to uncertainties on the strains in the range 10-
 472 15 μ strain for ε_V and 15-80 μ strain for $\varepsilon_{hk,l}$.

473 In interpreting the mechanical significance of the strain measurements it is important to remember
 474 that the grains ‘seen’ by the axial and radial detector banks for given hk,l peak belong to two different
 475 sub-sets of the total grain population. For example, the 10.8 peak in the axial diffraction pattern
 476 includes contributions from grains oriented such that one of the lattice planes (1018), (1108) or (0118)
 477 is normal to the loading direction, whereas the 10.8 peak in the radial diffraction pattern includes
 478 contributions from grains oriented such that one of these lattice planes is parallel to the loading
 479 direction (e.g. grains A and D in Fig. 1b). Moreover, whereas the angle between the lattice plane
 480 normal and loading direction is the same (0°) for all grains contributing to given hk,l peak in the axial
 481 diffraction pattern, grains contributing to given hk,l peak in the radial diffraction pattern can be at any
 482 rotational angle about the hk,l normal with respect to the loading direction. Since the single crystal
 483 elastic properties vary with lattice direction, it follows that the radial detector bank records diffraction
 484 from grains that are in different stress states. Numerical simulations of the elastic and plastic
 485 deformation of polycrystals under externally applied, axially symmetric loads show that this range in
 486 stress states may be substantial (e.g. Clausen et al., 1998; Oliver et al., 2004; Burnley, 2015). Given

the complexities that this presents for interpreting the radial single peak data, our interpretations of the single peak data are focused primarily on the data collected from the axial detector bank.

4. Results

The results of the experiments are tabulated in Supplementary document 2 (Tables S2.2-S2.10). This tabulation includes the calcite lattice parameters obtained from the Rietveld refinements at each load in both the axial and radial directions together with the d -spacings obtained from the single peak fits at each load in the axial direction only. Supplementary document 2 (Figs. S2.1-S2.9) also includes a set of figures for each experiment showing: (1) ε_a , ε_c and ε_V obtained from the Rietveld refinements in both axial and radial directions vs. applied stress, (2) sig-1 obtained from the Rietveld refinements in the axial direction vs. applied stress, and (3) ε_{hkl} in the axial direction vs. applied stress for each of the single peaks analysed.

4.1. 200°C results

The elastic strains evaluated from the lattice parameters given by the Rietveld refinements in the 200°C Solnhofen limestone and Carrara marble experiments are plotted as a function of applied stress in Fig. 3. The stress/strain curves for Solnhofen limestone (Fig. 3a) remain linear over the whole applied stress range. The permanent axial strain obtained from measurements of the initial and final length of the sample was <0.04%, that is, the deformation was essentially fully recoverable. In contrast the stress/strain curves for Carrara marble (Fig. 3b) show abrupt changes in slope at applied stresses of 14 MPa and 64.5 MPa. These are most pronounced in the ε_c data and are visible in both the axial and radial strains, although the change in slope at 64.5 MPa is most clearly seen in the radial data. Measurements of the initial and final length of the sample indicate a small permanent axial strain of 0.26%. The value of the sig-1 parameter increases linearly with applied load in both the Solnhofen limestone and Carrara marble experiments but with an abrupt increase in slope for Carrara marble at 64.5 MPa (Fig. 4).

The elastic strains evaluated from the single peak fits are plotted as a function of applied stress in

Fig. 5. In the Solnhofen limestone dataset (Figs. 5a-c) the stress/strain curves obtained from each peak analysed remain linear over the whole applied stress range. In the Carrara marble dataset (Figs. 5d-f) the stress/strain curves obtained from 00.6, 10.8 and 10.4 each show a sharp break in slope at 14 MPa. The break in slope at 64.5 MPa that was identified in the whole pattern fits is visible in the stress/strain curve for 10.2 (and less clearly in 21.5 and 31.4) as an abrupt reduction in the rate of increase of elastic strain with increasing applied stress. The stress/strain curves obtained from the other peaks analysed remain linear over the whole applied load range. At applied stresses greater than 14 MPa, the elastic strains obtained from 00.6 and 10.8 are much greater than the volumetric elastic strain, whereas those from 30.0, 11.0 and 21.1 are much less than the volumetric elastic strain.

We observed no variation in peak intensity with applied stress for any of the peaks analysed in the Solnhofen limestone dataset. In the Carrara marble dataset there is a very small increase in 00.6 peak intensity (in the axial detector bank) at the greatest stresses (Fig. 6) and a similar variation was observed for 10.8, but we observed no measurable changes in peak intensity for any of the other peaks.

4.2. Results at other temperatures

The elastic strains evaluated from the lattice parameters given by the Rietveld refinements for the Carrara marble experiments at temperatures other than 200°C are plotted as a function of applied stress in Fig. 7. At 25°C (Fig. 7a) the stress/strain curves are linear until the greatest stress (61 MPa). The sample failed mid-way through neutron counting at 61 MPa and so the data collected at this stress may be compromised by incipient macroscopic brittle failure. At 100°C (Fig. 7b) the slopes of the axial ϵ_a and ϵ_c stress/strain curves are very different at small stresses but abruptly become more similar at ~25 MPa. Measurements of the initial and final length of a separate sample that was subjected to two loading-unloading cycles at 100°C, the first to a maximum stress of 25 MPa and the second to 50 MPa, show that the deformation was fully recoverable to within measurement accuracy.

In the 320°-500°C experiments (Figs. 7c-e) the stress/strain curves are considered to show, like the 200°C data, two abrupt changes in slope as the applied stress was increased, although the load increments in some of the datasets were too large to demonstrate both of these definitively. The change

in slope at the smaller stress is identified by an abrupt increase in the difference between the slopes of the axial ε_a and ε_c stress/strain curves. This is evident in the 320°C data (Fig. 7c) at 6 MPa, while at 500°C (Fig. 7e) the curvature of the axial stress/strain curves at applied stresses less than 10 MPa suggests that it occurs at a very small applied stress (between 1 and 3 MPa). At 400°C (Fig. 7d) extrapolating the ε_a and ε_c axial stress/strain curves towards zero applied stress suggests that it occurs at an applied stress of <5 MPa. In the 320°-500°C experiments the change in slope of the stress/strain curves at large stress is more subtle but is evident at 320° and 400°C in the radial ε_c stress/strain curves and at 500°C in the axial ε_a and ε_c stress/strain curves. In each case there is an accompanying sharp increase in slope of the sig-1 vs. applied stress curves (Supplementary document 2, Figs. S2.5b, S2.6b, S2.7b).

At 600°C (Fig. 7f) the slope of the axial ε_c stress/strain curve is initially gentle and steepens up with increasing load but abruptly becomes gentle again (with subsequent steepening) at 21 MPa and at 34.5 MPa. The radial ε_c strains are contractional not extensional and the radial ε_c stress/strain curve shows the same abrupt changes of slope as the axial ε_c stress/strain curve.

The elastic strains obtained from the single peak fits to the Carrara marble data at temperatures other than 200°C are plotted as a function of applied stress in Supplementary document 2 (Figs S2.3-S2.8). Qualitatively, these show the same features as described for Carrara marble at 200°C. The increase in 00.6 peak intensity parallel to the loading direction at the greatest stresses is small but more obvious in the 400°C and 500°C experiments than at 200°C and is supported by the necessary accompanying decrease in 11.0 peak intensity (Fig. 8).

The elastic strains evaluated from the lattice parameters given by the Rietveld refinements for the 400°C Solnhofen limestone experiment are plotted as a function of applied stress in Fig. 9a, and the variation of the sig-1 parameter with applied stress in this experiment is shown in Fig. 9b. There is an abrupt increase in the slope of the axial ε_c stress/strain curve at ~88 MPa which corresponds to an increase in slope of the sig-1 vs. applied stress curve. This change in response is not visible in the radial stress/strain curves. The radial ε_c extensional strains are very large compared with those obtained in the other experiments. The stress/strain curves obtained from the single peak fits (Supplementary

document 2, Fig. S2.9) show the same break in slope at 88 MPa for 00.6 as observed in the axial ε_c stress/strain curve but all the other stress/strain curves are linear over the full range of applied stresses. No change in peak intensity with applied stress was observed for any of the peaks analysed.

