

The University of Akron

From the Selected Works of Caleb Holyoke

2013

Dislocation creep of polycrystalline dolomite

Caleb Holyoke

Andreas Kronenberg

Julie Newman



Available at: https://works.bepress.com/caleb_holyoke/9/



Dislocation creep of polycrystalline dolomite

Caleb W. Holyoke III ^{*}, Andreas K. Kronenberg, Julie Newman

Department of Geology and Geophysics, Texas A&M University, College Station, TX 77843, United States

ARTICLE INFO

Article history:

Received 23 May 2012

Received in revised form 6 December 2012

Accepted 17 January 2013

Available online 26 January 2013

Keywords:

Rheology

Dolomite

Carbonates

Strength of the continental crust

Experimental deformation

Dislocation creep

ABSTRACT

The field of dislocation creep and rheological parameters for coarse-grained ($d = 240 \mu\text{m}$) natural dolomite has been determined through experiments performed at temperatures of 700–1000 °C, effective pressures of 300–900 MPa and strain rates of $10^{-4}/\text{s}$ to $10^{-7}/\text{s}$. At low strain ($<7\%$), dolomite aggregates deform homogeneously and define a power law between strain rate and differential stress with a stress exponent of 3.0 ± 0.1 , but at higher strains, through-going, fine-grained ($<10 \mu\text{m}$) shear zones develop in the dolomite aggregates concomitant with strain weakening. Recrystallization is limited at low strain and microstructures observed in the low strain samples include undulatory extinction, twins, grain boundary bulging, limited recrystallization along twins and fluid inclusion trails. These same microstructures are present outside of the narrow, through-going shear zones in high strain samples; however, within the shear zones the grain size is small ($<10 \mu\text{m}$) with some larger porphyroclasts ($20\text{--}50 \mu\text{m}$). Shear zones nucleate at fine-grained zones formed at twin boundaries, twin–twin intersections and fluid inclusion trails and is likely due to a switch in deformation mechanism due to the large strength contrast between the fine-grained zones deforming by diffusion creep and the coarse-grained protolith. The activation energy (Q) for creep of coarse-grained dolomite at low strain is 145 kJ/mol. In contrast to other activation energies for dislocation and diffusion creep of minerals, Q for dislocation creep of dolomite is considerably less than that for diffusion creep (248 kJ/mol). The results of this study indicate that coarse-grained dolomite will initially deform by dislocation creep at natural strain rates and temperatures between 200 and 550 °C, but due to limited recovery mechanisms, fine-grained shear zones will nucleate and diffusion creep may control the rheology of these fine-grained shear zones in nature at temperatures above ~ 300 °C.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Carbonates, primarily calcite and dolomite, are commonly found in shear zones in the middle and upper crust and likely control the rheology of these zones. The deformation mechanisms and rheology of calcite aggregates have been explored extensively (Austin and Evans, 2009; de Bresser, 2002; Griggs and Miller, 1951; Griggs et al., 1953; Handin and Griggs, 1951; Heard and Raleigh, 1972; Herwegh et al., 2005; Renner et al., 2002; Rutter, 1972, 1974; Schmid et al., 1977; Schmid et al., 1980; Turner et al., 1956; Walker et al., 1990). However, deformation mechanisms and associated rheologies of dolomite aggregates have only recently been explored (Davis et al., 2008; Delle Piane et al., 2008); these studies provide a mechanical relationship for crystal plasticity and twinning at low temperatures and diffusion creep at high temperatures when grain size is small.

Davis et al. (2008) observed a temperature-dependent transition in the rheology of coarse-grained ($240 \mu\text{m}$) dolomite aggregates between low temperature plasticity and the onset of dislocation creep between 700 and 800 °C. However, due to decomposition of the

dolomite aggregates at the maximum temperature (850 °C) and pressure limitations (400 MPa) of the Heard-type gas confining medium rock deformation apparatus (gas apparatus) used in their study, they were unable to explore this deformation mechanism in detail and mechanical data are transitional between plasticity and dislocation creep fields. Earlier experiments by Neumann (1969) provide microstructural evidence of dislocation creep in coarse-grained ($700 \mu\text{m}$) dolomite aggregates at $T = 1000$ °C, but these experiments were performed using strong solid media (pyrophyllite) assemblies in the Griggs piston-cylinder rock deformation apparatus (Griggs apparatus) that do not allow accurate stress measurements (e.g. Stewart et al., 2013) and mechanical data were not reported. In this study, we performed an experimental investigation using the molten salt cell (MSC) and solid salt assembly (SSA) in a Griggs apparatus to characterize the rheology of coarse-grained dolomite aggregates deformed by dislocation creep.

2. Experimental study

We performed a series of experiments to characterize the strain rate ($\dot{\epsilon}$) and temperature dependence of flow strength of a coarse-grained natural dolomite aggregate (Madoc dolomite).

^{*} Corresponding author. Tel.: +1 979 458 3924.

E-mail address: holyoke@geo.tamu.edu (C.W. Holyoke).

2.1. Sample preparation and jacketing

The Madoc dolomite is a coarse- and equant-grained ($d \sim 240 \mu\text{m}$) dolomite aggregate with straight extinction when viewed optically with crossed Nicols, twins, fluid inclusion trails and few inclusions of quartz ($\ll 1\%$). Cores of Madoc dolomite (5 mm diameter) were collected from the same block of dolomite used as the starting material by Davis et al. (2008). These cores were cut to the approximate final length (10 mm) and cylinder ends were ground perpendicular to the cylinder axis. The cylinder ends of the alumina pistons were also ground perpendicular to the piston length and the lower piston length was adjusted so that the center of the dolomite cylinder would be at the same location as the thermocouple (Pt–Pt/10% Rh) weld. The dolomite cylinders were placed within Pt jackets, each with a layer (0.6 mm wall thickness) of Ag or Ni between the Pt jacket and annulus of the cylinder, for experiments performed below or above 850 °C, respectively. The conductive Ag or Ni layer is used to reduce temperature gradients along the insulating sample (± 5 – 10 °C, Holyoke, unpublished data), which are ± 20 °C without a thick metal layer (Tingle et al., 1993). Ni was not used at low temperatures because its strength becomes significant (40 MPa at 800 °C) and Ag was not used at higher temperatures due to its low melting point (~ 960 °C). One Ag or Ni disc was placed at each cylinder end in each experiment. Pt cups, which fit within the Pt jacket, were weld-sealed in all MSC experiments. In SSA experiments, a Pt disc was placed at the end of the cylinder end, outside of the inner Ag or Ni, and the ends of the Pt jacket were crimped over the cylinder end, which produces a mechanical seal at high pressure. After experiments performed using welded and mechanically sealed jackets, the Pt at the cylinder ends was always bowed out, indicating that both of these methods effectively prevented loss of CO_2 from the jacket and the CO_2 pore pressure could be determined from the dolomite decomposition reaction at equilibrium.

2.2. Apparatus and differential stress calibrations

All experiments were performed using a Griggs-type triaxial piston cylinder rock deformation apparatus (Holyoke and Kronenberg, 2010). The MSC technique was developed to eliminate contributions in load due to solid confining media surrounding cylindrical samples in a triaxial piston-cylinder apparatus (Green and Borch, 1989; Gleason and Tullis, 1993; Rybacki et al., 1998). A salt mixture (KCl/LiCl) is chosen that melts eutectically at experimental conditions, to replace the solid NaCl that normally surrounds the sample. The MSC technique also removes the Pb from the load column, which sharpens hit points in load records, in comparison with rounded hit points determined in SSA experiments associated with driving the load piston through the Pb. However, the removal of the Pb at the top of the load column by squeezing Pb from between the upper alumina piston and WC load piston in MSC experiments also leads to sample shortening of ~ 3 – 5% . Because of the strain sensitivity of dislocation creep in dolomite (discussed later), one experiment (D-5) was performed using

the MSC assembly without performing the Pb removal step. This procedure caused a rounded hit point and decreases the precision of stress determination during this experiment, but it allowed us to compare the mechanical data of samples with liquid or solid confining media at identical shortening strains.

2.2.1. Hit points in the MSC

In order to demonstrate that this modification of the MSC technique does not affect the accuracy of the force measurements collected in experiments performed without the pre-hit deformation stage, we performed an experiment on a nickel cylinder at 600 °C, $\dot{\epsilon} = 1.6 \times 10^{-4}/\text{s}$, and $P_c = 1000$ MPa (Table 1). Three deformation steps were performed in this experiment; the first deformation step was performed by advancing the load piston through the Pb and deforming the Ni cylinder to 12% strain. The hit point during this deformation step is rounded, similar to those in SSA experiments, but the Ni cylinder was surrounded by molten salt. After reaching the desired strain, the deformation piston was retracted. The first deformation step removes the Pb in the load column and couples the upper alumina piston to the WC load piston. While the load piston is retracted, molten salt is injected between the upper alumina piston and middle alumina piston. When the second and third deformation steps were performed, only molten salt was removed from the load column and the hit points were sharp, as is the case in a normal MSC experiment. Differential stresses increased slowly over the first 5% strain in the first deformation step and then the sample deformed at a nearly constant differential stress of ~ 150 MPa for the remainder of the experiment (Fig. 1a). Differential stresses in the second and third deformation steps increase rapidly in the first percent strain and then deform at a nearly constant differential stress (145 and 135 MPa in steps 2 and 3, respectively) for the remainder of each deformation step (Fig. 1a). The constant differential stress deformation in each of these experiments is the same within experimental error, but the slope of the elastic response of Ni to loading during the first deformation step is considerably lower than the elastic slopes determined during the second and third deformation steps, which had sharp, well-defined MSC hit points. The difference in apparent elastic behavior during the first step and the latter steps indicates complex behavior of the load column of the Griggs apparatus during the removal of Pb. We expect that simple, linear elastic response is best determined once Pb has been removed. Nevertheless, the constant stress deformation portion of all experiments is consistent, irrespective of these initial loading procedures.

