THE EFFECTS OF GRAIN SIZE ON THE STRENGTH OF MAGNESITE AGGREGATES DEFORMING BY LOW TEMPERATURE PLASTICITY AND DIFFUSION CREEP

A Thesis
Presented to
The Graduate Faculty of The University of Akron

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

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May, 2018
THE EFFECTS OF GRAIN SIZE ON THE STRENGTH OF MAGNESITE AGGREGATES DEFORMING BY LOW TEMPERATURE PLASTICITY AND DIFFUSION CREEP

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Thesis

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Magnesite is a common mineral found in altered peridotites and is much weaker than olivine, which may cause strain localization and deep focus earthquakes (Holyoke et al., 2014). Holyoke et al., (2014) determined the temperature and strain rate dependence of the strength of magnesite deforming by low temperature plasticity and diffusion creep mechanisms, but did not determine the grain size dependence of the strength of magnesite deforming by these mechanisms. In order to determine whether the strength of magnesite depends on grain size \(d\), we performed experiments on magnesite aggregates with \(d = 3, 6, 16 \text{ and } 80 \mu m\) for constant values of strain rate \(\dot{\varepsilon} = 10^{-5}/s\) at temperature \(T = 500 - 700 ^{\circ}C\), and pressures \(P\) of 0.2, 0.9, 2.4, 5.0 and 8.0 GPa, in the Griggs Apparatus and Deformation-DIA (D-DIA). At low temperatures microstructures were consistent with low temperature plasticity, which include extensive mechanical twinning. Strength of magnesite aggregates deformed at \(T = 500 ^{\circ}C\) and \(P = 0.9 \text{ GPa}\), \(\sigma\) decreases from 2.40 to 1.60 GPa as \(d\) increases from 3 to 80 \(\mu m\). At \(P = 2.4 \text{ GPa}\), \(\sigma\) decreases from 1.72 to 1.60 GPa as \(d\) increases over the same range. At \(P = 5.0 \text{ GPa}\), \(\sigma\) decreases from 2.73 to 2.69 GPa as \(d\) increases from 3 to 16 \(\mu m\). At \(P = 8.0 \text{ GPa}\), strengths are the same at all grain sizes. As pressure increases the grain size dependence of \(\sigma\) decreases. The grain size sensitivity exponent \(m_{\text{LTP}}\) decreases from \(m_{\text{LTP}} = 0.25\) (at \(P = 0.9 \text{ GPa}\)) to \(m_{\text{LTP}} = 0.08\) (\(P = 2.4 \text{ GPa}\)) to \(m_{\text{LTP}} = 0.008\) (\(P = 5.0 \text{ GPa}\)) and \(m_{\text{LTP}} = 0\) (\(P = 8.0 \text{ GPa}\)). These results demonstrate that the grain size sensitivity of low temperature plasticity deformation of magnesite is a function of pressure, and by inference, which may also be the case for low temperature plasticity of calcite. These results indicate that along much of the P-T path of
subducting slabs, grain size will not significantly affect magnesite aggregate strength if deforming by low temperature plasticity.

At higher temperatures ($T = 700 ^\circ C$) and low pressures ($P = 300$ MPa) the microstructures present are rounded grains and pore spaces around the grain boundaries which is consistent with diffusion creep deformation mechanism. When magnesite is deforming by diffusion creep the grain size sensitivity $m_d$ is $1.0 \pm .44$. The evolution of microstructures has a significant effect on the strength of the magnesite. Increased time at high temperatures causes an evolution from angular to rounded grains which caused the strength to decrease.

When extrapolated to natural conditions, the dominant deformation mechanism occurring in the subducting slab is diffusion creep. Furthermore, the viscosity of magnesite increases as the grain size increases, which could potentially cause strain localization in fine-grained zones of magnesite leading to the formation of deep focus earthquakes.
ACKNOWLEDGEMENTS

I would first like to thank my advisor, Dr. Caleb Holyoke for his time, patience, suggestions, and support throughout my graduate years at The University of Akron. Secondly, I would like to thank the National Science foundation for the grant that funded this study. I would also like to thank my committee members, Dr. LaVerne Friberg, and Dr. John Senko, for their feedback, and time invested throughout this process. Thank you to the collaborators on this grant, Dr. Kronenberg and Dr. Ratteron, for the research/writing suggestions.

A special thanks to Tom Quick for all of his help with the SEM, as well as his expertise on all of the lab equipment needed during this study. Also, thank you to Elaine Butcher for helping with the formatting of this thesis, as well as all of the other paperwork she has done for me throughout my years at The University of Akron.

My special thanks to my family and girlfriend, Audrey. Their support has helped me stay motivated, and determined throughout these hectic two years. Lastly, I would like to thank all of the graduate students, who made the journey of graduate school more memorable. A special thanks to Joe Millard, for his enriching conversations and support throughout countless hours in the lab.
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CHAPTER I
INTRODUCTION

Deep focus earthquakes occur at approximately 70 - 650 km in depth in the upper mantle of the earth (Frohlich, 1989), and most frequently occur in association with deep ocean trenches and volcanic arcs adjacent to subduction zones. Between 70-200 km earthquakes are common in several geographic regions, and likely caused by serpentine dehydration. The occurrence of deep focus earthquakes decreases exponentially at depths of 400 km, but beneath 400 km two thirds of the world’s earthquakes occur in the Tonga-Kermadec region (Frohlich, 1989). There are commonly fewer earthquakes between the depths of 300-450 kilometers within the earth, which is likely due to the olivine-spinel phase transition (Frohlich, 1989). However, earthquakes formed between 200-400 km within the earth are poorly understood. One possibility for these earthquakes is strain localization in carbonates formed by the alteration of peridotites.

Magnesite is a common alteration mineral formed from a reaction between CO\textsubscript{2} rich fluids and olivine/orthopyroxene in oceanic crust. Magnesium-rich carbonates have been observed in ultra-deep metamorphic collisional terrains and in mantle xenoliths (Dobrzhinetskaya et al., 2006; Sato and Katsura, 2001). Due to the stability of magnesite at high temperatures and pressures experienced in the subducting slab, once it is incorporated into the lithospheric mantle, it is likely to stay there as a carbon-bearing phase (Brenker et al., 2007).