571

572 5. Discussion

Plausible deformation processes that might influence the interpretation of the elastic strain measurements obtained in this study include: (1) elastic deformation, (2) twinning on the $e = \{01.8\}$ planes, (3) cleavage fracturing on the $r = \{10.4\}$ planes, and (4) non-crystallographically controlled fracturing. Mechanical twinning on the $f = \{01.2\}$ planes and the r -planes has also been reported in deformation experiments on single crystal calcite but this is very much subsidiary to e -twinning (Turner, 1954). The values of critical resolved shear stress for r -slip, f -slip and c -slip (De Bresser and Spiers, 1997) imply that at the greatest stresses and highest temperatures in this study the conditions for the onset of r -slip, and perhaps also f -slip and c -slip, may also have been exceeded (see Supplementary document 3, section S3.1.4).

To assess the relative significance of these deformation processes we have evaluated the directional variation of apparent elastic stiffness that is indicated by the single peak data and compared it with that predicted should any of these processes be active. The neutron diffraction measurements provide information about elastic strains not total strains. However, information about crystallographically controlled inelastic processes such as e -twinning or cleavage fracturing may be obtained indirectly from the rate of change of elastic strain with applied stress in differently oriented grains. If an inelastic process becomes active, the stresses and hence axial elastic strains ($\varepsilon_{ax,hkl}$) in the most favourably oriented grains for that process will increase less rapidly with increasing macroscopic applied stress (σ_{agg}) than during purely elastic deformation, that is, those grain orientations will appear anomalously stiff when stiffness is determined as $\Delta\sigma_{agg}/\Delta\varepsilon_{ax,hkl}$. Conversely, unfavourably oriented grains will become more stressed and experience greater elastic strains and so will appear anomalously compliant.

In the following we describe (1) the predicted directional variation of apparent elastic stiffness for the principal deformation processes listed above, (2) how the observed directional variation of

apparent elastic stiffness was obtained from the single peak neutron data, and (3) the results and their interpretation. Additional details of this analysis are provided in Supplementary document 3.

5.1. Predicted directional variation of apparent elastic stiffnesses

5.1.1. Elastic stiffness

Within a polycrystal that is under load the constraints imposed by neighbouring grains mean that the state of stress of any individual grain is triaxial. The predicted elastic response parallel to the direction of loading is therefore given by the triaxial form of Hooke's law (e.g. Dieter, 1988, p.50) which becomes in the experiment geometry

$$\sigma_{agg} = \frac{E_{hk.l}}{(1 - 2\nu_{hk.l})(1 + \nu_{hk.l})} [(1 - \nu_{hk.l})\varepsilon_{ax,hk.l} + 2\nu_{hk.l}\varepsilon_{rad,hk.l}] \quad (5)$$

where σ_{agg} is the macroscopic applied stress in the axial direction, $\varepsilon_{ax,hk.l}$ and $\varepsilon_{rad,hk.l}$ are the elastic strains of the grains contributing to the $hk.l$ peak in the axial diffraction pattern as measured in the axial and radial directions respectively, and $E_{hk.l}$ and $\nu_{hk.l}$ are $hk.l$ -specific diffraction elastic constants (e.g. Hutchings et al., 2005, p.206-207; Holden, 2013). By definition the diffraction elastic constants relate the $hk.l$ elastic strains to the macroscopic applied stress. They may be obtained from the single crystal elastic stiffness tensor using the same types of averaging approximations that are used to obtain volume-averaged values of Young's modulus (E_V) and Poisson's ratio (ν) for a polycrystal from the single crystal stiffness tensor of its component phase. However, because the grains contributing to given $hk.l$ diffraction peak are only a subset of the total grain population, the diffraction elastic constants are not generally the same as the elastic constants obtained from the whole grain population.

For a polycrystal of randomly oriented grains, if all grains are treated as experiencing the same strain (Voigt-averaging), $E_{hk.l}$ and $\nu_{hk.l}$ are the same for all $hk.l$ and hence are equal to the isotropic values of E_V and ν respectively as obtained by averaging over all grains using the Voigt approximation. Alternatively, if all grains are treated as experiencing the same stress (Reuss-averaging) then the diffraction elastic constants vary with $hk.l$. In this case the value of $E_{hk.l}$ is the same as the single crystal directional Young's modulus for that $hk.l$ (e.g. Nye, 1985, p.145). Howard and Kisi (1999) provide explicit expressions for $E_{hk.l}$ and $\nu_{hk.l}$ in terms of the single crystal elastic constants (Voigt-

622 averaging), and in terms of the single crystal elastic constants, h , k and l , and the unit cell parameters
 623 (Reuss-averaging).

624 Voigt- and Reuss-averaging only provide bounds on the diffraction elastic constants. The real
 625 values of $E_{hk,l}$ and $\nu_{hk,l}$ lie close to arithmetic mean or geometric mean of the Voigt and Reuss values
 626 (Matthies and Humbert, 1995). However, instead of using either of these means, more commonly $E_{hk,l}$
 627 and $\nu_{hk,l}$ are estimated using Kröner's self-consistent analysis (Kröner, 1958). This utilizes Eshelby's
 628 solution for the elastic field around an ellipsoidal inclusion embedded within a homogeneous medium
 629 (Eshelby, 1957) to account for the elastic interactions that occur between individual grains and their
 630 surroundings (for a brief but lucid description, see Gnäupel-Herold et al., 2012). Except for the case of
 631 an untextured polycrystal of a cubic phase, values of $E_{hk,l}$ and $\nu_{hk,l}$ given by Kröner's analysis must be
 632 evaluated numerically. A freely available application that does this for specified unit cell parameters
 633 and single crystal elastic stiffness tensor is ISODEC (Gnäupel-Herold, 2012).

634 Values of $E_{hk,l}$ obtained by Voigt- and Reuss-averaging and Kröner's analysis that are applicable for
 635 untextured calcite polycrystals at 200°C are shown for the diffraction peaks of interest in this study
 636 (Fig. 10a) in Fig. 10b. In Fig. 10b the Reuss-averaged values of $E_{hk,l}$ are shown on a stereographic
 637 projection and the Voigt-averaged and Kröner values are tabulated. While the amplitude of the
 638 variation of the Reuss-averaged $E_{hk,l}$ is greater than that of the Kröner $E_{hk,l}$, the shape of the directional
 639 variation is very similar. This is necessarily true if the Kröner values of $E_{hk,l}$ are close to the arithmetic
 640 mean of the Voigt and Reuss values because the Voigt value is independent of hk,l . The values of $\nu_{hk,l}$
 641 given by Kröner's analysis are also tabulated in Fig. 10b. The directional variation of these is small.

642 Values of $E_{hk,l}$ obtained by Voigt- and Reuss-averaging and Kröner's analysis at all the test
 643 temperatures used in this study are tabulated in Supplementary document 3 (section S3.1.2). In
 644 evaluating these we used the calcite single crystal elastic stiffness tensor measured as a function of
 645 temperature by Dandekar (1968). Unfortunately, Dandekar did not state explicitly whether he used the
 646 obverse or reverse setting of the rhombohedral lattice in hexagonal axes when he specified the
 647 components of this elastic stiffness tensor. This affects the sign of the c_{14} component, which Dandekar
 648 reported as negative. Ab initio calculations of the elastic stiffness of calcite, however, suggest that in

the obverse setting c_{14} is positive (Le Page et al., 2002). Accordingly, we obtained the magnitude of c_{14} from Dandekar but have reversed its sign so that it is positive. This is a significant step because switching the sign of c_{14} rotates the directional variation of elastic stiffness by 60° about the c -axis so that, for example, the grains contributing to the 01.2 axial peak change from being approximately the most compliant grains (obverse setting) to being approximately the most stiff (see Supplementary document 3, Fig. S3.1). As discussed below, the directional variation in elastic stiffness that we observe in those parts of our experiments in which we consider the deformation to be purely elastic supports the suggestion that Dandekar used the reverse setting.