2.2.2. Pressure sensitivity of the MSC and SSA load calibrations

Holyoke and Kronenberg (2010) demonstrated that differential stresses calculated from forces measured using the MSC and SSA in the Griggs apparatus are not accurate relative to those measured in the gas apparatus without correction. They reported calibrations for MSC and SSA experiments that correct for an increase in friction of the load column due to elastic strain of the load column during loading.

Table 1
List of metal deformation experiments.

Experiment	Assembly	Material	Temperature (°C)	Confining pressure (MPa)	Strain rate (s^{-1})	Strain (%)	Strength at $\epsilon = 5\%$ ^{a,b} (MPa)	Final strength ^b (MPa)
D-4	MSC	nickel	600	1000	1.5×10^{-4}	12	116	130
					1.5×10^{-4}	12	125	120
					1.5×10^{-4}	12	125	125
D-21	SSA	Mo	900	1500	1.6×10^{-5}	4	160	160
			800	1500	1.7×10^{-4}	8	245	260
			700	1480	1.7×10^{-4}	9	270	295

^a Unless total strain is less than 5%, then differential stress at the final strain is listed.

^b Corrected using methods described in Holyoke and Kronenberg (2010).

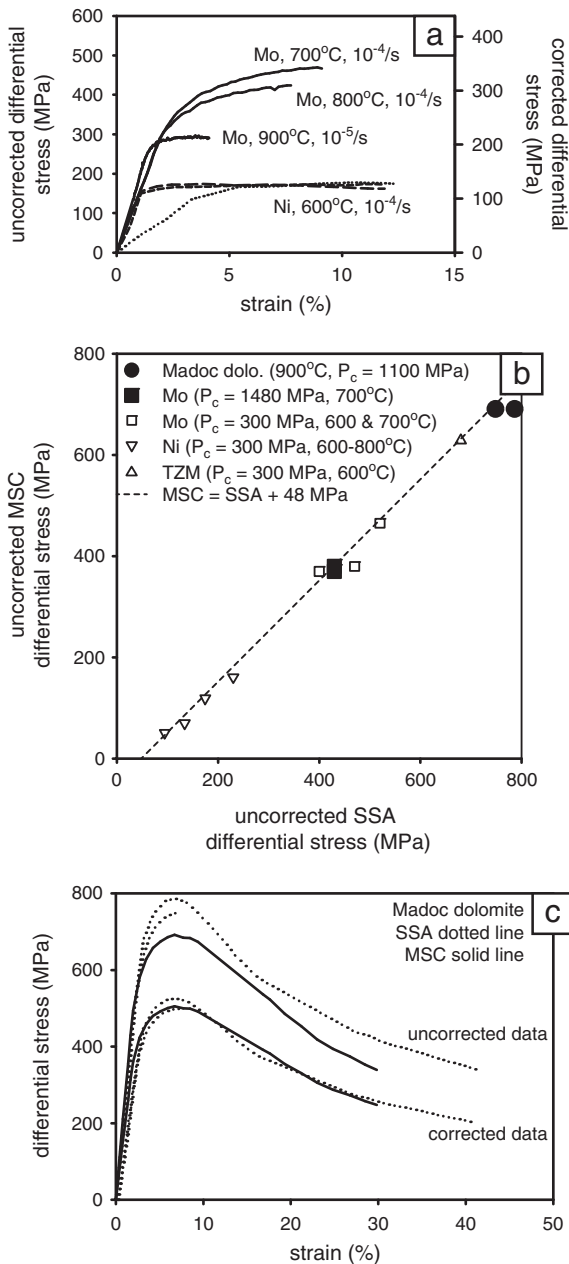


Fig. 1. Mechanical results for metals and dolomite using MSC and SSA methods at high confining pressures demonstrate the lack of pressure and temperature dependence of the Holyoke and Kronenberg (2010) calibrations. Differential stresses are labeled as uncorrected and corrected on the left and right axes, respectively, in all graphs of stress and strain data in this manuscript. (a) Differential stresses of the experiment performed on Mo at 700 °C/ $\dot{\epsilon} = 10^{-4}$ /s, 800 °C/ $\dot{\epsilon} = 10^{-4}$ /s and 900 °C/ $\dot{\epsilon} = 10^{-5}$ /s, decrease as a function of increasing temperature. The elastic portion of the stress-strain curve of the first deformation step of the experiment performed on Ni is considerably shallower than the elastic slopes of the second and third deformation steps. This difference is due to Pb in the load column during the first deformation step. However, constant stress deformation occurs at roughly the same value in all experiments. (b) The experiments performed at higher confining pressures (Mo – filled squares, Table 1) and temperature (Madoc dolomite, filled circles, Table 2) than the experiments used to develop the Holyoke and Kronenberg (2010) SSA calibration are in good agreement with the calibration, establishing that the calibration is insensitive to pressure and temperature. (c) Uncorrected differential stresses from experiments performed using the MSC (solid lines) and SSA (dotted lines) are considerably different. However, after application of the Holyoke and Kronenberg (2010) calibration, the peak stresses and rate of strain weakening are almost identical, indicating that the calibration is independent of strain.

Because increases in friction of the load column are systematic with load, the differential stresses from MSC and SSA experiments can be corrected reliably using the following equations, respectively:

$$\sigma_{\text{gas}} = 0.73 * \sigma_{\text{MSC}} (+/- 10 \text{ MPa}), \quad (1)$$

and

$$\sigma_{\text{gas}} = 0.73 * \sigma_{\text{SSA}} - 48 \text{ MPa} (+/- 30 \text{ MPa}). \quad (2)$$

The multiplication factor (0.73) in both equations is due to increased friction between the load column and confining pressure piston and apparatus components and elastic strain of the load column. The subtraction of 48 MPa from SSA results accounts for the strength of the solid salt assembly over temperatures of 400–800 °C. However, the confining pressures of experiments for the SSA calibration, performed at lower confining pressures than can be achieved by a gas apparatus (300–500 MPa), are considerably lower than those used in this study (generally > 1100 MPa). To test for any effects of pressure on these calibrations, we performed an additional experiment on a molybdenum cylinder using the SSA at the same temperature (700 °C) and strain rate ($\dot{\epsilon} = 1.6 * 10^{-4}$ /s) as was used in the calibration study of Holyoke and Kronenberg (2010), but at a higher confining pressure ($P_c = 1480$ MPa; Table 1). The differential stresses increase rapidly in the first 3% strain and, after yielding, continue to increase due to work hardening until the experiment was stopped (Fig. 1a). The uncorrected differential stress at $\epsilon = 5\%$ for this molybdenum cylinder is 480 MPa, essentially the same as the uncorrected differential stresses (470 and 490 MPa) measured for molybdenum cylinders in the SSA at low confining pressure (Fig. 1b). Therefore, we conclude that the SSA correction derived at low confining pressure by Holyoke and Kronenberg (2010) is applicable to differential stresses obtained at high confining pressure. This result is also consistent with the duplication of the Holyoke and Kronenberg (2010) calibrations at high confining pressures in other laboratories (Eric Goergen, Greg Hirth, personal communication). Note that we have presented additional data from the deformation steps performed during the same experiment at 800 °C and $\dot{\epsilon} = 1.7 * 10^{-4}$ /s and 900 °C and $\dot{\epsilon} = 1.7 * 10^{-5}$ /s. No low confining pressure experiments were performed using the SSA at these conditions; we present results of the calibration experiment only for use by other experimentalists to test our methods.

2.2.3. Temperature and strain sensitivity of the MSC and SSA load calibrations

The Holyoke and Kronenberg (2010) calibrations for MSC and SSA methods are based on comparisons of results obtained for metal cylinders deformed to low strains (<8%) in the gas apparatus and the MSC and SSA in the Griggs apparatus. Due to the upper temperature limitation of the gas apparatus, experiments were only conducted up to 800 °C, although the SSA is commonly used in experiments performed up to 900 °C and rarely as high as 1000 °C. Therefore, it is possible that the calibration differs at strains or temperatures outside of the original calibration range ($\epsilon < 8\%$, $T = 400\text{--}800$ °C). The mechanical data from two SSA and one MSC experiment performed at 900 °C, $P_c = 1150$ MPa and $\dot{\epsilon} = 1.7 * 10^{-4}$ /s on polycrystalline dolomite cylinders (as part of this study) can therefore be used to test for any changes in solid sample assembly strength with strain and temperature (Table 2). The uncorrected differential stresses of the SSA experiments are considerably higher than those of the MSC experiment at all strains and the rate of strain weakening after reaching the peak stress is also different (Fig. 1c). However, when the MSC and SSA corrections are applied to the mechanical data from these experiments, the peak corrected differential stresses of both SSA experiments (500 and 525 MPa) are well within experimental error (± 30 MPa) of the peak corrected differential stress of the MSC experiment (505 MPa, Fig. 1c). In addition, the rate of strain weakening is almost

Table 2

List of dolomite deformation experiments.