Holyoke, et al. (2014) determined that at lithospheric mantle temperatures and pressures, magnesite is much weaker than olivine and pyroxenes. This strength contrast
could cause strain localization causing the formation of deep focus earthquakes (Holyoke et al., 2014). They predicted that magnesite would deform by low temperature plasticity (LTP) mechanisms (kinking and/or dislocation glide) or diffusion creep along the pressure \((P)\)/temperature \((T)\) path of a subducting slab. However, they did not determine the grain size dependence of the strength of magnesite deforming by these mechanisms, but assumed that the grain size sensitivities would be similar to calcite, which has almost identical stress exponents and activation enthalpies to magnesite for the same deformation mechanisms. This experimental study was performed to determine if the strength of magnesite is dependent on grain size when deforming by low temperature plasticity or diffusion creep.

1.1 Magnesite deformation mechanisms

Fine-grained magnesite aggregates deform by dislocation glide and kinking at low temperatures \((T = 500 ^\circ C)\) at laboratory strain rates. These mechanisms are usually grouped and called low temperature plasticity. At temperatures lower than \(T = 650 ^\circ C\) and laboratory strain rates, fine-grained magnesite deforms by dislocation creep. At high temperatures \((T > 650 ^\circ C)\) and laboratory strain rates, magnesite aggregates deform by diffusion creep, but this mechanism only occurs in aggregates with very small grain sizes \((d < 8 \mu m)\), in laboratory controlled experiments (Holyoke et al., 2014). Diffusion creep produces rounded grains, pore spaces around the grains, as well as in the grains, and recrystallized grains along the grain boundaries.

Coarse-grained magnesite aggregates deform by low temperature plasticity at temperatures \(T < 600 ^\circ C\), at laboratory strain rates (Holyoke et al., 2014). Microstructures include kinking and extensive mechanical twinning (Holyoke et al., 2014). At high
temperatures \((T > 600 \, ^\circ C)\) and laboratory strain rates, the dominant deformation mechanism for coarse-grained magnesite is dislocation creep, a grain size sensitive deformation mechanism.
CHAPTER II
METHODS

2.1 Starting material

In order to determine the grain-size sensitivity of the strength of magnesite, experiments were performed over a range of temperatures \((T = 500 – 700 \, ^oC)\), pressures \((P = 300 – 8000 \, MPa)\) and three grain sizes \((d = 3, 16, \text{ and } 80 \, \mu m)\). The fine-grained magnesite cylinders were \(d = 3 \pm 1.3 \, \mu m\), which was measured from a grain size analysis (Fig 1a). The grains are angular with low porosity (1%), measured by the Archimedes method in water. The medium-grained magnesite, \(d = 16 \pm 0.9 \, \mu m\), was hydrostatically grown using cores of \(d = 3 \, \mu m\) magnesite, in the Griggs apparatus \((T = 850 \, ^oC \text{ and } P = 850 \, MPa)\) and is free of mechanical twinning and has high porosity (Fig. 1b). For the low temperature experiments, a coarse-grained magnesite, \(d = 80 \pm 2.6 \, \mu m\) was also used, and the grains are free of any mechanical twinning. The porosity of the coarse-grained magnesite aggregate is very low (<1%), measured by the Archimedes method in water (Fig. 1c). Hydrostatic experiments were also performed on magnesite cylinders with \(d = 3 \, \mu m\) to determine the rate of grain growth at 850 \(^oC\) for high temperature experiments. Grains were left to hydrostatically anneal for periods of \(t = 3,600, 21,600, \text{ and } 86,400 \, \text{seconds at } T = 850 \, ^oC \text{ and } P = 850 \, MPa.\)

Experiments to determine grain size dependence on magnesite deformation mechanisms were performed using the Deformation Dia (D-DIA), a cubic multi-anvil apparatus, or a Griggs-type piston deformation apparatus. Cylinders 1 mm in length
Figure 1. Polished SEM sections of starting materials for all experiments performed in this study. (a) fine-grained ($d = 3 \pm 1.3 \mu m$) natural Nevada, USA magnesite aggregate. (b) intermediate-grained ($d = 16 \pm 0.9 \mu m$) that was hydrostatically grown from the fine-grained Nevada magnesite aggregate. (c) coarse-grained ($d = 80 \pm 2.6 \mu m$) natural Nevada, USA magnesite aggregate.
and 1 mm in diameter were cored in preparation for the D-DIA apparatus and cylinders 10mm*5mm were cored for samples for the Griggs apparatus. The faces of all magnesite cylinders were ground perpendicular to the length of each cylinder. The samples were then bathed in water in an ultrasonic cleanser to remove any grit and dried in an oven for at least 24 hours at $T = 100 ^\circ C$ prior to putting into an assembly.

2.2 D-DIA Deformation Apparatus Experiments

A Durham-type assembly was used in all D-DIA experiments (Fig. 2). This assembly allows for stacked magnesite samples with different grain sizes to be deformed under identical temperatures and pressures. The cylinders of magnesite aggregates were placed in a nickel or platinum capsule. Hollow cylinders of BN/graphite were inserted inside of a mullite sphere with a soft fired pyrophyllite cradle. Two crushable alumina pistons were placed on both ends of the sample. Samples were separated from each other and the alumina pistons by three Pt/Rh disks placed at the ends of each cylinder (Fig. 2).

The D-DIA apparatus consists of upper and lower guide blocks, four wedge shaped thrust blocks, and six anvils (Wang et al., 2003). In the D-DIA control of the displacement of one anvil pair is provided by differential rams. The differential rams react against the platens driven by the main hydraulic ram, which creates hydrostatic pressurization of the experiment (Wang et al., 2003). During deformation, the top, bottom, and main rams are driven at a specific speed, so the strain rate and pressures remain constant (Durham et al., 2002; Wang et al., 2003). The velocities ($V$) of the two differential rams are controllable up to $V = 10^{-7}$ to $10^{-2}$ mm/s, and strain rates are typically $10^{-3}$ to $5 \times 10^{-6}$ s$^{-1}$ on a 1 * 1 mm cylindrical sample. The D-DIA has a maximum load of approximately 100 tons, and is capable of reaching temperatures of $T = 2000 ^\circ C$ and pressures of up to $P = 15$ GPa, which is comparable to about 450 kilometers within the Earth. Synchrotron
Figure 2. Schematic diagram of the Durham assembly used in the D-DIA deformation apparatus (after Durham et al., 2002).
x-rays were used to measure the length of the sample. Synchrotron radiation also allows for measurements of displacement (Wang et al., 2003). Images from alumina spectrum, which have differing absorption characteristics, were used to measure the strain and stress of each sample (Wang et al., 2003).