657

5.1.2. *Apparent elastic stiffness when inelastic processes are active*

The onset of a crystallographically-controlled inelastic process will alter the shape of the directional variation of apparent elastic stiffness because there are some grains that are more favourably oriented for the process (and so will appear stiffer) than others. We consider polycrystals in which grains that are well oriented for such a process are surrounded by grains that are less well oriented. The predictions are for processes that control the directional variations of apparent stiffness but that does not mean that other process are not simultaneously active.

The extent to which a grain is well oriented for e^+ -twinning is given by the magnitude of the Schmid factor (Eq. (1)) for twinning on the e -planes. The variation of this Schmid factor as a function of loading direction is shown in Fig. 10c. The neutron diffraction data do not discriminate between crystallographically equivalent loading directions and twin planes and therefore for each loading direction in Fig. 10c it is the maximum Schmid factor from all combinations of equivalent loading directions and twin planes that is shown. Of the grain orientations analysed in this study (axial diffraction patterns only), the most favourably oriented grains for e -twinning (Schmid factor most positive) are those contributing to the 10.2 peak while those contributing to the 00.6 peak cannot twin (Schmid factor negative). Also shown in Fig. 10c are loading directions for which the Schmid factors are positive on 0, 1, 2, or all 3 e -twin systems. We envisage three types of outcome for the apparent elastic stiffnesses when twinning is initiated depending upon how easy it is to accommodate the twin

676 strains within the microstructure.

- 677 (1) If accommodation is difficult then it may be that grains that have positive Schmid factors on more
 678 than one e -twin system are particularly favourably oriented. For the most difficult case, we expect
 679 the variation in apparent elastic stiffness to be similar to that given by the elastic stiffness tensor
 680 (Fig. 10b) but with a stronger maximum that lies (on the stereographic projection) closer to $\{30.0\}$
 681 along the $\{00.6\}$ - $\{30.0\}$ line in the middle of a field of grains with three positive Schmid factors.
 682 This field of grains with three positive Schmid factors is favoured over the other field of grains
 683 with three positive Schmid factors because these grains are elastically stiffer and therefore
 684 experience greater stress prior to the onset of twinning.
- 685 (2) If accommodation is easier so that grains with positive Schmid factors on two or three e -twin
 686 systems and not just three are sufficiently favourably oriented for twinning, we expect the
 687 apparent elastic stiffness to increase radially away from $\{00.6\}$ because the number of e -twin
 688 systems with positive Schmid factors increases approximately radially away from $\{00.6\}$.
- 689 (3) If accommodation is relatively easy then we expect the directional variation of apparent stiffness
 690 to be similar to that of the maximum Schmid factor for twinning, so that the apparent stiffness is
 691 greatest near $\{01.2\}$ and least at $\{00.6\}$.

692 Accommodation is most difficult in the absence of other inelastic processes. If in this situation some
 693 dilatancy helps to accommodate the twin strains, then one might expect the first type of outcome at the
 694 smallest stresses and temperatures perhaps giving way at greater stresses (and hence greater dilatancy)
 695 to the second type of outcome. The third type of outcome is envisaged to become important when the
 696 stresses/temperatures are sufficient to activate dislocation slip, and as such perhaps marks a switch
 697 from elastic twinning to permanent twinning.

698 The extent to which a grain is well oriented for r -slip is given by the magnitude of the Schmid
 699 factor for slip on the r -planes. The directional variation of the maximum Schmid factor for r -slip is
 700 shown in Fig. 10d. From the approximately radial decrease in Schmid factor away from $\{00.6\}$ we
 701 expect that the early stages of r -slip will show an apparent stiffness variation similar to that for the
 702 fully elastic case (Fig. 10b) but with a strengthening maximum at $\{00.6\}$. Assuming that twinning is

suppressed at fine grain size, this type of response is anticipated in the 400°C Solnhofen limestone experiment since that sample was loaded to much greater stresses than are required to activate r -slip.

The extent to which a grain is well oriented for cleavage fracturing on {10.4} may be assessed using Sohncke's normal stress law (Sohncke, 1869; Schmid and Boas, 1950, p.169-175). Rephrased for axial compression rather than axial extension, this simply notes that cleavage fracturing is favoured when the normal stress acting across the cleavage plane is small. The normal stress σ_n acting across the cleavage plane is given by

$$\sigma_n = \sigma_{agg} \cos^2 \chi \quad (6)$$

where χ is the angle between the loading direction and the normal to the cleavage plane (e.g. Dieter, 1988, p.250). The variation of $\cos^2 \chi$ with loading direction is shown in Fig. 10e. Again, since the neutron diffraction data do not discriminate between crystallographically equivalent loading directions and cleavage planes, for each loading direction it is the minimum value of $\cos^2 \chi$ from all combinations of equivalent loading directions and cleavage planes that is shown. Since grains with small $\cos^2 \chi$ are in a similar orientation to elastically stiff grains and therefore experience greater than average stress, while grains with large $\cos^2 \chi$ are in a similar orientation to elastically compliant grains and so experience less than average stress, the effect of limited cleavage fracturing on apparent stiffness is an intensification of the form of stiffness variation observed for purely elastic deformation.

If non-crystallographically-controlled fracturing (e.g. opening of grain boundaries, axial microcracking) has a significant influence on the stress distribution within the polycrystal, the data scatter about the stress/strain trends will increase for all grain orientations. From a general consideration of the form of fracture mechanism maps (e.g. Gandhi and Ashby, 1979) it is anticipated that at the deformation conditions of this study, the onset of cleavage fracturing will be at smaller stresses than axial microcracking.

5.2. Fitting the measured apparent elastic stiffnesses

The complexities associated with the interpretation of the radial data in the experiment geometry used in this study, and in particular, the fact that the measurements of $\epsilon_{rad,hk,l}$ come from grains that are

in a range of orientations with respect to the loading direction, none of which are in the same orientation as the grains used to obtain $\varepsilon_{ax,hk,l}$, make it difficult to utilize Eq. 5 and the values of $\nu_{hk,l}$. Consequently, since the macroscopic applied stress is uniaxial and the directional variation of $\nu_{hk,l}$ is small, in evaluating the measured apparent elastic stiffnesses we have used the uniaxial approximation of Eq. (5)

$$\sigma_{agg} = E_{hk,l} \varepsilon_{ax,hk,l} \quad (7)$$

The apparent elastic stiffness $E_{hk,l}$ of the hk,l subset of grains is then obtained by using linear regression to fit

$$\varepsilon_{ax,hk,l} = A_{hk,l} \sigma_{agg} \quad (8)$$

with $E_{hk,l} = A_{hk,l}^{-1}$. The fits were performed over stress intervals in which the variation of $\varepsilon_{ax,hk,l}$ with σ_{agg} was linear.