Experiment	Assembly	Material	Temperature (°C)	Confining pressure ^a (MPa)	Strain rate (s ⁻¹)	Strain (%)	Peak strength ^{b,c} (MPa)	Final strength ^c (MPa)
O-11	MSC ^d	Madoc dolomite	800	400	1.6×10^{-5}	6	445	445
D-5	MSC	Madoc dolomite	900	1120	1.4×10^{-4}	30	505 (7)	245
D-6	MSC	Madoc dolomite	1000	1350	1.6×10^{-6}	6	13	13
					1.6×10^{-5}	6	37 (2)	31
					1.6×10^{-4}	10	50	50
					1.6×10^{-6}	15	26	26
D-7	MSC	Madoc dolomite	900	1120	Hyd.	NA	NA	NA
D-8	MSC	Madoc dolomite	900	1150	1.6×10^{-6}	6	60	60
					1.6×10^{-5}	5	137	137
					1.6×10^{-4}	6	260 (4)	250
					1.6×10^{-6}	6	60	60
D-9	MSC	Madoc dolomite	1000	1350	1.6×10^{-5}	4	93	93
			900	1120	1.6×10^{-5}	4	220 (3)	215
			800	980	1.6×10^{-5}	4	350	350
D-10	SSA ^e	Madoc dolomite	900	1130	1.6×10^{-4}	7	500	500
D-11	SSA	Madoc dolomite	900	1150	1.6×10^{-4}	41	525 (7)	200
D-12	SSA	Madoc dolomite	900	1140	1.7×10^{-5}	33	390 (5)	135
D-13	SSA	Madoc dolomite	900	1150	1.5×10^{-6}	35	265 (4)	55
D-14	SSA	Madoc dolomite	900	1150	1.4×10^{-7}	10	85 (4)	60
D-15	SSA	Madoc dolomite	900	1150	1.6×10^{-6}	7	170 (4)	145
D-17	SSA	Madoc dolomite	900	1150	1.8×10^{-5}	6	370	370
D-19	SSA	Madoc dolomite	700	970	6.4×10^{-7}	5	390	390
D-22	SSA	Madoc dolomite	1000	1350	1.8×10^{-5}	14	200 (3)	50

^a $P_{\text{eff}} = 900$ MPa for all experiments, except O-11 where $P_{\text{eff}} = 300$ MPa.^b Strain in parentheses, if different than final strain.^c Corrected using methods described in Holyoke and Kronenberg (2010).^d Molten salt cell assembly.^e Solid salt assembly.

identical (Fig. 1c). The uncorrected peak differential stresses also plot along the MSC vs. SSA calibration relation (Fig. 1b). These results demonstrate that the MSC and SSA calibrations provide accurate stresses to within ± 10 MPa (MSC) or ± 30 MPa (SSA) over the strain, temperature, pressure conditions typically achieved in the Griggs apparatus.

2.3. Experimental procedure

The experiments to determine the rheology of dolomite deforming by dislocation creep were performed over a broad range of temperatures (700–1000 °C), confining pressures (P_c , 400–1350 MPa) and strain rates (10^{-4} – 10^{-7} /s, Table 2). Dolomite begins to dissociate at ~ 500 °C and room pressure (Wyllie and Huang, 1976) and generates a CO_2 pore pressure (P_p) at the conditions of experiments. Therefore, we varied confining pressure to maintain a constant effective pressure (P_{eff}) of 900 MPa, where $P_{\text{eff}} = P_c - P_{\text{CO}_2}$ (Fig. 2), with the exception of one experiment performed to duplicate an experiment performed by

Davis et al. (2008) in the gas apparatus at $T = 800$ °C, $P_c = 400$ MPa and $\dot{\epsilon} = 1.6 \times 10^{-5}$ /s.

All experiments were performed using the molten salt cell (MSC) or solid salt assembly (SSA) in a Griggs apparatus according to the methods described in Holyoke and Kronenberg (2010). The strength of the Ag–Pt or Ni–Pt jacketing (< 10 MPa) is significantly less than the dolomite at all conditions and no corrections for jacket strength were made to the mechanical data. The mechanical data were corrected for background packing friction, frictional forces in the load column and assembly strength (SSA experiments only).

Temperature and pressure were increased from room conditions to the final experimental conditions over a period of approximately 4 h. The assembly was heated by a resistive graphite furnace and temperatures were held within ± 2 °C in all experiments. After reaching the desired temperature and pressure in SSA experiments, the deformation piston was advanced at a constant rate until the sample was deformed to the desired strain. In all MSC experiments, except D-5, a pre-hit deformation cycle was performed to remove any Pb between the WC load piston and upper alumina piston before deforming the sample at the desired strain rate. Removal of the Pb improves the quality of the hit point and allows accurate measurement of elastic response of the samples, but it also leads to sample shortening of $\sim 5\%$ prior to the portion of the experiment performed to determine rheological parameters. After reaching the desired experimental strain, each sample was quenched under load to 200 °C and then returned to room temperature and pressure in approximately 1 h.

2.4. Sample and mechanical data analysis

After reaching room temperature and pressure, the sample was removed from the assembly and impregnated with epoxy. Each sample was then cut along a plane parallel to the direction of maximum compressive stress and perpendicular to any planar shear zone that may have developed at high strain. Thin sections for optical and TEM analyses were prepared from these sample halves. Differential stresses were calculated from force measurements collected during

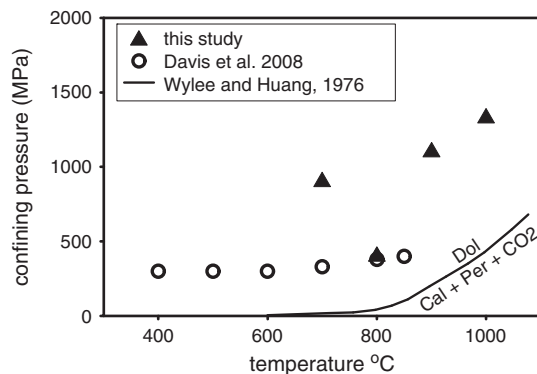


Fig. 2. Pressure and temperature conditions of all experiments performed using the Madoc dolomite in this study (black triangles) and Davis et al. (2008, open circles). The dolomite dissociation reaction from Wyllie and Huang (1976) was used to estimate P_{CO_2} at all experimental conditions ($P_{\text{CO}_2} = P_c$ at the line).

the experiments and corrected according to the methods of Holyoke and Kronenberg (2010).

3. Results

Two types of experiments were performed on Madoc dolomite cylinders to determine the rheology of coarse-grained polycrystalline dolomite: single-deformation-step experiments and multi-deformation-step experiments (Table 2). The single-deformation-step experiments were performed to determine how stress and microstructures evolve as a function of strain. While the multi-deformation-step experiments were initially performed to determine rheological parameters, they were not used to determine these parameters because we learned that strain became localized in all samples deformed to total strains >8%.

3.1. Single-deformation-step mechanical data

Single-deformation-step experiments were performed at $T = 700\text{--}1000\text{ }^{\circ}\text{C}$, $P_{\text{eff}} = 900\text{ MPa}$ and $\dot{\epsilon} = 10^{-4}\text{--}10^{-7}/\text{s}$ to total strains of 5–41% (Table 2) using both the MSC and SSA. Differential stresses increased rapidly in the first 2% strain prior to yielding in all experiments. The dolomite work hardened somewhat until reaching a peak stress at $\epsilon \sim 5\text{--}8\%$. The corrected peak differential stresses varied from 85 to 525 MPa. In all experiments performed to $\epsilon > 8\%$, after reaching the peak differential stress, the dolomite began to strain weaken, in some cases by as much as 75% of the peak stress, until the experiment was stopped. None of the experiments achieved a constant stress following the onset of strain weakening.

3.2. Strain rate- and temperature-stepping experiments

Strain rate- and temperature-stepping experiments were performed to determine the strain rate and temperature sensitivities, respectively, of dolomite flow strength using the MSC. Two strain rate-stepping experiments were performed: one at $900\text{ }^{\circ}\text{C}$ and $P_c = 1150\text{ MPa}$ (D-8) and one at $1000\text{ }^{\circ}\text{C}$ and $P_c = 1350\text{ MPa}$ (D-6). Each sample was deformed to low strain (3–5%) at $\dot{\epsilon} = 1.6 \times 10^{-4}/\text{s}$ to remove Pb from the load column (i.e., the pre-hit procedure) and the differential stresses during these deformation steps are not reported. The stepping experiments were performed by deforming the dolomite cylinder to low strain (5–10%) at $\dot{\epsilon} \sim 1.6 \times 10^{-6}/\text{s}$, $1.6 \times 10^{-5}/\text{s}$, $1.6 \times 10^{-4}/\text{s}$ and then at $1.6 \times 10^{-6}/\text{s}$ again before quenching the experiment. The differential stresses measured in the experiment performed at $900\text{ }^{\circ}\text{C}$ and $P_c = 1150\text{ MPa}$ were 60, 137, 260 and 60 MPa, respectively, for the same sequence of imposed strain rates (Table 2, Fig. 4a). The corrected differential stresses measured in the experiment performed at $1000\text{ }^{\circ}\text{C}$ and $P_c = 1350\text{ MPa}$ were 13, 37, 50 and 26 MPa, respectively, for the same strain rates listed above (Table 2, Fig. 4b). In all cases, differential stresses increased with increasing strain rate, but differential stresses in individual deformation steps were significantly lower than those measured in single deformation step experiments performed at the same conditions.

Each deformation step of the temperature-stepping experiment (D-9) was performed at $\dot{\epsilon} = 1.6 \times 10^{-5}/\text{s}$, at temperatures of 1000, 900 and $800\text{ }^{\circ}\text{C}$ (Table 2). A pre-hit deformation stage was also performed at $1000\text{ }^{\circ}\text{C}$ and $\dot{\epsilon} = 1.6 \times 10^{-4}/\text{s}$ to low strain ($\sim 3\%$) and these data are not reported. Confining pressure was decreased between each deformation step to maintain a constant $P_{\text{eff}} = 900\text{ MPa}$ after decreasing the temperature to the temperature of the subsequent deformation step ($P_{\text{eff}} = P_c - P_{\text{CO}_2}$, as equilibrium P_{CO_2} at sequential temperatures are decreased). The dolomite cylinder was unloaded and maintained hydrostatically during these temperature and pressure changes. Corrected differential stresses were 93, 220, 350 MPa for the deformation steps performed at 1000, 900 and $800\text{ }^{\circ}\text{C}$, respectively (Fig. 4c). As temperature decreased, differential stress increased, consistent with a thermally activated process. However, all differential stresses in individual