X-radiographs were collected at the D-DIA apparatus at conditions of \( T = 500 \, ^\circ C \). In both images, magnesite aggregate cylinders \( d = 3 \, \mu m \) and \( d = 80 \, \mu m \) were stacked. At lower pressures (\( P = 2.4 \, GPa \)) magnesite cylinders \( d = 80 \, \mu m \) deformed by 42\%, while the magnesite with grain size of \( d = 3 \, \mu m \) deformed by 27\%, under identical conditions (Fig. 3a). At much higher pressures, \( P = 8.0 \, GPa \) both of the grain size strained the exact same amount (20\%) in relation to time (Fig. 3b).

Experiments using the D-DIA were performed at \( T = 500 \, ^\circ C \), pressures ranging from \( P = 2.4 \, 8.0 \, GPa \) and \( \dot{\varepsilon} = 1.6 \times 10^{-5} / s \). In experiments performed on fine/coarse-grained magnesite, and fine/medium-grain stacked experiments the starting materials were first pressurized, over the period of \( \sim 5 \) hours, to \( P = 7.4 \, GPa \) and then the temperature was increased to \( T = 500 \, ^\circ C \). In a pressure stepping experiment, the pressure was increased to \( P = 7.4, 5.0, \) and then 2.4 GPa. The cylinders were deformed until constant differences in both cylinders strain rates were observed. The cylinders were then quenched, and depressurized to room conditions. After the samples were removed from the D-DIA apparatus, the samples were submerged in A/B thin section epoxy and sectioned parallel to the maximum compression stress direction. The sample halves were then polished using a series of silicon grit sizes (16 \( \mu m \), 8 \( \mu m \) and 3 \( \mu m \)) on glass plates, sonicated, and dried at room conditions for SEM analyses.
Figure 3. (a) Starting magnesite cylinders with $d = 3$ and 80 µm (left). At $P = 2.4$ GPa the magnesite cylinder with $d = 80$ µm deforms by 42% while the magnesite cylinder with $d = 3$ µm deforms by 27% (right). (b) Starting magnesite cylinders with $d = 3$ and 80 µm (left). Both of the magnesite cylinders deformed by the same strain (right). (Mag_007 and Mag_017, $T = 500$ °C, $P = 2.4$ and 8.0 GPa, $V = 0.003$ mm/s).
2.3 Griggs apparatus experiments

2.3.1 Solid salt assembly

Solid salt assemblies (SSA) were used in the Griggs apparatus. Experiments were performed at $T = 500 - 700 \, ^\circ C$, $P = 300 - 900 \, MPa$, and $\dot{\varepsilon} = 1.6 \times 10^{-5} \, s^{-1}$ (Fig. 4). In order to make magnesite aggregates of $d = 3$, 6, and 16 µm, respectively, fine-grained magnesite ($d = 3 \pm 1.3 \, \mu m$) cylinders were held hydrostatically at $T = 850 \, ^\circ C$ and $P = 850 \, MPa$ for periods of $t = 3,600, 21,600, and 86,400$ seconds, respectively prior to changing the P/T to the desired conditions for deformation. The Griggs deformation apparatus applies a force to the sample with constant displacement rates of $0.66 \, cm/hr$ to $6.6 \times 10^{-5} \, cm/hr$ which results in $\dot{\varepsilon} = 1.6 \times 10^{-4}$ to $1.6 \times 10^{-9} \, s^{-1}$. (Holyoke et al., 2014). The Griggs apparatus is capable of reaching pressures up to $P = 2.0 \, GPa$.

Magnesite cylinders for Griggs experiments are 10.16 mm in length and 5.08 mm in diameter and then the faces were ground perpendicular to maximum compression stress using silicon carbide grit ($d = 16 \, \mu m$) cleaned in an ultrasonic cleansing fluid and left to dry in an oven at $T = 100 \, ^\circ C$ for at least 24 hours. The sample is surrounded by a series of hollow cylinders of NaCl, soft fired pyrophyllite, and graphite and the sample is wrapped in either a Pt or Ag can (Holyoke et al., 2014). The temperature was measured near the samples with a Pt/Pt 10% Rh in mullite tubing. The cylinder was inserted into an Ag can, which has Ag disks inserted on either side of the sample, and then crimped. Crimping forms a mechanical weld during pressurization of the assembly, upon removal from the assembly after the experiment the Ag can was bowed out, which means that the mechanical welding prevented loss of CO$_2$ from the jacket (Holyoke et al., 2014).

Magnesite cylindrical samples were brought to hydrostatic conditions ($T = 850 \, ^\circ C$ and $P = 850 \, MPa$), and left to anneal until desired intermediate grain size was observed. The magnesite cylinder was deformed at ($T = 500 - 800 \, ^\circ C$, $P = 0.30 - 0.9 \, GPa$) after the
Figure 4. Schematic diagrams of assemblies used in Griggs deformation apparatus. Left, is the (SSA or solid salt assembly). Right, is the (MSC or molten salt cell assembly) that uses a eutectic salt mixture of KCl/LiCl that is placed around the magnesite cylinder.
hydrostatic experiments. After deformation, the samples were quenched over a period of an hour, and then cut along a plane parallel to maximum compressive stress. Sample halves were then prepared for SEM analyses using a series of different silicon carbide grit sizes with \( d = 16 \, \mu m, 8 \, \mu m \) and \( 3 \, \mu m \), ultrasonically bathed in water, and then polished with silicon carbide grit with \( d = 0.3 \, \mu m \).

2.3.2 Molten salt cell assembly

For experiments that needed higher mechanical data resolution a molten salt cell assembly (MSC) was used (Fig. 4). In this study, the MSC assembly was used for temperatures ranging from \( T = 700 - 800 \, ^\circ C \) and a constant pressure of \( P = 300 \, MPa \). Hydrostatic grain growth experiments were performed prior to deformation at \( T = 800 \, ^\circ C \) for annealing periods of \( t = 3,600 \) seconds and then deformed an anneal period of \( 21,600 \) seconds and deformed, and then annealed for \( 86,400 \) seconds and then deformed. Single step deformation experiments were also performed on cylinders of magnesite using the MSC at \( T = 700 \, ^\circ C \) and \( P = 300 \, MPa \). The MSC assembly uses a KCl/LiCl eutectic mixture that becomes molten at experimental conditions (Holyoke and Kronenberg, 2010).