To make it easier to compare the directional variation of the observed apparent elastic stiffnesses with the predictions, we used ten values of $E_{hk,l}$ (one for each peak) obtained within each stress interval to fit an apparent elastic stiffness tensor for that interval. To be consistent with the neglect of Poisson constraint effects in Eq. (7) we assumed homogeneous stress. With this approximation, $E_{hk,l}$ for a trigonal class 3m material may be written in terms of the components of the single crystal elastic compliance tensor (s_{ij}), the lattice parameters (a , c), and h , k and l , as (Howard and Kisi, 1999)

$$A_{hk,l} = E_{hk,l}^{-1} = b_{1,hk,l} s_{11} + b_{2,hk,l} s_{33} + b_{3,hk,l} (2s_{13} + s_{44}) + b_{4,hk,l} s_{14} \quad (9)$$

where

$$b_{1,hk,l} = [16(H^2 + HK + K^2)^2] / [4H^2 + 4HK + 4K^2 + 3L^2]^2]$$

$$b_{2,hk,l} = 9L^4 / [4H^2 + 4HK + 4K^2 + 3L^2]^2]$$

$$b_{3,hk,l} = [12(H^2 + HK + K^2)L^2] / [4H^2 + 4HK + 4K^2 + 3L^2]^2]$$

$$b_{4,hk,l} = [8(3^{1/2})(2H^3 + 3H^2K - 3HK^2 - 2K^3)L] / [4H^2 + 4HK + 4K^2 + 3L^2]^2]$$

$$H = h/a \quad ; \quad K = k/a \quad ; \quad L = l/c$$

Hence multiple regression of the observed values of $A_{hk,l}$ on $b_{1,hk,l}$, $b_{2,hk,l}$, $b_{3,hk,l}$, and $b_{4,hk,l}$, while forcing the intercept of the fit to be zero, allows s_{11} , s_{33} , $(2s_{13} + s_{44})$, and s_{14} to be evaluated. From these four terms $E_{hk,l}$ may be plotted for any orientation using (Nye, 1985, p.145)

$$E_{hk.l}^{-1} = (1 - l_3^2)^2 s_{11} + l_3^4 s_{33} + l_3^2 (1 - l_3^2) (2s_{13} + s_{44}) + 2l_2 l_3 (3l_1^2 - l_2^2) s_{14} \quad (10)$$

where l_1 , l_2 and l_3 are the cosines of the angles between the $hk.l$ plane normal and the orthogonal axes x_1 , x_2 and x_3 respectively (in which x_1 and x_3 are parallel to the a_1 and c crystallographic axes respectively and x_2 is defined with the right-hand rule).

Since the homogeneous stress approximation cannot be precisely true, our focus in performing these fits is to capture the shape of the directional variation in apparent elastic stiffness rather than the precise magnitude of those stiffnesses. As noted above, the shape of this variation obtained using this approximation should be the same as that obtained using more realistic averaging schemes.

765

766 5.3. Apparent elastic stiffness results and interpretation

The directional variation of the apparent elastic stiffnesses obtained in the 200°C experiments is shown in Fig. 11, and selected results at other temperatures are shown in Fig. 12. A full set of results is given in Supplementary document 3 (section S3.2). By the side of each figure the values of $E_{hk.l}$ obtained using Eq. (8) are listed, while the contours in the stereographic projections show the directional variation of $E_{hk.l}$ obtained using Eqs. (9)-(10). Choosing stress intervals over which the variation of $\epsilon_{ax,hk.l}$ with σ_{agg} was linear generally ensured that the fits to Eq. (8) were tightly constrained, although in a few cases (when the range of elastic strains over the stress interval was small) the data scatter was too large to attempt a fit for one or more of the $\{hk.l\}$. The correlation coefficients for the fits to Eq. (9) were generally very high (> 0.98) but given the limitations of the homogeneous stress approximation, meaningful assessment of the quality of the fits is challenging (for further comments see Supplementary document 3, section 3.2.2). Since we use the fits to Eq. (9) simply to identify significant changes in the shape of the directional variation in apparent stiffness, the key requirement (which is satisfied) is that the locations of stiffness maxima and minima and general magnitude of the stiffness variations that are shown by the contours on the stereographic projections is in agreement with the listed values of $E_{hk.l}$.

The directional variation of apparent elastic stiffness in the 200°C Solnhofen limestone dataset (Fig. 11a) is very similar to that predicted for purely elastic deformation provided c_{14} is positive (Fig. 10b).

784 The slope of the applied stress vs. axial volumetric elastic strain curve (Fig. 3a) gives $E_V = 79.74$ GPa
 785 which is close to the value of $E_{V,Kröner} = 78.13$ GPa and so supports the interpretation that the
 786 deformation of the sample was purely elastic. Our results are therefore in agreement with the
 787 conclusion of Le Page et al. (2002) that in the obverse setting of the calcite rhombohedral lattice in
 788 hexagonal axes c_{14} is positive, and that the negative values of c_{14} reported by Dandekar (1968) for
 789 calcite imply that he used the now non-standard reverse setting.

790 The 200°C Carrara marble data at $\sigma_{agg} < 14$ MPa (Fig. 11b) also has a stiffness variation consistent
 791 with elastic deformation. The rather larger amplitude of this variation compared with the Solnhofen
 792 limestone data (Fig. 11a) may indicate that there was also some cleavage fracturing of particularly
 793 favourably oriented grains but the very small range of elastic strains over this small stress interval
 794 means that the quality of the fits to the least well constrained peaks (30.0, 31.4 and 11.0) is insufficient
 795 to be definitive. At $\sigma_{agg} > 64.5$ MPa (Fig. 11d) the variation of apparent stiffness matches that of the
 796 maximum Schmid factor for e -twinning (Fig. 10c). At intermediate stresses (Fig. 11c) the apparent
 797 stiffness increases radially away from {00.6} as predicted for twinning in those grains that have
 798 positive Schmid factors for twinning on two or more e -twin systems. That stresses in these grains were
 799 relieved (at least temporarily) is indicated by the abrupt off-loading seen in the whole pattern radial ε_c
 800 strains at 14 MPa (Fig. 3b) because this implies that stresses were being relieved in grains loaded
 801 parallel to the {00.6} lattice planes (e.g. grains contributing to the 30.0 and 11.0 peaks in the axial
 802 diffraction patterns). The radial gradient of apparent stiffness is large initially (14-18 MPa, Fig. 11c)
 803 but is much smaller at greater stresses (Supplementary document 3, Fig. S3.11). This suggests that
 804 with increasing stress the rate of formation of new twins declined, perhaps as the supply of twin nuclei
 805 in favourably oriented grains was exhausted. The absence of any measurable changes in diffraction
 806 peak intensity at these stresses (Fig. 6) means that the volume fraction of twins must have been small,
 807 that is, the twins must have been sparse or very thin. At 64.5 MPa a new inelastic process that assisted
 808 in accommodating twinning became active. The abrupt change in the rate of increase of the sig-1
 809 parameter at ~ 850 μ strain (Fig. 4) implies the onset of a defect-generating process at this stress. The
 810 hint of an increase in intensity of the 00.6 peak in the axial direction at this stress (Fig. 6) is consistent

811 with the onset of twinning texture development because twinning rapidly rotates *c*-axes that are at a
 812 high angle to the loading direction towards that loading direction (Spiers, 1979), although termination
 813 of the experiment at small permanent strains ($<0.3\%$) interrupted this texture development at a very
 814 early stage. Hence we interpret that while 14 MPa marks the onset of elastic twinning, 64.5 MPa marks
 815 the onset of permanent twinning accommodated by dislocation activity. Since this sample was not
 816 unloaded from a stress less than 64.5 MPa, the fully elastic nature of the deformation up to that stress is
 817 an inference but this interpretation is consistent with the fully elastic deformation observed in the
 818 sample that was unloaded from 50 MPa at 100°C.

819 The Carrara marble data at temperatures other than 200°C are consistent with the interpretation of
 820 the 200°C data, although in most experiments measurements were not acquired at a sufficient number
 821 of loads at very small stresses to demonstrate the initial purely elastic phase of deformation. An
 822 exception is the test at 25°C (Fig. 12a) which has a stiffness variation consistent with purely elastic
 823 deformation through to abrupt macroscopic failure at 61 MPa. Again the Young's modulus obtained
 824 from the applied stress vs. axial volumetric elastic strain curve (Fig. 7a), $E_V = 82.24$ GPa, is very close
 825 to $E_{V,Kr\ddot{o}ner} = 82.51$ GPa, supporting the interpretation that the deformation of the sample was purely
 826 elastic. At small stresses at 100°C (Fig. 12b) and at 320°, 400° and 500°C (Supplementary document
 827 3, Figs. S3.12-14) there is a strong maximum in apparent stiffness within the more highly stressed of
 828 the two fields of grains that have positive Schmid factors for twinning on all three *e*-twin systems (Fig.
 829 10c). At greater stresses at 100° and 320°C the variation in stiffness changes to the radial pattern
 830 described at 200°C (Supplementary document 3, Figs. S3.10, S3.12). At 400°C the variation of
 831 apparent stiffness at $\sigma_{agg} > 52$ MPa (Fig. 12c) is an intense form of the maximum Schmid factor for *e*-
 832 twinning pattern (Fig. 10c). Indeed the grains with greatest Schmid factor have negative apparent
 833 stiffnesses implying that they were off-loading. In this experiment the increasing 00.6 peak intensity
 834 (and accompanying decreasing 11.0 peak intensity) in the axial diffraction pattern which begins at
 835 52 MPa (Fig. 8) provides stronger evidence for the onset of twinning texture development than
 836 observed at 200°C. The stress/strain curves at large stresses at 500°C and at all stresses at 600°C are
 837 too nonlinear to fit apparent stiffnesses using the methods adopted here.