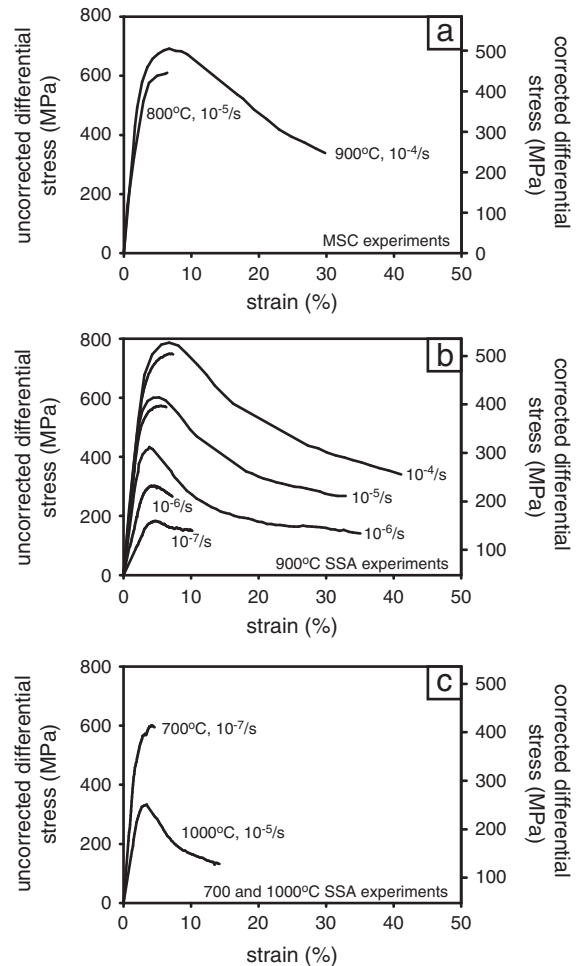


Fig. 3. Differential stresses in experiments performed on Madoc dolomite at all conditions ($T = 700\text{--}1000\text{ }^{\circ}\text{C}/\dot{\epsilon} = 10^{-7}\text{--}10^{-4}/\text{s}$) in the MSC (a) and SSA (b, c) increase rapidly over the first 1–2% strain and after reaching a peak stress, begin to strain weaken at strains greater than 5–8%.

deformation steps of temperature-stepping experiments (strains of 4% in each step) were significantly lower than those measured at the same low strain in single-deformation-step experiments performed at the same conditions.

3.3. Microstructures

We outline the deformation microstructures at the optical and TEM scales as they relate to intracrystalline creep mechanisms, which predominate at low strains, in this paper, leaving detailed optical and TEM analyses of microstructures and strain localization to a separate study (Holyoke et al., in preparation). In low strain ($< 8\%$) samples, deformation is relatively homogeneous (Fig. 5a) and microstructures at the optical scale include some patchy extinction, serrated grain boundaries and limited recrystallization at some grain boundaries and twin intersections, twins and along trails of fluid inclusions (Fig. 6a). At the TEM scale, the original, coarse dolomite grains have high dislocation densities while recrystallized grains have few or no dislocations (Fig. 6b). The appearance of the grain boundaries is indicative of recrystallization-accommodated dislocation creep (i.e., grain boundary bulging leading to reductions in dislocation density), as observed in quartz and feldspar (Hirth and Tullis, 1992; Stipp et al., 2010; Tullis and Yund, 1987). Anastomosing, fine-grained ($< 10\text{ }\mu\text{m}$, Fig. 6c), through-going shear zones are observed in samples deformed to strains greater than 8% (Figs. 5b/c). Shear zones cross cut some grains and follow grain boundaries in other portions of the samples. In the highest

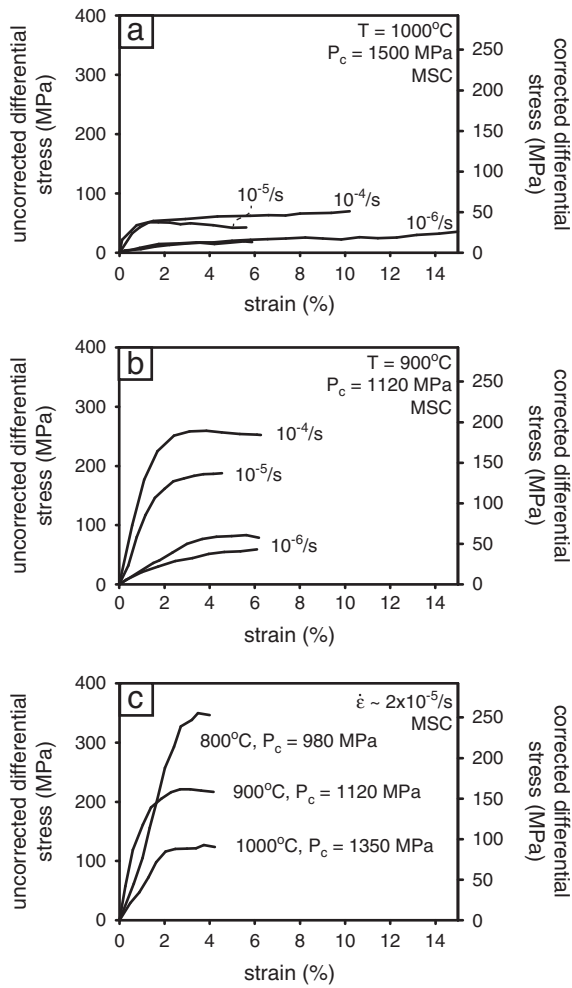


Fig. 4. Differential stresses in strain rate stepping experiments performed at (a) 1000 °C/ P_c = 1500 MPa (D-6) and (b) 900 °C/ P_c = 1120 MPa (D-8) increase systematically with increasing strain rate. (c) Differential stresses increase with decreasing temperature (1000–800 °C, $\dot{\epsilon}$ = 10^{-5} /s) in the temperature-stepping experiment (D-9). Differential stresses in all stepping experiments were lower than those measured at similar strains in individual deformation step experiments (Fig. 3a–c) performed at the same conditions (Table 2).

strain samples, the narrow shear zones are well developed and transect the sample (Fig. 5c), but microstructures outside of the shear zones in these samples are similar to those observed in low-strain samples. Relict shear zones in conjugate orientations, similar to those observed at intermediate strain, are also observed in some samples (Fig. 5c). Grain sizes in these shear zones are relatively uniform ($<10 \mu\text{m}$), but larger (20–50 μm) porphyroclasts are also present within the shear zones (Fig. 6d).

4. Discussion

All Madoc dolomite samples deformed homogeneously by dislocation creep at low ($<8\%$) strains, but nucleation of fine-grained shear zones, accompanied by strain weakening, caused heterogeneous deformation within the dolomite aggregates at strains greater than 8%. In the following, we discuss the methods used to determine the low-strain rheology associated with dislocation creep, the rheological parameters, and the implications of the rheological evolution to naturally deformed dolomites.

4.1. Experimental technique

The most precise method to determine differential stresses in high pressure experiments is the MSC (Holyoke and Kronenberg, 2010). However, one limitation of this method is the necessity of a pre-hit deformation stage to remove Pb from the load column to generate a sharp hit point. If the materials of interest deform homogeneously at all strains, then the pre-hit will not significantly alter the microstructure of that material, such as the experiment performed on a nickel cylinder (Fig. 2), whose strength quickly reaches steady-state values for each deformation step at total strains up to 36%. However, if the rheology and microstructure of the material of interest are sensitive to total strain (i.e., the material does not deform homogeneously or the deformation mechanisms change in response to microstructural changes), then the pre-hit deformation stage will affect the stresses measured in subsequent deformation steps.

We observed the development of shear zones in dolomite sample deformed strains above 8% during single deformation stage experiments over a wide range of peak differential stresses (85–525 MPa). These shear zones developed at all temperatures (700–1000 °C) and strain rates (10^{-4} – 10^{-7} /s) explored in this study. Neumann (1969) observed limited recrystallization in a narrow zone in a coarse-grained

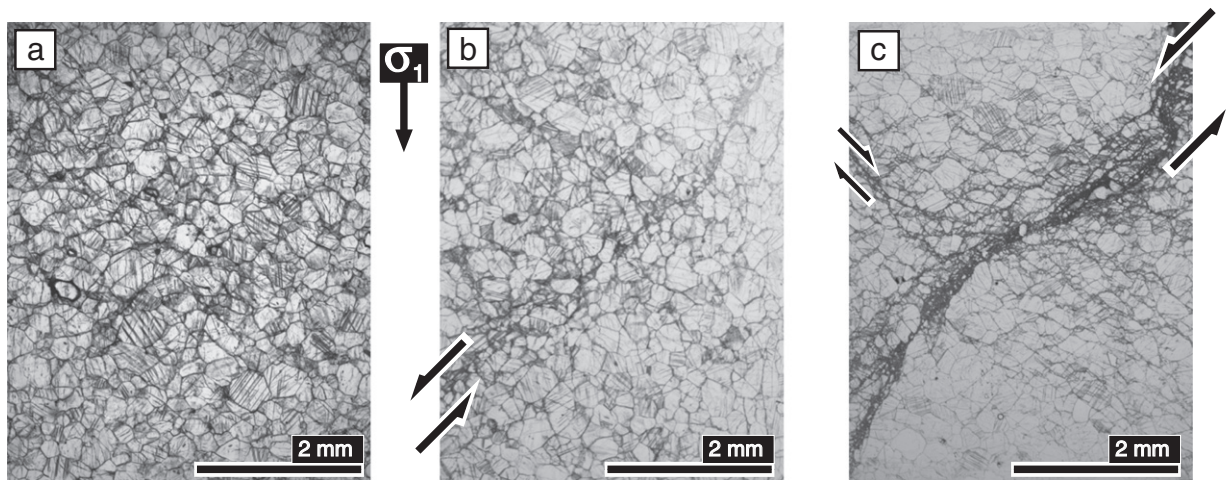


Fig. 5. Plane polarized light sample-scale photomicrographs of three samples with different total strains (7, 10 and 41%) illustrate the development of shear zones within the dolomite aggregates. (a) At low sample strain (7%), deformation of the dolomite aggregate is relatively homogeneous (D-10, 900 °C, P_c = 1130 MPa, $\dot{\epsilon}$ = 1.6×10^{-4} /s). (b) At intermediate sample strain (10%), strain localizes within thin, fine-grained zones that cross-cut the sample (shear arrows), cross-cutting some grains or following grain boundaries elsewhere (D-14, 900 °C, P_c = 1150 MPa, $\dot{\epsilon}$ = 1.6×10^{-7} /s). (c) At higher sample strain (41%), strain is highly localized within a well-developed, through-going shear zone (large shear sense arrows) that cross-cuts the sample. Relict shear zones (small shear sense arrows) are also observed in conjugate orientations (D-11, 900 °C, P_c = 1130 MPa, $\dot{\epsilon}$ = 1.6×10^{-4} /s).