The sample was wrapped in an Ag wrap and then inserted into a platinum can with two platinum cups on each side of the can. These cups were welded to the can using a jeweler’s microscopic welder. Welding the cups to the can prevents the molten salt mixture from coming in contact with the sample. The sample was then placed into a MSC assembly, which uses hollow cylinders of NaCl, soft fired pyrophyllite, a KCl/LiCl salt mixture, and a resistant graphite furnace to heat the sample. The MSC uses a mullite thermocouple with Pt/Pt-Rh 10% wires (thermocouple type S) to measure temperature throughout the experiment. The assembly was placed into a pressure vessel and brought
up to the desired temperature and pressure. Calibration for the differential stress measurements for the MSC is:

$$\sigma_{\text{actual}} = 0.73 \times \sigma_{\text{measured}} - 50 \text{ MPa}$$

After the sample was deformed to the desired strain, the sample was brought to room temperature over the period of $t \sim 60$ minutes and cut parallel to maximum compression stress. The sample was then ground and sample halves for SEM analysis were prepared.

2.4 Grain size analysis

Images obtained from the SEM were used to trace grains in order to perform grain size analyses for every experiment. Approximately 200 grains were traced in Adobe Photoshop software. The sample is first traced with the background disabled from view. Next, the image is analyzed using Image SXM. In Image SXM the scale is set by converting pixels into micrometers. Next, the image is inverted, and then the particle analysis can be completed. Image SXM records: selected area, x-y center, perimeter length, angle, major axis, mean density, standard deviation, modal density, and integrated density (Barbery, 2017). With the measurements of the average axes length, the average grain size (diameters) of each magnesite sample was calculated.

2.5 Thin section preparation for SEM.

Scanning electron microscope (SEM) analyses were performed to observe microstructures, and grain sizes of the deformed magnesite aggregate cylinders. For the SEM, the deformed cylinders of magnesite were cut parallel to the maximum compressional direction and then ground on glass plates using a series of decreasing
silicon carbide grit sizes with (16 µm, 8 µm, and 3 µm). The samples were sonicated after every grit size to ensure a homogeneous grind on each sample. The samples were then polished using $d = 0.3$ µm silicon carbide grit on a polishing wheel and sonicated to remove any excess grit, and left to dry for a period of at least 24 hours prior to being carbon coated and analyzed in the SEM.
CHAPTER III
RESULTS

3.0 Results

Experiments were performed on magnesite aggregate cylinders over a range of temperatures \( T = 500 - 800 \, ^\circ C \), pressures \( P = 0.3 - 8.0 \, \text{GPa} \) with a constant strain rate of \( \dot{\varepsilon} = 1.6 \times 10^{-5} \, \text{s}^{-1} \) and grain sizes \( d = 3 \pm 1.2 - 80 \pm 2.4 \, \mu m \), to determine if grain size sensitivity plays a role on the strength of magnesite (Tables 1 and 2). Six different types of experiments were performed; 1) hydrostatic grain growth experiments in the Griggs apparatus, 2) single deformation step experiments on stacked cylinders in the D-DIA, 3) a pressure stepping experiment on stacked cylinders in the D-DIA, 4) single step experiments at high pressures in the Griggs apparatus, 5) single step experiments at low pressures in the Griggs apparatus, and 6) grain size stepping experiments in the Griggs apparatus. The results of these experiments are discussed in the following sections.

3.1 Hydrostatic grain growth experiments

The magnesite samples were held hydrostatically in the Griggs apparatus at \( T=850^\circ C \) and \( P = 850 \, \text{MPa} \) for annealing periods \( t \) of \( t = 3,600, 21,600, \) and \( 86,400 \) seconds in order to determine the relationship of grain growth. This growth rate was used to increase the grain size by a desired amount in subsequence experiments prior to deformation (Fig. 5). The grain size of magnesite at \( t = 3,600 \) seconds was similar to the starting material.
Table 1. List of all experiments for magnesite performed at $T = 500 \, ^\circ C$.

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<th>Confining pressure (GPa)</th>
<th>Grain size (µm)</th>
<th>Differential stress (MPa)</th>
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<td>-</td>
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<td>15.5</td>
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<tr>
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<td>D-DIA</td>
<td>Nevada Magnesite</td>
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<tr>
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<td>1900</td>
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<tr>
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<td>3</td>
<td>1900</td>
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<td>Nevada Magnesite</td>
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<td>0.9</td>
<td>3</td>
<td>2400</td>
<td>1.6 * 10^{-5}</td>
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<tr>
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<td>Griggs</td>
<td>Nevada Magnesite</td>
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<td>16</td>
<td>1600</td>
<td>1.6 * 10^{-5}</td>
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Table 2. List of all experiments for magnesite deformed at $T \geq 700 \, ^\circ C$.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Assembly</th>
<th>Anneal time (hours)</th>
<th>Material</th>
<th>Temperature (°C)</th>
<th>Confining pressure (GPa)</th>
<th>Grain size (µm)</th>
<th>Differential stress (MPa)</th>
<th>Strain rate ($s^{-1}$)</th>
<th>Strain (%)</th>
</tr>
</thead>
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<tr>
<td>Z-86</td>
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<td>Nevada</td>
<td>700</td>
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<td></td>
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<td></td>
<td>700</td>
<td>0.30</td>
<td>6.6</td>
<td>177</td>
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</tr>
<tr>
<td>Z-97</td>
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<td>-</td>
<td>Nevada</td>
<td>800</td>
<td>0.30</td>
<td>3.1</td>
<td>151</td>
<td>$1.6 \times 10^{-5}$</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>Magnesite</td>
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<td>5.4</td>
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<td></td>
<td></td>
<td>24</td>
<td></td>
<td>800</td>
<td>0.30</td>
<td>7.5</td>
<td>180</td>
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<td>6.4</td>
<td>255</td>
<td>$1.6 \times 10^{-5}$</td>
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<tr>
<td>Z-107</td>
<td>SSA</td>
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<td>Nevada</td>
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<td>3.2</td>
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<td></td>
<td></td>
<td></td>
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</tbody>
</table>
At $t = 21,600$ seconds the grain size was $d \sim 6 \pm 1.6 \mu m$, and at $t = 86,400$ seconds the grain size was $d \sim 16 \pm 0.9 \mu m$ (Fig 1, Tables 1 and 2).

3.2 Low temperature D-DIA single step experiments

Four single deformation-step experiments were performed on stacked magnesite cylinders using the D-DIA at Argonne National Laboratory in Chicago, IL. All experiments were deformed at $T = 500^\circ C$ at a pump displacement rate of $V = .003$ mm/s which corresponds to $\dot{\varepsilon} \sim 10^{-5}$ s$^{-1}$. Two low pressure ($P = 2.4$ GPa) experiments (Mag_005 and Mag_015), one intermediate pressure ($P = 5.0$ GPa) experiment (Mag_011), and one high pressure ($P = 8.0$ GPa) experiment (Mag_017) were performed (Table 1).