838 The 400°C Solnhofen limestone data at $\sigma_{agg} > 85$ MPa (Fig. 12d) shows an apparent stiffness
 839 variation that has an intense maximum at $\{00.6\}$, and is consistent with a stress distribution within the
 840 sample that is essentially elastic but under modification by r -slip (Fig. 10d). The apparent stiffness
 841 variation at smaller stresses is similar but with a much less intense maximum at $\{00.6\}$
 842 (Supplementary document 3, Fig. S3.16). The latter implies that the onset of r -slip was at stresses
 843 smaller than 85 MPa. There is possibly a change in slope of the stress/strain curves at ~ 30 MPa visible
 844 in the axial and radial ε_a strains (Fig. 9a) and axial $\{00.6\}$ and $\{10.4\}$ strains (Supplementary
 845 document 2, Fig. S2.9). If this marks the onset of r -slip in optimally oriented grains (Schmid factor =
 846 0.5), it corresponds to a critical resolved shear stress for r -slip of ~ 15 MPa. The published temperature
 847 dependence of the critical resolved shear stress for r -slip gives 13 MPa at 400°C (De Bresser and
 848 Spiers, 1997). The lack of significant peak-broadening at $\sigma_{agg} < 85$ MPa implies that the activity of r -
 849 slip, if initiated at ~ 30 MPa, remained low. If the enhanced activity initiated at 85 MPa is due to the
 850 onset of a new, r -slip-accommodating dislocation process as the peak-broadening data suggest (Fig.
 851 9b), that new dislocation process would have a critical resolved shear stress of ~ 42.5 MPa. A candidate
 852 is low temperature f -slip ($\{1012\}\langle 0221\rangle\langle 2201\rangle$) which has a critical resolved shear stress
 853 (extrapolated from 300°C) of ~ 36.5 MPa at 400°C (De Bresser and Spiers, 1997). The directional
 854 variation of the maximum Schmid factor for low temperature f -slip is not sufficiently different from r -
 855 -slip to discriminate between the two on the basis of apparent elastic stiffnesses without further tests on
 856 Solnhofen limestone using smaller applied load increments and at additional temperatures. The
 857 permanent strain of this sample after loading to 182 MPa was only 0.21% and so it is only the onset of
 858 dislocation slip processes that is observed. This is consistent with the absence of measurable peak
 859 intensity changes. The apparent stiffness fits imply that twinning was not a significant influence on the
 860 stresses within this sample. This is consistent with observations that stresses greater than ~ 300 MPa
 861 are required for the onset of permanent twinning in Solnhofen limestone (Rowe and Rutter, 1990), but
 862 it is also noteworthy that there is no evidence for precursory elastic twinning at smaller stresses either.
 863
 864 *5.4. Potential influence of fracturing?*

865 The calculated apparent elastic stiffnesses imply that crystallographically controlled fracturing, if it
 866 occurred at all, was not an important influence on the distribution of stress within our samples.
 867 Moreover, the limited scatter of data away from the σ_{agg} vs. $\epsilon_{ax,hkl}$ trends suggests that non-
 868 crystallographically controlled intragranular fracturing was also not an important influence on the
 869 distribution of stress. This is consistent with previously reported values of the stress required for the
 870 onset of dilatancy in Carrara marble and Solnhofen limestone which are ~ 60 MPa and ~ 250 MPa
 871 respectively at atmospheric pressure and temperature (e.g. data compilations of Baud et al., 2000;
 872 Schubnel et al., 2005). Nevertheless, this does not exclude the possibility that some dilatancy helped to
 873 accommodate those deformation processes that did control the stress distribution.

874 The nucleation of microfractures during elastic twinning in calcite is well-documented (e.g.
 875 Federov and Tyalin, 1981; Federov et al., 1988), and elastic twin nucleation at the tips of propagating
 876 fractures has also been observed (Finkel et al., 1976). Evidence of twin-induced fracturing or fracture-
 877 induced twinning is often present in twin microstructures (e.g. Olsson and Peng, 1976; Vajdova et al.,
 878 2012, Fig. 11b), although it is not always clear which induced which. Our observation that within
 879 Carrara marble the stresses are dominated by twinning rather than cleavage fracturing suggests that in
 880 our experiments twinning predominantly precedes fracture. This is consistent with models of fracture-
 881 induced twinning which suggest that in calcite it is easier to continue extending a cleavage crack rather
 882 than to form a crack tip twin (Clayton and Knap, 2013). However, this is not to say that localized
 883 microfracturing at the scale of individual twins did not occur during the twinning process.

884 Some grain boundary dilatancy almost certainly accompanied the deformation of our samples.
 885 Thermal stresses generated during heating by the thermal expansion anisotropy of calcite can produce
 886 measurable grain boundary dilatancy for temperature changes as small as 50°C (Luque et al., 2011).
 887 Numerical models of the distribution of stresses within thermally cycled calcite polycrystals are able to
 888 reproduce this observation, and also suggest that dilatancy increases with increasing grain size and
 889 with increasing textural isotropy, although it is more significant during cooling than heating
 890 (Shushakova et al., 2013). Samples of the same Carrara marble that we used in our study, which were
 891 slowly heated to 300° or 600°C and then rapidly quenched, show only a very small permanent

dilatancy in the 300°C cycle but a 2% increase in permanent porosity (induced along the grain boundaries and not as intragranular fractures) in the 600°C cycle (Delle Piane et al., 2015). It follows that some opening of the grain boundaries occurred during the heating of our samples, particularly in the tests on Carrara marble. Further grain boundary dilatancy undoubtedly occurred during loading. Dilatancy of this kind is not easily observed by the neutron diffraction techniques we used. However, if it has a significant influence on twin nucleation, there may be some measurable confining pressure sensitivity of the onset of elastic twinning.

5.5. *Twinning piezometry*

The stresses required for what we infer to be (based on the interpretation of our apparent stiffness fits) the onset of elastic and permanent twinning in the Carrara marble experiments, are shown in Fig. 13. We have defined the onset of elastic twinning as the stress at which the difference between the slopes of the axial ε_a and ε_c stress/strain curves abruptly increases (e.g. at the arrowed point labelled ‘E’ in Fig. 3b). This occurs at small stresses (<15 MPa) and hence for onset of elastic twinning to be clearly defined data from several load steps at small stresses are required. This requirement is only satisfied for the 200°, 320° and possibly the 500°C datasets (Figs. 3b, 7c, 7e). However, extrapolation of the ε_a and ε_c axial stress/strain curves obtained at 100°, 400° and 600°C back towards zero load implies that the onset of elastic twinning in these tests was also at very small loads (<5 MPa) (Figs. 7b, 7d, 7f). At 200°C there is a hint of a precursory elastic twinning event at 8 MPa visible in the radial ε_c stress/strain curve (Fig. 3b). The onset of permanent twinning was identified in the tests at temperatures below 600°C by an abrupt increase in slope of the sig-1/stress curve (e.g. Fig. 4), which in all cases was accompanied by a change in slope of the radial ε_c stress/strain curve and/or the axial ε_a and ε_c stress/strain curves (e.g. at the arrowed point labelled ‘P’ in Fig. 3b and Fig. 7e). The two points shown for 600°C in Fig. 13 are the two stresses (at $\sigma_{agg} > 10$ MPa) at which there is an abrupt change in slope of the axial and radial ε_c stress/strain curves (Fig. 7f).