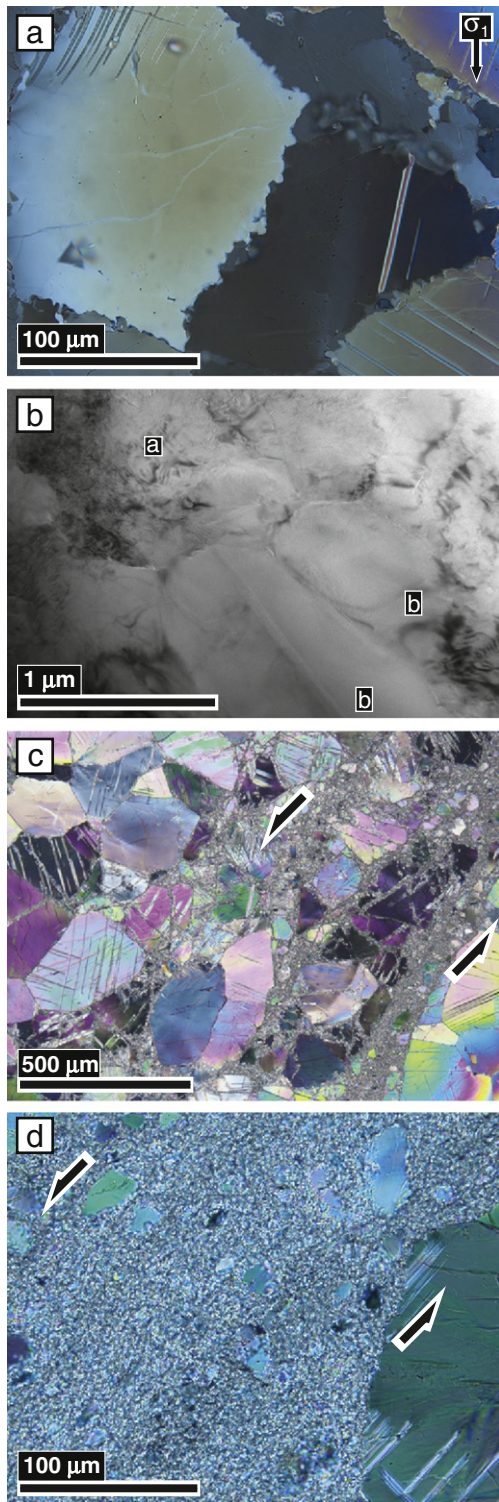


Fig. 6. Images of dolomite samples deformed to low, intermediate and high sample strains demonstrate the transition from homogeneous strain to localized strain. (a) At low strain or away from shear zones in higher strain samples, the microstructures include twins, undulatory extinction and very limited grain boundary migration (cross-polarized light photomicrograph, D-14, 900 °C, $P_c = 1150$ MPa, $\dot{\epsilon} = 1.6 \times 10^{-7}$ /s). (b) At the TEM scale, original dolomite grains (a) have high dislocation densities and recrystallized grains (b) are generally free of dislocations (bright-field TEM image, D-17, $\epsilon = 6\%$, 900 °C, $P_c = 1130$ MPa, $\dot{\epsilon} = 1.6 \times 10^{-5}$ /s). (c) At higher sample strain (10%), fine-grained shear zones are observed along grain boundaries or cutting across larger grains (cross-polarized light photomicrograph, D-14, 900 °C, $P_c = 1150$ MPa, $\dot{\epsilon} = 1.6 \times 10^{-7}$ /s). (d) At the highest sample strain (41%), through-going fine-grained shear zones cross cut the sample. The grain size inside of the shear zone is extremely small ($< 5 \mu\text{m}$) with some larger ($< 20 \mu\text{m}$), irregularly-shaped porphyroclasts (cross-polarized light photomicrograph, D-11, 900 °C, $P_c = 1130$ MPa, $\dot{\epsilon} = 1.6 \times 10^{-4}$ /s).

dolomite aggregate (Dover Plains dolomite) deformed at 1000 °C to $\epsilon = 30\%$, much as observed in our samples. Barber et al. (1994) deformed one sample of Crevola dolomite within the dislocation creep field at 900 °C and $\sim 10^{-5}$ /s and observed minor strain weakening beginning at low strain ($\sim 5\%$ and a differential stress of ~ 300 MPa), but they did not discuss the recrystallization process or comment on the optical microstructures, focusing instead on TEM-scale defects and dislocation substructures. The strain dependence of the strengths observed in all experimental studies of dolomite aggregates deformed by dislocation creep is likely due to the formation of small dynamically recrystallized grains that begin to control the rheology of the bulk sample, probably due to a change in dominant deformation mechanism. The strain weakening caused by the formation of these dynamically recrystallized grains is the reason that corrected differential stresses are lower in the strain rate- and temperature-stepping experiments (Fig. 5a–c) than corrected differential stresses in single-deformation-step experiments performed at the same temperatures and strain rates using the SSA (Fig. 4b and c). The pre-hit deformation step of these multi-deformation-step MSC experiments likely alters the microstructure of the dolomite aggregates; thus, subsequent deformation steps characterize the rheology of both the protolith and shear zones, which makes these experiments unsuitable for characterizing the rheology of dolomite deforming by dislocation creep. As a result of these complexities, we have chosen to determine the rheological parameters of dolomite dislocation creep using the peak differential stresses from individual experiments performed using the SSA and MSC, rather than using data obtained from the stepping experiments. The mechanical data from the single-deformation-step experiments were analyzed to determine the stress exponent (n) and activation energy (Q) of an Arrhenius type flow law:

$$\dot{\epsilon} = A\sigma^n \exp\left(\frac{-Q}{RT}\right) \quad (3)$$

where A is the pre-exponential term ($\text{MPa}^{-n}\text{s}^{-1}$), σ is the differential stress (MPa), R is the universal gas constant and T is temperature (K).

4.2. Strain rate and temperature sensitivity

In order to determine the strain rate sensitivity of the strength of coarse-grained dolomite, we have compared the mechanical data from all experiments performed on Madoc dolomite at 900 °C and $P_c \sim 1150$ MPa. This set of experiments contains the broadest range of differential stresses (85–525 MPa) and strain rates (1.7×10^{-4} /s to 1.7×10^{-7} /s). The relationship between strain rate and stress used to determine the strain rate sensitivity based on Eq. (3) is:

$$\ln \dot{\epsilon} = n \ln \sigma + \left(\ln A - \frac{Q}{RT} \right). \quad (4)$$

Therefore, the stress exponent is the slope of the relationship between $\ln \dot{\epsilon}$ and $\ln \sigma$.

The slope of this relationship for experiments performed at 900 °C is 3.0 ± 0.1 if the highest stresses measured at the highest strain rate ($\dot{\epsilon} = 1.7 \times 10^{-4}$ /s) are excluded from the fit to the data (Fig. 7a, Table 2). The high differential stress data obtained at the highest strain rate (500–525 MPa) are nearly equal to those of samples deformed by crystal plasticity and twinning mechanisms (600–700 MPa) and appear to represent transitional deformation, both by dislocation creep and crystal plasticity mechanisms. The stress exponent (n) of 3.0 (± 0.1) is consistent with microstructures of these samples, which indicate that samples were deformed by dislocation creep mechanisms.

The temperature sensitivity of the rheology of the coarse-grained dolomite aggregates deformed by dislocation creep was determined using multiple experiments performed at a single set of conditions and determining differential stresses at low strains. If the mechanical data from a series of experiments performed at the same strain rate

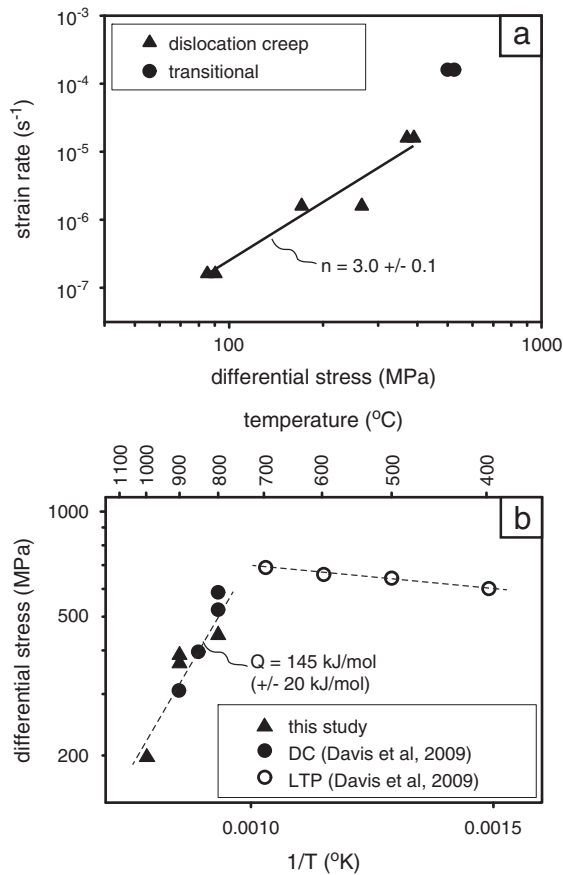


Fig. 7. (a) The relationship between strain rate and differential stress (measured at low strain) of single-deformation-step experiments performed on the Madoc dolomite at 900 °C is linear at $\dot{\epsilon} = 10^{-7}$ – 10^{-5} /s, resulting in a value of 3.0 (± 0.1) for the stress exponent n . The differential stresses (500–525 MPa) of the single-deformation-step experiments performed at $\dot{\epsilon} = 10^{-4}$ /s do not fit the same relationship as the lower differential stress data. These high differential stress data are transitional between low temperature plasticity and dislocation creep. (b) The relationship between the natural log of differential stress and inverse absolute temperature at a constant strain rate is linear over the range of the experiments performed in this study (800–1000 °C, $\dot{\epsilon} = 1.6 \times 10^{-5}$ /s). The activation energy (Q) derived from single-deformation-step experiments is 145 kJ/mol (± 40 – 10 kJ/mol) for $n = 3.0$.