Mag_005 was a low pressure experiment. A cylinder of $d = 3 \mu m$ magnesite was deformed at $T = 500^\circ C$, $P = 2.4$ GPa and $\dot{\varepsilon} \sim 10^{-5}$ s$^{-1}$. The magnesite had a differential stress of 1.8 GPa and was strained by 29% its original length (Table 1, Fig. 6).

The second low pressure experiment was Mag_015. Experiment Mag_015 was a stacked experiment with magnesite cylinders of $d = 3 \mu m$ and $d = 16 \mu m$. Mag_015 was deformed at $T = 500^\circ C$, $P = 2.4$ GPa and $\dot{\varepsilon} \sim 10^{-5}$ s$^{-1}$. The magnesite cylinder had a differential stress of 2.0 GPa. The magnesite cylinder with $d = 3 \mu m$ only strained by 24% and the magnesite cylinder with $d = 16 \mu m$ strained by 33%. (Table 1, Fig. 7).

Microstructures in samples deformed at low pressures ($P = 2.4$ GPa) include mechanical twins. In all experiments grains became more elongate relative to maximum compression stress direction (Fig. 8a).

One intermediate pressure ($P = 5.0$ GPa) experiment (Mag_011) was stacked magnesite cylinders of $d = 3 \mu m$ and $d = 16 \mu m$. The magnesite cylinders deformed at $T = 500^\circ C$ and $\dot{\varepsilon} \sim 10^{-5}$ s$^{-1}$. The experiment had a stress of 2.7 GPa. The magnesite cylinder
Figure 5. Magnesite grain average diameter (µm) as a function of time (seconds) at hydrostatic conditions of $T = 850 \, ^\circ\!C$ and $P = 850 \, \text{MPa}$.
Figure 6. Experiment strain rate of fine grained magnesite cylinders of \( d = 3 \, \mu m \) is \( \dot{\varepsilon} = 3.9 \times 10^{-4}/s \). The peak differential stress is \( \sigma = 1.8 \) GPa. (Mag_005, \( T = 500 \, ^\circ C \), \( P = 2.4 \) GPa, \( V = 0.003 \) mm/s).
Figure 7. Strain rates of fine and medium grained magnesite cylinders differ at $P = 2.4$ the medium grained magnesite cylinder starts to deform at a faster strain rate ($\dot{\varepsilon} = 1.80 \times 10^{-5}$/s) than the fine grained magnesite cylinder ($\dot{\varepsilon} = 1.40 \times 10^{-5}$/s). The peak differential stress was 2.0 GPa. (Mag_015, $T = 500 \, ^\circ$C, $P = 2.4$ GPa, $V = 0.003$ mm/s).

Figure 7. Experiment (Mag_015) was performed on cylinders of natural magnesite with $d = 3 \, \mu$m and $d = 16 \, \mu$m at $T = 500 \, ^\circ$C and $P = 2.4$ GPa using the D-DIA. The cylinders are stacked, so strain can be observed under identical conditions. Magnesite with grain size $d = 16 \, \mu$m deformed by 33% while the $d = 3 \, \mu$m cylinder of magnesite deformed by only 24%. The cylinder had a differential stress of 2.0 GPa. (Mag_015, $T = 500 \, ^\circ$C, $P = 2.4$ GPa, $V = 0.003$ mm/s).
with \( d = 3 \, \mu m \) deformed by 23% while the magnesite cylinder with \( d = 16 \, \mu m \) magnesite deformed by 29% of its original length (Table 1, Fig. 9).

Microstructures in samples deformed at intermediate pressures are similar to those observed in Mag_015, which include mechanical twins. In all experiments grains became more elongate relative to maximum compression stress direction. (Fig. 8b).

A final single-step experiment (Mag_017) was performed at high pressure (\( P = 8.0 \, \text{GPa} \)) at \( T = 500 \, ^\circ\text{C} \), and \( \dot{\varepsilon} = 10^{-5}\,\text{s}^{-1} \). Experiment Mag_017 was a stacked magnesite cylinder of \( d = 3 \, \mu m \) and \( d = 80 \, \mu m \). Mag_017 had a stress of 2.4 GPa (Table 1, Fig. 10). The cylinder with \( d = 3 \, \mu m \) strained by 20% and so did the cylinder of magnesite with \( d = 80 \, \mu m \) (Table 1, Fig. 10).

Microstructures in samples deformed at \( P = 8.0 \, \text{GPa} \) include mechanical twins. The magnesite grains also became more elongate perpendicular to maximum compression stress direction (Fig. 8b).

### 3.3 Low temperature D-DIA pressure stepping experiment

A pressure-stepping experiment was performed using the Durham assembly in the D-DIA on Mag_007 at \( T = 500 \, ^\circ\text{C} \), pressures of \( P = 7.4, 5.0, \) and 2.4 GPa at a displacement rate of \( V = .003 \, \text{mm/s} \) on stacked magnesite cylinders \( d = 3 \, \mu m \) and \( d = 80 \, \mu m \) (Table 1). The experiment was first brought to \( P = 7.4 \, \text{GPa} \) and the sample was deformed. The pressure was lowered to 5.0 GPa and then deformed, and then 2.4 GPa and deformed a final time. Since this experiment was a stepping experiment, the microstructures only reflect the final step deformed at \( P = 2.4 \, \text{GPa} \). At \( P = 2.4 \, \text{GPa} \) the differential stress was 1.7 GPa. The magnesite cylinder with \( d = 3 \, \mu m \) strained by 28% while the magnesite cylinder \( d = 80 \, \mu m \) strained by 42% of its original length (Figs. 3 and 11).
Figure 8. (a) Experiment Mag_005, magnesite cylinder of $d = 3 \, \mu$m deformed at $T = 500 \, ^\circ\text{C}$ and $P = 2.4 \, \text{GPa}$, the grains became more elongate relative to compression (arrow). (b) Magnesite (Mag_011) cylinder of $d = 16 \, \mu$m deformed at $T = 500 \, ^\circ\text{C}$ and $P = 5.0 \, \text{GPa}$, mechanical twinning (arrow) is present in many of the grains, as well as the grains becoming more elongate (c) Magnesite (Mag_017) cylinder of $d = 80 \, \mu$m deformed at $T = 500 \, ^\circ\text{C}$ and $P = 8.0 \, \text{GPa}$. Extensive mechanical twinning (arrow) is present.
Figure 9. Strain rates of fine and medium grained magnesite cylinders differ at $P = 5.0$ the medium grained magnesite cylinder starts to deform at a faster strain rate ($\dot{\varepsilon} = 2.1 \times 10^{-5}/s$) than the fine grained magnesite cylinder ($\dot{\varepsilon} = 1.6 \times 10^{-4}/s$). The peak differential stress was 2.7 GPa. (Mag_011, $T = 500 \, ^\circ C$, $P = 5.0 \, GPa$, $V = 0.003 \, mm/s$).
Figure 10. Strain rates of fine and coarse grained magnesite cylinders at $P = 8.0$ GPa the fine and coarse grained magnesite deform at the same strain rate ($\dot{\varepsilon} = 1.6 \times 10^{-5}$). The peak differential stress was 2.4 GPa. (Mag_017, $T = 500$ °C, $P = 8.0$ GPa, $V = 0.003$ mm/s).
Microstructures at the SEM scale Nevada magnesite deformed at \( T = 500 \, ^\circ\text{C} \) and \( P = 2.4\text{-}7.4 \, \text{GPa} \) include significantly flattened grains relative to the starting material. The grains in the magnesite cylinder with \( d = 3 \, \mu\text{m} \) sample are not significantly flattened.