Depending upon how effective grain boundary dilatancy or other deformation processes were in relieving the thermal stresses generated during heating, the samples heated to different temperatures

919 may have been in different stress states at the start of loading. This complicates interpretation of the
 920 temperature variation of the stresses for the onset of twinning. Given that at atmospheric pressure only
 921 small temperature changes are required to initiate dilatancy, and that once formed ongoing opening of
 922 boundary cracks probably prevents significant further increases in internal stress (Shushakova et al.,
 923 2013), we suspect that within our dataset this effect is small at the higher temperatures. Yet it is
 924 noteworthy that no elastic twinning was observed at 25°C, and hence perhaps some thermally-induced
 925 boundary dilatancy is needed for the onset of elastic twinning. The onset of elastic twinning at 100°C
 926 at an anomalously small stress may perhaps be explained by limited crack formation along boundaries
 927 during heating, thereby providing plentiful locally stressed crack tip sites to serve as twin nuclei.

928 In common with studies on engineering materials that undergo twinning, we find that the onset of
 929 twinning during loading is abrupt. If elastic twinning is an early stage in the development of a
 930 permanent twin, the value of up to ~10 MPa which is adopted as a critical resolved shear stress in
 931 some calcite piezometers, is consistent with the stresses that we have obtained for the onset of elastic
 932 twinning at 200°-320°C. This stress is not, however, a critical resolved shear stress because the onset
 933 of elastic twinning within a grain is more strongly influenced by the number of its *e*-twin systems that
 934 have positive Schmid factors than by the magnitude of those Schmid factors. The onset of permanent
 935 twinning is governed by the magnitude of the Schmid factor on the most favourably oriented *e*-twin
 936 system within the twinning grains. Since it is the permanent twins that are examined when the calcite
 937 twinning piezometer is applied to natural deformation microstructures, perhaps the stress required for
 938 permanent twinning is more relevant when seeking to generalize empirical piezometers (e.g that of
 939 Rowe and Rutter, 1990) to incorporate microstructural variables. Given that this stress is tied to
 940 dislocation processes, one may anticipate that it is temperature dependent and has a Hall-Petch-type
 941 grain size dependence.

942

943 **6. Conclusions**

944 We have performed uniaxial compression experiments on Carrara marble (at 25°-600°C) and
 945 Solnhofen limestone (at 200° and 400°C) within a neutron beam-line to establish if the onset of

946 mechanical twinning in calcite polycrystals could be observed using neutron diffraction before
 947 macroscopic brittle failure of the samples. By collecting neutron diffraction patterns at different
 948 applied loads, we have evaluated and compared the elastic strain versus applied stress response of
 949 several sub-sets of differently oriented grains in order to identify the deformation processes
 950 responsible for the observed behaviour. We interpret the results in the following way.

- 951 (1) In the experiments at 25°C on Carrara marble and at 200°C on Solnhofen limestone the
 952 deformation response was purely elastic. This requires the sign of the elastic stiffness component
 953 c_{14} to be positive when the obverse setting of the calcite rhombohedral lattice in hexagonal axes is
 954 used, in agreement with ab initio calculations of the elastic properties of calcite (Le Page et al.,
 955 2002).
- 956 (2) In all the Carrara marble tests at temperatures higher than 25°C the deformation response was
 957 dominated by twinning. The onset of elastic twinning in grains with two or more *e*-twin systems
 958 with positive Schmid factors for twinning was observed at applied stresses of less than 15 MPa.
 959 The rate of accumulation of elastic twin strain decreased with increasing strain until twinning in
 960 grains with large Schmid factors on one of their *e*-planes abruptly began to dominate the
 961 distribution of stresses within the sample. This change in response was accompanied by an
 962 increased rate of diffraction peak broadening and is interpreted to correspond with the onset of
 963 permanent twinning accommodated by dislocation slip. The stress required for the onset of both
 964 elastic twinning and permanent twinning decreases with increasing temperature.
- 965 (3) In the Solnhofen limestone test at 400°C there is no evidence for twinning. Instead *r*-slip was
 966 initiated, possibly at ~30 MPa. However, the onset of enhanced rates of diffraction peak
 967 broadening was not until 85 MPa and so we infer that significant dislocation activity on the *r*-slip
 968 systems did not occur until other slip systems became active.

969 We conclude that the onset of twinning and other dislocation processes can be observed in calcite
 970 rocks using these techniques. The approach provides new experimental information about twinning
 971 that is otherwise difficult to obtain. In particular, by performing experiments on samples with different
 972 microstructures, the influence of different microstructural variables on the onset of twinning can be

973 directly assessed and potentially accommodated into a more generally applicable calcite piezometer.
 974 Using observations from differently oriented sub-sets of grains to identify the onset of twinning and to
 975 obtain information about how the twin strains are accommodated does not provide everything needed
 976 for a full micromechanical description of twinning. As noted by others (e.g. Preuss et al., 2010),
 977 detailed criteria for twin nucleation and growth are difficult to identify from such observations. Hence
 978 there remains a need for integrating grain-ensemble-averaging information of the kind that can be
 979 obtained from neutron diffraction experiments with the kind of grain scale information that can be
 980 obtained from microstructural studies and high spatial resolution synchrotron X-ray strain scanning.

981

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990

991 **Appendix A. Supplementary data**

992 Supplementary data related with this article can be found at http://dx.doi.org/10.1016/j.jsg.*****.

993

994 *Supplementary document 1.* Summary of calcite crystallographic information used in this study.

995 *Supplementary document 2.* Full tabulation with supporting figures of the data reported in this study.

996 *Supplementary document 3.* Predicted directional variation of apparent elastic stiffness for different
 997 calcite deformation processes (relevant to the present study), together with the results (with
 998 interpretative comments) of the apparent stiffness fits obtained in this study.

999

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Figure captions

Fig. 1. (a) Plan view of the geometry of the neutron experiments. The sample is mounted horizontally in the loading frame and positioned with the loading axis at 45° to the incident beam. Two detector banks with a fixed scattering angle of $2\theta = 90^\circ$ are located, one on either side of the sample. The detector bank to the right of the sample collects diffraction data from grains which have a scattering vector parallel to the loading direction (axial direction), while the detector bank to the left of the sample simultaneously collects diffraction data from grains which have a scattering vector normal to the loading direction (radial direction). (b) Within the sample differently oriented grains A and B both have a set of lattice planes satisfying the Bragg condition for the axial detector bank and therefore

1297 contribute towards two different peaks within the diffraction pattern recorded by that detector bank.
 1298 Likewise differently oriented grains C and D contribute towards two different peaks within the
 1299 diffraction pattern collected by the radial detector bank.

1300

1301 **Fig. 2.** Typical diffraction patterns obtained at 200°C from Carrara marble (left) and Solnhofen
 1302 limestone (right). These were both collected in the axial detector bank from samples under 1 MPa
 1303 applied stress. Note that the lower and upper figures of each pair cover different d -spacing ranges and
 1304 that the intensity scales are different in each plot. In each plot the crosses are the diffraction data, the
 1305 solid line is the calculated profile from the Rietveld refinement, and the lower line is the difference
 1306 between the observed and calculated profile. The single peaks analysed in this study are labelled; those
 1307 labelled in smaller font size are peaks that produce potentially usable but poorer quality datasets.

1308

1309 **Fig. 3.** Elastic strains evaluated from the lattice parameters (a , c , V) given by the whole pattern
 1310 Rietveld refinements for the experiments at 200°C on (a) Solnhofen limestone and (b) Carrara marble.
 1311 $1000 \mu\text{strain} = 0.1\%$ strain. The uncertainties in the strains that arise from the uncertainties in the lattice
 1312 parameters are smaller than the size of the symbols. The linear fits shown on Fig. 3a are of the
 1313 volumetric strain data (crosses) against applied stress. The arrows on Fig. 3b highlight the stress
 1314 positions of two changes in response identified from the radial strain data (this figure) and sig-1 data
 1315 (Fig. 4), which are interpreted to mark the onset of elastic twinning (E) and permanent twinning (P) in
 1316 the Carrara marble sample.