but different temperatures are compared, then the activation energy can be determined from the following relationship based on Eq. (3):

$$\ln \sigma = \left(\frac{Q}{nR} \right) \left(\frac{1}{T} \right) - \frac{\ln \dot{\epsilon}}{n}. \quad (5)$$

The slope of the relationship between $\ln \sigma$ and $1/T$ is equal to the activation energy (Q) divided by the stress exponent and universal gas constant. Taking $n = 3.0$, the activation energy (Q), based on both data from the gas apparatus (Davis et al., 2008) and data from this study, is 145 (± 40 – 10) kJ/mol. This value is considerably lower than the value (410 kJ/mol) reported by Davis et al. (2008), which was determined by the same method as used in this study (Fig. 7b, Table 2), but assuming $n = 7$. Because of the limited conditions (800–850 °C) of the dislocation creep field accessible at modest P_c (< 400 MPa), Davis et al. (2008) were unable to determine the strain rate sensitivity of dislocation creep in dolomite and they adopted a relatively large value of n (Eq. (7)) similar to that reported for calcite dislocation creep (de Bresser, 2002). Our data indicate that the strain rate sensitivity of the rheology of dolomite deforming by dislocation creep ($n = 3.0 \pm 0.1$) is far closer to values predicted by dislocation creep theories (Poirier, 1985).

The activation energy (145 kJ/mol) for dislocation creep in dolomite aggregates is lower than the activation energy for diffusion creep in dolomite aggregates (280 kJ/mol) determined by Davis et al. (2008). It is generally believed that rate-controlling processes of intragranular creep will be governed by larger activation barriers than grain boundary processes of diffusion creep and grain boundary sliding. For example, activation energies for dislocation creep of polycrystalline calcite and olivine (420 and 400–500 kJ/mol, respectively) are greater than those determined for diffusion creep of the same monomineralic aggregates (190 and 335–375 kJ/mol, respectively, Hirth and Kohlstedt, 2003; Schmid et al., 1980; Walker et al., 1990). The consequence of differing relative magnitudes of activation energies for dislocation creep and diffusion creep of dolomite and other earth materials is that their temperature sensitivities alter the topology of the fields of these creep mechanisms on deformation mechanism maps.

The relative magnitudes of activation energies of dislocation and diffusion creep for dolomite deformation are unusual. Further research is necessary to understand the rate-controlling mechanisms of dislocation and diffusion creep of dolomite, before we can explain the relative magnitudes of their activation energies. A number of complicating factors may be involved. Dislocation glide and twinning appear to require higher stresses at higher temperatures (Davis et al., 2008). The recovery mechanisms (e.g., dislocation climb and dynamic recrystallization) in dolomite aggregates may not operate at rates sufficient to prevent work hardening, leading to strain accommodation by twinning. In addition to dynamic recrystallization at grain boundaries via bulge nucleation processes, similar bulge nucleation along fluid inclusion trails appears to be involved in the formation of fine-grained material which is much weaker than the coarse-grained regions of dolomite samples, leading to strain localization in fine-grained zones. Internal creep processes of dolomite may be influenced by cation order–disorder reactions, while grain boundary processes may be less sensitive to cation order–disorder.

The temperature dependence we report for dislocation creep of dolomite ($Q = 145$ kJ/mol) may reflect intrinsic temperature sensitivities of intracrystalline deformation processes and their dependence on changing order–disorder with temperature. Dolomite disorder increases from $s = 0.934$ (800 °C) to $s = 0.74$ (1000 °C) ($s = 1$ is perfectly ordered) over the range of temperatures used to determine the activation energy in this study (Antao et al., 2004; Reeder and Wenk, 1983).

We had anticipated a non-linear temperature dependence due to the combined temperature effects on dislocation creep mechanisms and changing cation order–disorder. However, the data set is well fit by a linear relationship in $\ln \sigma$ and $1/T$ space (Eq. (5), Fig. 7b). Any temperature dependence of dislocation creep due to disorder is either small or follows a relationship that is not readily distinguished from an Arrhenius law. Thus, the apparent activation energy of creep may be a combination of two functions that lead to an Arrhenius $\ln \sigma - 1/T$ law.

Cation order/disorder reactions are likely to be less important during natural deformation of dolomite at lower temperatures and strain rates than in the high temperature and strain rate experiments reported here. The apparent activation energy ($Q = 145$ kJ/mol) for dislocation creep may nevertheless apply to deformation in the Earth if cation order/disorder reactions do not affect dislocation creep in our experiments. In any case, the low activation energy measured in this study ($Q = 145$ kJ/mol) for dislocation creep relative to Q (280 kJ/mol) for diffusion creep, cannot be readily explained by cation order/disorder reactions unless the rate-controlling step of dislocation creep is favored by cation ordering.

4.3. Deformation mechanism map and naturally deformed dolomite aggregates

The mechanical data of coarse-grained polycrystalline dolomite deforming by dislocation creep is well fit by Eq. (3) using the rheological

parameters determined above (Fig. 8a). In order to predict the dominant deformation mechanisms of coarse-grained dolomite aggregates deforming in nature, we constructed a deformation mechanism map in differential stress-temperature space (Fig. 8b) using the dislocation creep flow law of this study, the flow law reported for diffusion creep (Davis et al., 2008):

$$\dot{\epsilon} = A\sigma^n d^{-m} \exp\left(\frac{-Q}{RT}\right), \quad (6)$$

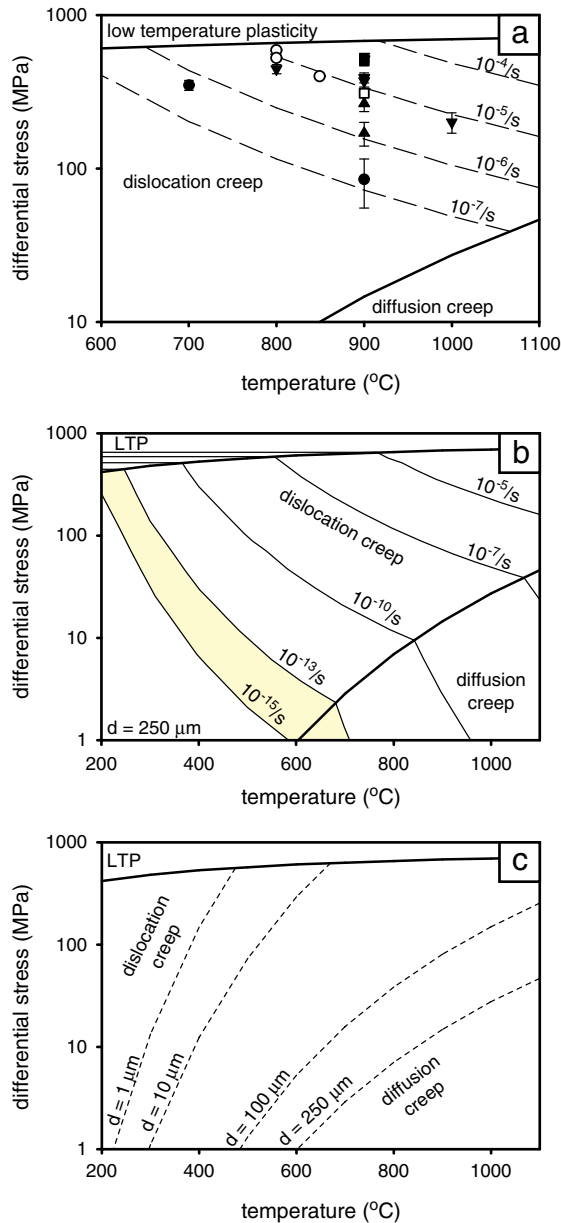


Fig. 8. (a) The peak stresses of single-deformation-step experiments at $T = 700\text{--}1000\text{ }^{\circ}\text{C}$, $\dot{\epsilon} = 10^{-4}\text{--}10^{-7}/\text{s}$ are well fit by a temperature vs. differential stress deformation mechanism map constructed using the flow law for dolomite deforming by dislocation creep (Eq. (3), parameters in Table 3). (b) A deformation mechanism map constructed using the dislocation creep flow law of this study and the low temperature plasticity and diffusion creep flow laws of Davis et al. (2008) indicates that naturally-deformed, coarse-grained dolomite aggregates will initially deform by dislocation creep over a wide range of conditions. (c) Decreasing grain size of dolomite shifts the dislocation creep–diffusion creep boundary to lower temperatures ($d = 100, 10$ and $1\text{ }\mu\text{m}$ shown). This transition indicates that, as fine-grained ($d \sim 10\text{ }\mu\text{m}$) shear zones nucleate, the rheology of these shear zones at higher temperatures ($> 300\text{ }^{\circ}\text{C}$) will be governed by diffusion creep.

where d is grain size and m is the grain size exponent, and a relationship that fits the low temperature plasticity data of Davis et al. (2008):

$$\dot{\epsilon} = A\sigma^n, \quad (7)$$

where values of parameters are given in Table 3. Both Davis et al. (2008) and Delle Piane et al. (2008) developed diffusion creep flow laws using fine-grained synthetic dolomites over similar temperatures ($600\text{--}800\text{ }^{\circ}\text{C}$), effective pressure (300 MPa) and strain rates ($10^{-4}\text{--}10^{-6}/\text{s}$). The flow stresses measured in both studies are nearly identical at corresponding conditions as are rheological parameters n and m (Table 3); yet, these studies report activation energies that are different (368 and 280 kJ/mol, respectively). We note, however, that data presented in Fig. 7 of Delle Piane et al. (2008) yield an activation energy of 310 kJ/mol, which is within experimental errors of the value published by Davis et al. (2008). Deformation mechanism maps are essentially the same if we replace the diffusion creep law of Davis et al. (2008) by that of Delle Piane et al. (2008), but we have used Davis et al. (2008) out of personal preference.