3.4 Single deformation step experiments at high pressure

Two single-step, low-temperature experiments (Z-74 and Z-77) were performed on Nevada magnesite cylinders (\( d = 3 \, \mu\text{m} \) and \( d = 16 \, \mu\text{m} \)) using the solid salt assembly in the Griggs apparatus. Experiment Z-74 was performed on magnesite with a grain size of \( d = 3 \pm 1.3 \, \mu\text{m} \) at \( T = 500 \, ^\circ\text{C} \), \( P = 0.9 \, \text{GPa} \) and \( \dot{\varepsilon} = 1.6 \times 10^{-5} \, \text{s}^{-1} \). Z-74 had a differential stress of 2.4 GPa, and was strained to \( \sim 14\% \) of its original length (Fig. 12).

Microstructures observed at the SEM scale include flattened grains and minor mechanical twinning (Fig. 13a).

Another experiment (Z-77) was performed on magnesite cylinders with (\( d = 16 \, \mu\text{m} \)). Experiment Z-77 was annealed for \( t = 86,400 \) seconds at \( T = 850 \, ^\circ\text{C} \). The sample was deformed at \( T = 500 \, ^\circ\text{C} \), \( P = 0.9 \, \text{GPa} \), and \( \dot{\varepsilon} = 10^{-5} \, \text{s}^{-1} \). Experiment Z-77 had a final differential stress of 1.6 GPa and strained by \( \sim 10\% \) its original length (Fig. 12).

Microstructures observed in SEM images of Nevada magnesite with \( d = 16 \, \mu\text{m} \) deformed at low temperature include flattened grains relative to the starting material. Extensive mechanical twinning was also observed in the magnesite cylinder with \( d = 16 \, \mu\text{m} \) sample. No evidence of grain boundary migration or dynamic recrystallization was observed in either of the samples from these experiments (Fig. 13b).
Figure 11. Strain rates of fine and coarse grained magnesite cylinders are nearly identical at $P = 7.4$ GPa. However, at $P = 5.0$ GPa the coarse grained magnesite cylinder starts to deform at a faster strain rate ($\dot{\varepsilon} = 5.8 \times 10^{-4}$/s) than the fine grained magnesite cylinder ($\dot{\varepsilon} = 2.0 \times 10^{-4}$/s) and at $P = 2.4$ GPa the difference in strain rates in the fine grained is coarse grained magnesite is ($\dot{\varepsilon} = 3.8 \times 10^{-4}$/s). (Mag_007, $T = 500^\circ$C, $P = 2.4-7.4$ GPa, $V = 0.003$ mm/s).
Figure 12. Stresses of fine and medium grained magnesite cylinders at $P = 0.9$ GPa decreases from $\sigma = 2.4$ GPa with magnesite of $d = 3$ µm to $\sigma = 1.6$ GPa with magnesite of $d = 16$ µm. (Z-74 and Z-77, $T = 500$ °C, $P = 0.9$ GPa, $\dot{\varepsilon} = 10^{-5}$ s$^{-1}$).
Figure 13. (a) Experiment Z-74, magnesite cylinder of $d = 3 \, \mu m$ deformed at $T = 500 \, ^oC$ and $P = 0.9 \, GPa$, the grains became more elongate relative to compression. (b) Experiment Z-77, magnesite cylinder of $d = 16 \, \mu m$ deformed at $T = 500 \, ^oC$ and $P = 0.9 \, GPa$, mechanical twinning is present in many of the grains.
3.5 High temperature single step experiments at low pressure

Two single-step experiments (Z-102 and Z-107) were performed in a solid salt assembly in the Griggs apparatus on magnesite aggregates. Experiment Z-102 was annealed for \( t = 21,600 \) seconds and had a final grain size of \( d = 6.4 \) µm, the sample was then deformed at \( T = 700 \) °C, \( P = 300 \) MPa, and \( \dot{\varepsilon} = 1.6 \times 10^{-5} \text{s}^{-1} \). Experiment Z-102 was strained by \( \sim 8 \% \) had a final differential stress of 255 MPa (Fig. 14).

Experiment Z-107 was annealed for a period of \( t = 3,600 \) seconds and had a final grain size of \( d = 3.2 \) µm, the magnesite cylinder was then deformed at \( T = 700 \) °C, \( P = 300 \) MPa, and \( \dot{\varepsilon} = 1.6 \times 10^{-5} \). The experiment was deformed to 6 % strain and had a differential stress of 305 MPa (Fig. 14).

Microstructures observed at the SEM scale for Nevada magnesite aggregates deformed in the Griggs apparatus at \( T = 700 \) °C and \( P = 300 \) MPa include moderate rounding of grains, and pore spaces around grain boundaries, as well as pores within the grains of deformed magnesite (Figure 15).

3.6 High temperature grain stepping experiments at low pressure

Axial compression, grain-size stepping experiments were performed on magnesite cylinders (Z-86 and Z-97) using the Griggs apparatus (Table 2). Experiment Z-86 was performed at \( T = 700 \) °C, \( P = 300 \) MPa, and \( \dot{\varepsilon} = 1.6 \times 10^{-5} \). During this grain size stepping experiment, the magnesite core was annealed and deformed three times. The first annealing period was 3,600 seconds. The differential stress after subsequent deformation was 207 MPa (\( d = 3.1 \) µm). The following annealing period was 21,600 seconds and the strength was 273 MPa (\( d = 4.7 \) µm). The final annealing period was 86,400 seconds and the differential stress after subsequent deformation was 177 MPa (\( d = 6.6 \) µm). The
Figure 14. Stresses of magnesite cylinders with $d = 3.2$ and $6.4 \, \mu m$ at $P = 300 \, MPa$ increases from $\sigma = 255 \, MPa$ with magnesite of $d = 6.4 \, \mu m$ to $\sigma = 305 \, MPa$ with magnesite of $d = 3.2 \, \mu m$. (Z-102 and Z-107, $T = 700 \, ^{\circ}C$, $P = 300 \, MPa$, $\dot{\varepsilon} = 10^{-5} \, s^{-1}$).
Figure 15. Magnesite (Z-101) cylinder $d = 6.4 \, \mu m$ deformed at $T = 700 \, ^\circ C$ and $P = 300 \, MPa$. Microstructures include moderately rounded grains and pore spaces around the grain boundaries.
grain sizes for each of the deformation steps are based on the grain size growth rate at the conditions of annealing (Fig. 16).