1317

1318 **Fig. 4.** The variation of sig-1 (a measure of strain-broadening of the diffraction peaks) in the axial
 1319 direction during loading in the 200°C experiments. The values of sig-1 in each experiment have been
 1320 normalized by the value of sig-1 in that experiment at the least applied stress (1 MPa). To facilitate
 1321 comparison between the two samples, the sig-1 data are plotted against ε_V in the axial direction; the
 1322 plots with applied stress on the x -axis are given in Supplementary document 2 (Figs. S2.1b, S2.2b).
 1323 The dashed lines show linear trends and are not fits. Note the abrupt increase in rate of strain-

broadening in the Carrara marble data at an applied stress of 64.5 MPa (arrowed point at $\sim 850 \mu\epsilon$), which is interpreted to mark the onset of permanent twinning.

Fig. 5. Elastic strains evaluated from the d -spacings given by the single peak fits for eight peaks within the diffraction patterns recorded by the axial detector in the experiments at 200°C on (a)-(c) Solnhofen limestone and (d)-(f) Carrara marble. The data for 21.1 and 11.0 are similar to 30.0 (see Supplementary document 2, Figs. S2.1f, S2.2f). The horizontal lines on the symbols in the key to each plot show the uncertainty in strains that arise from the uncertainty in d -spacing. In each case the volumetric strain ϵ_V obtained from the whole pattern Rietveld refinements (Figs. 3a,b) is shown for reference. The arrows show the stress positions of the changes in response that were identified from the Carrara marble whole pattern fits (Fig. 3b).

Fig. 6. Variation in 00.6 and 30.0 peak intensity with applied stress in the Carrara marble experiment at 200°C (axial detector bank). The intensities have been normalized by the measured intensity for the indicated peak at 1 MPa. The fluctuations in normalized intensity reflect the uncertainty of the fitted intensity but at the greatest stresses there is a small increase in 00.6 intensity. The arrows show the stress positions of the changes in response that were identified from the Carrara marble whole pattern fits (Fig. 3b).

Fig. 7. Elastic strains evaluated from the lattice parameters (a , c , V) given by the whole pattern Rietveld refinements for the Carrara marble experiments at temperatures other than 200°C. The uncertainties in the strains that arise from the uncertainty in the lattice parameters are smaller than the size of the symbols. The arrows indicate changes in response identified by abrupt changes in slope and (at the greatest stresses in the 320°-500°C experiments) by the sig-1 data (Supplementary document 2, Figs. S2.5b, S2.6b, S2.7b). These are interpreted as marking the onset of elastic twinning (E) and permanent twinning (P).

1351 **Fig. 8.** Variation in 00.6 and 11.0 peak intensity with applied stress in the Carrara marble experiment
 1352 at 400°C (axial detector bank). The intensities have been normalized by the measured intensity for the
 1353 indicated peak at 1 MPa. The arrow shows the applied stress at which a change in sample response was
 1354 noted in the analysis of the whole pattern fits for this experiment (Fig. 7d). Above this stress there is an
 1355 increase in the 00.6 intensity and a corresponding decrease in 11.0 intensity.

1356

1357 **Fig. 9.** Results from the 400°C Solnhofen limestone experiment. (a) Elastic strains evaluated from the
 1358 lattice parameters (a , c , V) given by the whole pattern Rietveld refinements. The uncertainties in the
 1359 strains that arise from the uncertainties in the lattice parameters are smaller than the size of the
 1360 symbols. (b) The variation of the sig-1 parameter with applied stress. The values of sig-1 have been
 1361 normalized by the value of sig-1 at 1 MPa. The dashed lines show linear trends and are not fits. The
 1362 arrow highlights the stress at which there is an abrupt change in slope of the axial ε_c stress/strain curve.

1363

1364 **Fig. 10.** (a) Normals to the calcite lattice planes examined in this study plotted on an upper
 1365 hemisphere, equal angle projection. (b) Variation in directional Young's modulus as obtained from the
 1366 calcite single crystal elastic stiffnesses of Dandekar (1968) but with the sign of c_{14} reversed. The
 1367 diffraction elastic constants given by Kröner's analysis for a calcite polycrystal containing randomly
 1368 oriented grains are listed for the lattice planes of interest on the right, together with the volume-
 1369 average values of Young's modulus obtained assuming homogeneous stress ($E_{V,Reuss}$), homogeneous
 1370 strain ($E_{V,Voigt}$), and as given by Kröner's analysis ($E_{V,Kröner}$). (c) Variation of the Schmid factor for e^+ -
 1371 twinning with loading direction. The contours show the maximum Schmid factor obtained for any
 1372 given loading direction from all combinations of equivalent loading directions and e -planes. The
 1373 dashed lines demarcate regions where 0, 1, 2, and 3 of the differently oriented e -planes have positive
 1374 Schmid factors for twinning. (d) Variation of the Schmid factor for r^- -slip with loading direction.
 1375 Again it is the maximum Schmid factor obtained from all combinations of equivalent loading
 1376 directions and r -planes that is shown. (e) Variation of the minimum value of $\cos^2\chi$ with loading
 1377 direction as obtained from all combinations of equivalent loading directions and r -planes. The

1378 magnitude of the normal stress on the cleavage plane (r -plane) is directly proportional to $\cos^2\chi$, where
 1379 χ is the angle between the loading direction and the normal to the cleavage plane.

1380

1381 **Fig. 11.** Directional variation of apparent elastic stiffness in the 200°C experiments plotted on upper
 1382 hemisphere, equal angle stereographic projections, (a) for Solnhofen limestone, and (b)-(d) for Carrara
 1383 marble over three different intervals of applied stress. The tabulated E_{hkl} (in GPa) were obtained from
 1384 linear fits to the axial elastic strain vs. applied stress data given in Supplementary document 2 (Tables
 1385 S2.2, S2.3) and shown graphically in Fig. 5. The contours show the variation of E_{hkl} given by the
 1386 stiffness tensor fitted to these tabulated E_{hkl} assuming homogeneous stress. The dots are the normals to
 1387 the analysed lattice planes (Fig. 10a).

1388

1389 **Fig. 12.** Results from some of the apparent elastic stiffness fits obtained for the experiments at
 1390 temperatures other than 200°C. These are presented in the same way as the plots shown in Fig. 11, and
 1391 are for Carrara marble at (a) 25°C, (b) 100°C (small stresses), and (c) 400°C (large stresses), and for
 1392 Solnhofen limestone at (d) 400°C (large stresses). The axial elastic strain vs. applied stress data used in
 1393 the fits is given in Supplementary document 2 (Tables S2.4, S2.5, S2.7, S2.10).

1394

1395 **Fig. 13.** The stresses at the onset of elastic and permanent twinning in Carrara marble (grain size
 1396 150 μm). The curves show trends in the data and are not fits. The apparent elastic stiffnesses were not
 1397 analysed in the 600°C experiment. Hence which of the two points shown at this temperature marks the
 1398 onset of permanent twinning is unknown. In each experiment the onset of permanent twinning was at
 1399 an axial volumetric elastic strain of $< 0.1\%$.

Fig. 1. (a) Plan view of the geometry of the neutron experiments. The sample is mounted horizontally in the loading frame and positioned with the loading axis at 45° to the incident beam. Two detector banks with a fixed scattering angle of $2\theta = 90^\circ$ are located, one on either side of the sample. The detector bank to the right of the sample collects diffraction data from grains which have a scattering vector parallel to the loading direction (axial direction), while the detector bank to the left of the sample simultaneously collects diffraction data from grains which have a scattering vector normal to the loading direction (radial direction). (b) Within the sample differently oriented grains A and B both have a set of lattice planes satisfying the Bragg condition for the axial detector bank and therefore contribute towards two different peaks within the diffraction pattern recorded by that detector bank. Likewise differently oriented grains C and D contribute towards two different peaks within the diffraction pattern collected by the radial detector bank.