Construction of the σ – T deformation mechanism map for dolomite indicates that at natural strain rates ($10^{-13}\text{--}10^{-15}/\text{s}$) and temperatures below $200\text{ }^{\circ}\text{C}$, coarse-grained ($d \sim 250\text{ }\mu\text{m}$) dolomite will deform by low temperature plasticity (Fig. 8b). However, at these high differential stresses ($> 400\text{ MPa}$) dolomite aggregates may also fail by brittle fracture, with the extent of plastic versus brittle processes depending on pressure. With increasing temperature ($200\text{--}250\text{ }^{\circ}\text{C}$), dolomite is predicted to deform by dislocation creep and, depending on the strain rate and confining pressure, by components of crystal plasticity or brittle failure (Fig. 8b). At temperatures above $250\text{ }^{\circ}\text{C}$, natural strain rates and presumably high effective pressures, dolomite will deform by dislocation creep (Fig. 8b). Diffusion creep does not become the dominant deformation mechanism in coarse-grained ($d \sim 250\text{ }\mu\text{m}$) dolomite aggregates until temperatures above $600\text{ }^{\circ}\text{C}$. Decreasing the grain size shifts the boundary between dislocation and diffusion creep to lower temperatures (Fig. 8c). Fine-grained ($< 10\text{ }\mu\text{m}$) dolomite aggregates may continue to deform by dislocation creep at temperatures up to $300\text{ }^{\circ}\text{C}$, but above $300\text{ }^{\circ}\text{C}$, diffusion creep is predicted to be the predominant deformation mechanism (Fig. 8c). One implication of this observation is that comminution of dolomite in transitional brittle–ductile faults may alter fault strengths through mixed fracture and dislocation creep processes. If grain size refinement continues to be important at high temperatures through dynamic recrystallization, in the absence of cracking, dislocation creep may also give way to diffusion creep.

The positive-sloped, convex-down boundary between dislocation creep and diffusion creep of dolomite aggregates in σ – T space (Fig. 8b and c) is very different from the dislocation creep–diffusion creep boundaries of other crystalline solids, such as calcite or olivine (Hirth and Kohlstedt, 2003; Rutter, 1995), or metals (Ashby, 1972) which have negative-sloped, convex-up dislocation–diffusion creep boundaries. This result is solely due to the inversion of the activation energies of dislocation creep and diffusion creep in dolomite compared with relative values of activation energies of dislocation and diffusion creep in calcite, olivine and metals (for which the activation energy of dislocation creep is generally greater than that of diffusion creep). Further research will be required to understand the creep

Table 3
Flow law parameters used for calculation of deformation mechanism maps.

Deformation mechanism	Equation	A (MPa $^{-n}\text{s}^{-1}$)	n	m	Q (kJ mol $^{-1}$)
Low temperature plasticity	7	2.31×10^{-143}	49	–	–
Dislocation creep	3	1.50×10^{-6}	3	–	145
Diffusion creep	6	1.74×10^9	1.28	3	280
(Davis et al., 2008)					
Diffusion creep	6	–	1.3	2.6	368/310 ^a
(Delle Piane et al., 2008)					

^a See text for discussion.

activation energies of dolomite deformed by dislocation creep and diffusion creep before we can learn how widespread this behavior may be for crystalline solids. However, the growth of the diffusion creep field at the expense of the dislocation creep field at finer grain sizes is consistent with the grain size sensitivity of the rheology of diffusion creep in other materials, and has similar geologic consequences for natural deformation of rocks of varying grain sizes.

4.4. Dolomite vs. calcite rheology

Dolomite and calcite are observed in naturally deformed rocks as different stratigraphic layers or mixed within single formations (Delle Piane et al., 2008; Wells et al., 2011; Woodward et al., 1988). Studies of naturally deformed carbonates have concluded that dolomite accommodates less strain than calcite, especially at low temperatures (Wells et al., 2011; Woodward et al., 1988), indicating that calcite is weaker than dolomite at these conditions. In order to compare the predicted rheologies of dolomite and calcite deforming at natural conditions, we constructed grain size–stress (d – σ) deformation mechanism maps for three temperatures (200, 400 and 600 °C, Fig. 9a–c, respectively) using the same rheologies for dolomite as for our σ – T deformation mechanism maps. The calcite grain size–stress relations are plotted using flow laws for diffusion creep accommodated by volume diffusion/dislocation processes (Walker et al., 1990), grain boundary diffusion/sliding (Herwegh et al., 2003) and cross slip-controlled dislocation creep (de Bresser, 2002).

At 200 °C, the strength of dolomite at all grain sizes (0.1 μ m to 1 cm) is considerably greater than calcite, consistent with studies of carbonates deformed in upper levels of the crust (Wells et al., 2011; Woodward et al., 1988). At 400 °C, dolomite is still stronger than calcite at fine grain sizes, but fine-grained dolomites are similar in strength or weaker than coarse-grained calcite marbles. At 600 °C, the strength of dolomite is generally stronger than calcite at grain sizes <1 cm, but both carbonates are very weak (<10 MPa) relative to those predicted by creep laws for common crustal silicates, such as quartz (Gleason and Tullis, 1995). Previous workers (Davis et al., 2008, 2011; Delle Piane et al., 2008) speculated that at high temperatures and natural strain rates, dolomites may be weaker than calcite marbles, depending on their grain sizes. Grain growth in dolomite is several orders of magnitude slower than it is in calcite (Davis et al., 2011). Thus, calcite marbles may undergo grain growth and deform in the dislocation creep regime. If grain growth and deformation are simultaneous, nucleation of calcite grains during dynamic recrystallization and grain growth may lead to grain sizes that favor mixed dislocation creep and diffusion creep at the boundaries between these deformation mechanism fields (de Bresser et al., 1998, 2001). In contrast, grain growth of dolomite is sluggish, and fine-grained dolomites may deform largely by diffusion creep. Delle Piane et al. (2008) reported field observations of strain partitioning between layers of dolomite and calcite, with a weaker, higher strain dolomite host surrounding calcite layers that were folded and boudinaged at high temperatures (~700 °C). Our experimental results are consistent with these observations when grain sizes of dolomite units are significantly smaller than those of coexisting calcite units.

5. Conclusions

Coarse-grained dolomite deforms by dislocation creep at high temperatures (700–1000 °C), constant P_{eff} (900 MPa) and strain rates $= 1.7 \times 10^{-7}$ – 1.7×10^{-4} /s with peak differential stresses at low strain (<8%) from 525 to 85 MPa. The low strain mechanical data were used to determine the rheological parameters of a dislocation creep flow law with $A = 1.5 \times 10^{-6}$ ($\pm 2.7 \times 10^{-7}$), $n = 3 \pm 0.1$, and $Q = 145 \pm 20$ kJ/mol. Microstructures observed within the coarse-grained dolomite aggregate at low strain include undulatory extinction, serrated grain boundaries, twins, limited recrystallization

at grain boundaries, twin intersections and along fluid inclusion trails. Dolomite samples deformed to strains >8% strain-weakened with the development of through-going fine-grained shear zones, which likely deform by diffusion creep. Microstructures outside of these shear zones reflect continued dislocation creep processes, consistent with those observed in low strain samples. These results indicate that:

1. Deformation of dolomite by dislocation creep appears to be limited to small strain deformations, while fine-grained dynamically recrystallized dolomite that develops at the edges of porphyroclasts leads to strain localization if the temperatures are high enough for diffusion creep to become the dominant deformation mechanism within these fine-grained zones.

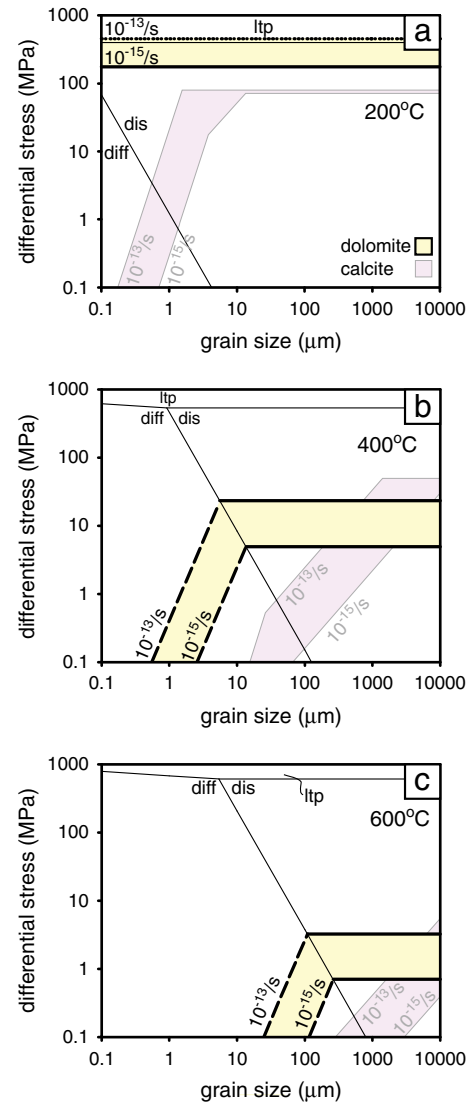


Fig. 9. Strengths of dolomite (yellow shaded zones) at natural strain rates (10^{-15} – 10^{-13} /s) and three temperatures (200, 400 and 600 °C) were calculated to construct deformation mechanism maps in grain size–differential stress space using the dislocation creep flow law of this study and diffusion creep and crystal plasticity flow laws of Davis et al. (2008). Flow laws for calcite (pink shaded zones, references in text) were used to calculate the calcite strengths at the same conditions in order to compare the strengths of calcite and dolomite at natural conditions. (a) The strengths of dolomite at all grain sizes (0.1 μ m–1 cm) are greater than those of calcite when deformed at 200 °C and natural strain rates. Brittle behavior may also occur if the confining pressure is not high enough to prevent crack growth. (b) At 400 °C and natural strain rates, the strength of polycrystalline dolomite is greater than polycrystalline calcite at grain sizes less than ~1 mm, but calcite is somewhat stronger at coarser grain sizes. (c) At 600 °C, the strength of polycrystalline dolomite is greater than polycrystalline calcite at grain sizes less than 5 mm, but is similar at coarser grain sizes. The strengths of both carbonates at these conditions are <10 MPa.