Experiment Z-97 was performed at $T = 800 \, ^\circ C$, $P = 300 \, MPa$, and $\dot{\varepsilon} = 1.6 \times 10^{-5}$. During this grain size stepping experiment, the magnesite core was annealed and deformed three times. The first annealing period was 3,600 seconds. The differential stress after subsequent deformation was 151 MPa ($d = 3.1 \, \mu m$). The following annealing period was 21,600 seconds and the strength was 275 MPa ($d = 5.4 \, \mu m$). The final annealing period was 86,400 seconds and the differential stress after subsequent deformation was 180 MPa ($d = 7.5 \, \mu m$). The grain sizes for each of the deformation steps are based on the grain size growth rate at the conditions of annealing, and the data was normalized using the flow law to 700 °C (Fig. 16).

Microstructures observed at the SEM scale for Nevada magnesite aggregates deformed in stepping experiments at $T = 700 \, ^\circ C$, $P = 300 \, MPa$, and $\dot{\varepsilon} = 1.6 \times 10^{-5} s^{-1}$ include extensive rounding of grains, pore spaces around grain boundaries, as well as pores within the grains of the deformed magnesite. The grain size-stepping experiment samples have more extensive rounding of grains than the single-step deformation experiments (Fig. 18).
Figure 16. Stresses of magnesite cylinders with $d = 3.1$ increases in strength from $\sigma = 207$ MPa with magnesite of $d = 3.1 \mu$m to $\sigma = 273$ MPa with magnesite of $d = 4.7 \mu$m. In the final step, the strength decreased to $\sigma = 177$ MPa with magnesite of $d = 6.6 \mu$m ($Z-86$, $T = 700 ^\circ C$, $P = 300$ MPa, $\dot{\varepsilon} = 10^{-5}$ s$^{-1}$).
Figure 17. Stresses of magnesite cylinders with $d = 3.1$ increases in strength from $\sigma = 151$ MPa with magnesite of $d = 3.1$ µm to $\sigma = 275$ MPa with magnesite of $d = 5.4$ µm. In the final step, the strength decreased to $\sigma = 180$ MPa with magnesite of $d = 7.5$ µm ($Z-97 T = 700 ^\circ C, P = 300$ MPa, $\dot{\varepsilon} = 10^{-5}$ s$^{-1}$).
Figure 18. Magnesite (Z-86) cylinder $d = 6.6$ mature microstructures from stepping experiments include extensively rounded grains and pore spaces around and within the magnesite grains.
4.1 Grain size dependence of low temperature plasticity deformation mechanisms

Natural magnesite aggregates were deformed \((d = 3, 16, \text{ and } 80 \, \mu\text{m})\) to understand how grain size affects the strength of the magnesite deforming at \(T = 500 \, ^\circ\text{C}\) at both high and low pressures \((P = 0.9 - 8.0 \, \text{GPa})\). There was a strength contrast during deformation that found as the grain size increases the strength decreases which is consistent with low temperature plasticity. Microstructural analyses also provided insight that magnesite is grain size dependent when deforming by low temperature plasticity, as extensive mechanical twinning and a flattening of grains were present during every experiment. At low pressures \((P = .90 \, \text{GPa})\), magnesite is much more grain size sensitive, but at higher pressures the grain size sensitivity becomes negligible on the strength of the magnesite aggregates deforming by low temperature plasticity deformation mechanisms.

The dependence on strength and grain size for low temperature plasticity can be described by:

\[
\sigma_y = \sigma_i + kd^{m_{\text{LTP}}} \tag{eq. 1}
\]

(Olsson, 1974) where \(\sigma_y\) is the yield stress, \(\sigma_i\) and \(k\) are constants for a given set of test conditions, and \(d\) is the mean grain size. This relationship is used to demonstrate how yield stress is dependent on grain size. The grain size sensitivity exponent \((m_{\text{LTP}})\) was determined from the relationship between stress and grain size of the deformed magnesite aggregates (Fig. 19). The \(m_{\text{LTP}}\) values along with microstructural data are
Figure 19. Grain size sensitivity of the strength of magnesite aggregates deforming by low temperature plasticity at \( T = 500 \, ^\circ C \) and pressures ranging from \( P = 0.9 \) – 8.0 GPa.
characteristic of low temperature plasticity deformation mechanisms occurring in magnesite at low pressures.

The grain size sensitivity exponent ($m_{\text{LTP}}$) for magnesite deforming by low temperature plasticity decreases from $m_{\text{LTP}} = 0.25$ (at $P = 0.9$ GPa) to $m_{\text{LTP}} = 0.08$ ($P = 2.4$ GPa) to $m_{\text{LTP}} = 0.008$ ($P = 5.0$ GPa) and $m_{\text{LTP}} = 0$ ($P = 8.0$ GPa) (Fig. 20). These results demonstrate that the grain size sensitivity of low temperature plasticity deformation of magnesite decreases with increasing pressure and, due to their similarities, calcite and other common carbonates likely behave similarly within the subducting slab (Fig. 21). Although no previous $m_{\text{LTP}}$ value has been calculated for magnesite, a calculation of grain size exponent ($m_{\text{LTP}}$) for marble deforming by low temperature plasticity has been previously calculated by ($m_{\text{LTP}} = 0.5$; Olson et al., 1974) with conditions of $T = 500$ °C and low pressures of $P = 2.0$ GPa. This grain size dependence is attributed to the Hall-Petch mechanism of dislocation pileup at grain boundaries causing cracking or slip across grain boundaries (Olsson, 1974). The shear stress of the concentration may also initiate dislocation glide (Olsson, 1974). However, increasing pressure may inhibit gliding associated with dislocation pileups at grain-boundaries which may be the cause of the decreased grain size dependence at higher pressures.