Fig. 2. Typical diffraction patterns obtained at 200°C from Carrara marble (left) and Solnhofen limestone (right). These were both collected in the axial detector bank from samples under 1 MPa applied stress. Note that the lower and upper figures of each pair cover different d -spacing ranges and that the intensity scales are different in each plot. In each plot the crosses are the diffraction data, the solid line is the calculated profile from the Rietveld refinement, and the lower line is the difference between the observed and calculated profile. The single peaks analysed in this study are labelled; the labels in smaller font size are peaks that produce potentially usable but poorer quality datasets.

Fig. 3. Elastic strains evaluated from the lattice parameters (a , c , V) given by the whole pattern Rietveld refinements for the experiments at 200°C on (a) Solnhofen limestone and (b) Carrara marble. 1000 μstrain = 0.1% strain. The uncertainties in the strains that arise from the uncertainties in the lattice parameters are smaller than the size of the symbols. The linear fits shown on Fig. 3a are of the volumetric strain data (crosses) against applied stress. The arrows on Fig. 3b highlight the stress positions of two changes in response identified from the radial strain data (this figure) and sig-1 data (Fig. 4), which are interpreted to mark the onset of elastic twinning (E) and permanent twinning (P) in the Carrara marble sample.

Fig. 4. The variation of sig-1 (a measure of strain-broadening of the diffraction peaks) in the axial direction during loading in the 200°C experiments. The values of sig-1 in each experiment have been normalized by the value of sig-1 in that experiment at the least applied stress (1 MPa). To facilitate comparison between the two samples, the sig-1 data are plotted against ϵ_V in the axial direction; the plots with applied stress on the x -axis are given in Supplementary document 2 (Figs. S2.1b, S2.2b). The dashed lines show linear trends and are not fits. Note the abrupt increase in rate of strain-broadening in the Carrara marble data at an applied stress of 64.5 MPa (arrowed point at $\sim 850 \mu\epsilon$), which is interpreted to mark the onset of permanent twinning.

Solnhofen limestone, 200°C

Carrara marble, 200°C

Fig. 5. Elastic strains evaluated from the d -spacings given by the single peak fits for eight peaks within the diffraction patterns recorded by the axial detector in the experiments at 200°C on (a)-(c) Solnhofen limestone and (d)-(f) Carrara marble. The data for 21.1 and 11.0 are similar to 30.0 (Supplementary document 2, Figs. S2.1f, S2.2f). The horizontal lines on the symbols in the key to each plot show the uncertainty in strains that arise from the uncertainty in d -spacing. In each case the volumetric strain ϵ_V obtained from the whole pattern Rietveld refinements (Figs. 3a,b) is shown for reference. The arrows show the stress positions of the changes in response that were identified from the Carrara marble whole pattern fits (Fig. 3b).

Fig. 6. Variation in 00.6 and 30.0 peak intensity with applied stress in the Carrara marble experiment at 200°C (axial detector bank). The intensities have been normalized by the measured intensity for the indicated peak at 1 MPa. The fluctuations in normalized intensity reflect the uncertainty of the fitted intensity but at the greatest stresses there is a small increase in 00.6 intensity. The arrows show the stress positions of the changes in response that were identified from the Carrara marble whole pattern fits (Fig. 3b).

Fig. 7. Elastic strains evaluated from the lattice parameters (a , c , V) given by the whole pattern Rietveld refinements for the Carrara marble experiments at temperatures other than 200°C. The uncertainties in the strains that arise from the uncertainty in the lattice parameters are smaller than the size of the symbols. The arrows indicate changes in response identified by changes in slope and (at the greatest stresses in the 320°-500°C experiments) by the sig-1 data (Supplementary document 2, Figs. S2.5b, S2.6b, S2.7b). These are interpreted as marking the onset of elastic twinning (E) and permanent twinning (P).

Fig. 8. Variation in 00.6 and 11.0 peak intensity with applied stress in the Carrara marble experiment at 400°C (axial detector bank). The intensities have been normalized by the measured intensity for the indicated peak at 1 MPa. The arrow shows the applied stress at which a change in sample response was noted in the analysis of the whole pattern fits for this experiment (Fig. 7d). Above this stress there is an increase in the 00.6 intensity and a corresponding decrease in 11.0 intensity.

Fig. 9. Results from the 400°C Solnhofen limestone experiment. (a) Elastic strains evaluated from the lattice parameters (a , c , V) given by the whole pattern Rietveld refinements. The uncertainties in the strains that arise from the uncertainties in the lattice parameters are smaller than the size of the symbols. (b) The variation of the sig-1 parameter with applied stress. The values of sig-1 have been normalized by the value of sig-1 at 1 MPa. The dashed lines show linear trends and are not fits. The arrow highlights the stress at which there is an abrupt change in slope of the axial ϵ_c stress/strain curve.

Fig. 10. (a) Normals to the calcite lattice planes examined in this study plotted on an upper hemisphere, equal angle projection. (b) Variation in directional Young's modulus as obtained from the calcite single crystal elastic stiffnesses of Dandekar (1968) but with the sign of c_{14} reversed. The diffraction elastic constants given by Kröner's analysis for a calcite polycrystal containing randomly oriented grains are listed for the lattice planes of interest on the right, together with the volume-average values of Young's modulus obtained assuming homogeneous stress ($E_{V,Reuss}$), homogeneous strain ($E_{V,Voigt}$), and as given by Kröner's analysis ($E_{V,Kröner}$). (c) Variation of the Schmid factor for e^+ -twinning with loading direction. The contours show the maximum Schmid factor obtained for any given loading direction from all combinations of equivalent loading directions and e -planes. The dashed lines demarcate regions where 0, 1, 2, and 3 of the differently oriented e -planes have positive Schmid factors for twinning. (d) Variation of the Schmid factor for r -slip with loading direction. Again it is the maximum Schmid factor obtained from all combinations of equivalent loading directions and r -planes that is shown. (e) Variation of the minimum value of $\cos^2 \chi$ with loading direction as obtained from all combinations of equivalent loading directions and r -planes. The magnitude of the normal stress on the cleavage plane (r -plane) is directly proportional to $\cos^2 \chi$, where χ is the angle between the loading direction and the normal to the cleavage plane.

Fig. 11. Directional variation of apparent elastic stiffness in the 200°C experiments plotted on upper hemisphere, equal angle stereographic projections, (a) for Solnhofen limestone, and (b)-(d) for Carrara marble over three different intervals of applied stress. The tabulated $E_{hk,l}$ (in GPa) were obtained from linear fits to the axial elastic strain vs. applied stress data given in Supplementary document 2 (Tables S2.2, S2.3) and shown graphically in Fig. 5. The contours show the variation of $E_{hk,l}$ given by the stiffness tensor fitted to these tabulated $E_{hk,l}$ assuming homogeneous stress. The dots are the normals to the analysed lattice planes (Fig. 10a).

Fig. 12. Results from some of the apparent elastic stiffness fits obtained for the experiments at temperatures other than 200°C. These are presented in the same way as the plots shown in Fig. 11, and are for Carrara marble at (a) 25°C, (b) 100°C (small stresses), and (c) 400°C (large stresses), and for Solnhofen limestone at (d) 400°C (large stresses). The axial elastic strain vs. applied stress data used in the fits is given in Supplementary document 2 (Tables S2.4, S2.5, S2.7, S2.10).

Fig. 13. The stresses at the onset of elastic and permanent twinning in Carrara marble (grain size 150 μm). The curves show trends in the data and are not fits. The apparent elastic stiffnesses were not analysed in the 600°C experiment. Hence which of the two points shown at this temperature marks the onset of permanent twinning is unknown. In each experiment the onset of permanent twinning was at an axial volumetric elastic strain of $< 0.1\%$.

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