2. The activation energy (Q) of dislocation creep of dolomite is lower than the activation energy of diffusion creep of dolomite.
3. Extrapolating our results to geologic strain rates, dislocation creep is likely the dominant deformation mechanism in coarse-grained dolomite deformed at temperatures up to $\sim 550^\circ\text{C}$.
4. Extrapolating our results to geologic strain rates, diffusion creep may be the dominant deformation mechanism in fine-grained dolomite at temperatures greater than 300°C .

Acknowledgments

This study was funded by the American Reinvestment and Recovery Act via a grant to JN, AK and CH from the National Science Foundation (EAR-0911586). CH would like to thank Rachel Wells for discussions on the rheology of dolomite and calcite in natural settings and sharing a program to calculate calcite deformation mechanism maps. Thanks to Bernhard Stockhert and Johannes de Bresser for in depth and helpful reviews.

References

- Antao, S.M., Mulder, W.H., Hassan, I., Crichton, W.A., Parise, J.B., 2004. Cation disorder in dolomite, $\text{CaMg}(\text{CO}_3)_2$, and its influence on the aragonite plus magnesite $\leftrightarrow$ dolomite reaction boundary. *American Mineralogist* 89, 1142–1147.
- Ashby, M.F., 1972. First report on deformation-mechanism maps. *Acta Metallurgica et Materialia* 20, 887–897.
- Austin, N., Evans, B., 2009. The kinetics of microstructural evolution during deformation of calcite. *Journal of Geophysical Research* 114.
- Barber, D.J., Wenk, H.R., Heard, H.C., 1994. The plastic-deformation of polycrystalline dolomite – comparison of experimental results with theoretical predictions. *Materials Science and Engineering A* 175, 83–104.
- Davis, N.E., Kronenberg, A.K., Newman, J., 2008. Plasticity and diffusion creep of dolomite. *Tectonophysics* 456, 127–146.
- Davis, N.E., Newman, J., Wheelock, P.B., Kronenberg, A.K., 2011. Grain growth kinetics of dolomite, magnesite and calcite: a comparative study. *Physics and Chemistry of Minerals* 38, 123–138.
- de Bresser, J.H.P., 2002. On the mechanism of dislocation creep of calcite at high temperature: Inferences from experimentally measured pressure sensitivity and strain rate sensitivity of flow stress. *Journal of Geophysical Research* 107, 1–16.
- de Bresser, J.H.P., Peach, C.J., Reijers, J.P.J., Spiers, C.J., 1998. On dynamic recrystallization during solid state flow: effects of stress and temperature. *Geophysical Research Letters* 25, 3457–3460.
- de Bresser, J.H.P., Ter Heege, J.H., Spiers, C.J., 2001. Grain size reduction by dynamic recrystallization: can it result in major rheological weakening? *International Journal of Earth Sciences* 90, 28–45.
- Delle Piane, C., Burlini, L., Kunze, K., Brack, P., Burg, J.P., 2008. Rheology of dolomite: large strain torsion experiments and natural examples. *Journal of Structural Geology* 30, 767–776.
- Gleason, G.C., Tullis, J., 1993. Improving flow laws and piezometers for quartz and feldspar aggregates. *Geophysical Research Letters* 20, 2111–2114.
- Gleason, G.C., Tullis, J., 1995. A flow law for dislocation creep of quartz aggregates determined with the molten-salt cell. *Tectonophysics* 247, 1–23.
- Green, H.W., Borch, R.S., 1989. A new molten-salt cell for precision stress measurement at high-pressure. *European Journal of Mineralogy* 1, 213–219.
- Griggs, D., Miller, W.B., 1951. Deformation of Yule marble. Part I. Compression and extension experiments on dry Yule marble at 10,000 atmospheres confining pressure, room temperature. *Geological Society of America Bulletin* 62, 853–862.
- Griggs, D., Turner, F.J., Borg, I., Sosoka, J., 1953. Deformation of Yule Marble. Part 5. Effects at 300-Degrees-C. *Geological Society of America Bulletin* 64, 1327–1342.
- Handin, J.W., Griggs, D., 1951. Deformation of Yule marble. Part II. Predicted fabric changes. *Geological Society of America Bulletin* 62, 863–886.
- Heard, H.C., Raleigh, C.B., 1972. Steady-state flow in marble at 500° to 800°C . *Geological Society of America Bulletin* 83, 935–956.
- Herwegh, M., Xiao, X.H., Evans, B., 2003. The effect of dissolved magnesium on diffusion creep in calcite. *Earth and Planetary Science Letters* 212, 457–470.
- Herwegh, M., de Bresser, J.H.P., ter Heege, J.H., 2005. Combining natural microstructures with composite flow laws: an improved approach for the extrapolation of lab data to nature. *Journal of Structural Geology* 27, 503–521.
- Hirth, G., Kohlstedt, D., 2003. Rheology of the Upper Mantle and Mantle Wedge; A View from the Experimentalists, Inside the Subduction Factory. *American Geophysical Union, Washington, DC, United States*, pp. 83–105.
- Hirth, G., Tullis, J., 1992. Dislocation creep regimes in quartz aggregates. *Journal of Structural Geology* 14, 145–159.
- Holyoke III, C.W., Kronenberg, A.K., 2010. Accurate differential stress measurement using the molten salt cell and solid salt assemblies in the Griggs apparatus with applications to strength, piezometers and rheology. *Tectonophysics* 494, 17–31.
- Holyoke III, C.W., Kronenberg, A.K., Newman, J., in preparation. Microstructural evolution during strain localization in dolomite aggregates.
- Neumann, E.R., 1969. Experimental recrystallization of dolomite and comparison of preferred orientations of calcite and dolomite in deformed rocks. *Journal of Geology* 77, 426–438.
- Poirier, J., 1985. *Creep of Crystals: High-temperature Deformation Processes in Metals, Ceramics and Minerals*. Cambridge University Press, Cambridge.
- Reeder, R.J., Wenk, H.R., 1983. Structure refinements of some thermally disordered dolomites. *American Mineralogist* 68, 769–776.
- Renner, J., Evans, B., Siddiqi, G., 2002. Dislocation creep of calcite. *Journal of Geophysical Research* 107, 1–16.
- Rutter, E.H., 1972. Influence of interstitial water on rheological behavior of calcite rocks. *Tectonophysics* 14, 13–33.
- Rutter, E.H., 1974. Influence of temperature, strain rate and interstitial water in experimental deformation of calcite rocks. *Tectonophysics* 22, 311–334.
- Rutter, E.H., 1995. Experimental study of the influence of stress, temperature, and strain on the dynamic recrystallization of Carrara Marble. *Journal of Geophysical Research* 100, 24,651–24,663.
- Rybacki, E., Renner, J., Konrad, K., Harbott, W., Rummel, F., Stockhert, B., 1998. A servohydraulically-controlled deformation apparatus for rock deformation under conditions of ultra-high pressure metamorphism. *Pure and Applied Geophysics* 152, 579–606.
- Schmid, S.M., Boland, J.N., Paterson, M.S., 1977. Superplastic flow in finegrained limestone. *Tectonophysics* 43, 257–291.
- Schmid, S.M., Paterson, M.S., Boland, J.N., 1980. High temperature flow and dynamic recrystallization in Carrara Marble. *Tectonophysics* 65, 245–280.
- Stewart, E.D., Holyoke III, C.W., Kronenberg, A.K., 2013. High pressure deformation experiments using solid confining media and Griggs piston-cylinder methods: appraisal of stress and deformation in talc assemblies. *Tectonophysics*. <http://dx.doi.org/10.1016/j.tecto.2012.12.004>.
- Stipp, M., Tullis, J., Scherwath, M., Behrmann, J.H., 2010. A new perspective on paleopiezometry: dynamically recrystallized grain size distributions indicate mechanism changes. *Geology* 38, 759–762.
- Tingle, T.N., Green, H.W., Young, T.E., Kocynski, T.A., 1993. Improvements to Griggs-type apparatus for mechanical testing at high-pressures and temperatures. *Pure and Applied Geophysics* 141, 523–543.
- Tullis, J., Yund, R.A., 1987. Transition from cataclastic flow to dislocation creep of feldspar; mechanisms and microstructures. *Geology* 15, 606–609.
- Turner, F.J., Griggs, D.T., Clark, R.H., Dixon, R.H., 1956. Deformation of Yule marble. Part VII. Development of oriented fabrics at 300°C – 500°C . *Geological Society of America Bulletin* 67, 1259–1294.
- Walker, A.N., Rutter, E.H., Brodie, K.H., 1990. *Experimental Study of Grain-size Sensitive Flow of Synthetic, Hot-pressed Calcite Rocks, Deformation Mechanisms, Rheology and Tectonics*. Geological Society of London, London, United Kingdom, pp. 259–284.
- Wells, R.K., Holyoke III, C.W., Wojtal, S.F., Newman, J., 2011. Low temperature rheology of calcite and dolomite: experiment and nature. Abstract MR11B-2174 Presented at 2011 Fall Meeting, AGU, San Francisco, Calif., 5–9 Dec.
- Woodward, N.B., Wojtal, S., Paul, J.B., Zadins, Z.Z., 1988. Partitioning of deformation within several external thrust zones of the Appalachian Orogen. *Journal of Geology* 96, 351–361.
- Wyllie, P.J., Huang, W.L., 1976. Carbonation and melting reactions in system $\text{CaO-MgO-SiO}_2\text{-CO}_2$ at mantle pressures with geophysical and petrological applications. *Contributions to Mineralogy and Petrology* 54, 79–107.