These results indicate that along much of the P-T path of subducting slabs, grain size will not significantly affect magnesite strength. Since there is an opposite effect of increasing temperature and increasing confining pressure on the strength of magnesite due to grain size differences, the strength of magnesite deforming by low temperature plasticity is likely a complicated function of depth of burial, and will not significantly affect magnesite strength along most of the subducting slab.
Figure 20. Grain size dependence ($m_{\text{LTP}}$) of magnesite and calcite deforming at $T = 500$ °C, and pressures of $P = 0.2, 0.9, 2.4, 5.0, \text{ and } 8.0$ GPa. As the pressure increases, the $m_{\text{LTP}}$ value exponentially decreases, indicating that at higher pressures grain size sensitivity on the strength of magnesite decreases.
4.2 Grain size dependence on diffusion creep deformation mechanisms

Grain size stepping experiments and single-deformation step experiments were performed on a natural magnesite aggregate at $\dot{\varepsilon} = 1.6 \times 10^{-5}\text{s}^{-1}$ at $T = 700-800\,^\circ\text{C}$ and $P = 300\,\text{MPa}$. The microstructures observed were rounding of the grains, pores around the grain boundaries, and pores within the grains, which is indicative of diffusion creep deformation mechanism. Experiments Z-86 and Z-97 were brought to conditions and then immediately deformed. After that deformation step the sample was left to anneal for a period of $t = 21,600\,\text{s}$, which caused the strength to drastically increase, with the increasing grain size. The final step was left to anneal for $t = 86,400\,\text{s}$ to achieve a grain size of $d = 6.4\,\mu\text{m}$. After the 86,400 second period, the strength of the magnesite decreased, which is unexpected for carbonates deforming by diffusion creep. The reason the strength decreased is likely due to the evolution of the microstructures during the three deformation steps. The microstructures showed the grains becoming extensively rounded and porous when left to anneal, which is dependent on temperature as well as time left at conditions.

In single deformation experiments (Z-102 and Z-107) the magnesite was deformed after just 3,600 and 21,600 seconds, and did not hydrostatically grow for 24 hours as in experiments Z-86 and Z-97, so the microstructures were not able to fully evolve. The grains were more angular with less pore spaces causing the strength of these grains to be higher than expected results. Davis et al., (2011) also observed this same microstructural evolution on synthetic magnesite.

The dependence on the strength and grain size for diffusion creep is described by the following flow law (Schmid et al., 1977).

$$\dot{\varepsilon} = A*\sigma^n d^{-m} \exp (-H/RT) \quad (\text{eq. 2})$$
Figure 21. Graph, illustrating the grain size dependence \( (m_d) \) on the strength of magnesite deforming by diffusion creep with conditions of \( T = 700 \, ^\circ C \), and \( P = 300 \, MPa \). As the grain size increases the strength of magnesite deforming by diffusion creep also increases \( (m_d = 1.0 \pm 0.44) \).
Where $\dot{\varepsilon}$ is strain rate, $A$ is a constant, $\sigma_n$ is differential stress, and $n$ is the stress exponent, $d$ is mean grain size and $-m_d$ is the grain size dependence, $H$ is energy, $R$ is a gas constant, $T$ is the absolute temperature. The $m_d$ value for magnesite in this study was calculated by taking the natural log of the flow law:

$$\ln \sigma = \frac{m_d}{n} \ln d \quad -(\ln A + \ln \varepsilon + Q/R \, \ln T)$$

The calculated value for the grain size sensitivity of magnesite deforming by diffusion creep is $m_d = 1.0 \pm .44$ which is considerably lower than Schmid et al. (1977), which calculated a value of $m_d = 3$. The $m_d$ value calculated in this study is consistent with grain boundary sliding ($m_d = 1-2$) instead of body Nebarrow- Herring or grain boundary diffusion creep ($m_d = 3$, Fig 21).

4.4 Extrapolation to nature

To extrapolate my experimental results to natural conditions I used the diffusion creep flow law from Holyoke et al. (2014), and used my new calculated $m_d$ value for diffusion creep (eq. 2). I calculated the strength of magnesite deforming by diffusion creep over a range of grain sizes of ($d = 1 – 1000 \, \mu m$).

The natural conditions used in the extrapolation of my data were strain rates of $\dot{\varepsilon} = 1 \times 10^{-14} \, \text{s}^{-1}$, temperatures following the average natural geothermal gradient ($T = 25 \, ^\circ \text{C}$ per kilometer within the Earth), pressures following the average natural pressure gradient ($P = 30 \, \text{MPa per kilometers within the Earth}$) and grain sizes of $d = 1, 10, 100, \text{and} 1000 \, \mu m$ (Figure 22). At all grain sizes, the deformation mechanism of magnesite aggregates with the lowest viscosities is diffusion creep, which indicated that the dominant deformation mechanism in the subducting slab will be diffusion creep.
Figure 22. A comparison of the viscosity of magnesite deforming naturally in a subducting slab by low temperature plasticity ($d = 3 \mu m$), dislocation creep ($d = 3 \mu m$), and diffusion creep with grain sizes varying from ($d = 1 – 1000 \mu m$). Throughout most of the subducting slab diffusion creep will be the dominant deformation mechanism.
CHAPTER V
CONCLUSIONS

A set of experiments were performed on natural magnesite aggregates with grain sizes ranging from \((d = 3 – 80 \, \mu m)\) at \(\varepsilon = 10^{-5} \text{s}^{-1} (T = 500 \, ^\circ\text{C})\) and a range of pressures \((P = 0.9 – 8.0 \, \text{GPa})\). At these conditions magnesite deforms by low temperature plasticity. The strength of these grain sizes is likely highly dependent on grain size, but this dependence decreases with increasing pressure.

Another set of experiments were performed on natural magnesite aggregates with grain sizes ranging from \((d \sim 3 – 7 \, \mu m)\) at \(\dot{\varepsilon} = 10^{-5} \text{s}^{-1}, (T = 700 \, ^\circ\text{C})\) and \(P = 0.3 \, \text{GPa}\). The microstructures in these aggregates include pore spaces around the grain boundaries and pores within the magnesite grains, which is consistent with diffusion creep or grain boundary sliding. The strength of these aggregates also increases with increasing grain size. The rate of strength increases with increasing grain size is consistent with grain boundary sliding.
REFERENCES


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APPENDIX A
LIST OF EXPERIMENTS

The following appendix is a list of all experiments performed in this experimental study. All of these experiments include both the experiments that were used in this study and the experiments that were not used in this study, for various reasons, to determine the m value for magnesite.


Table A1. List of all experiments performed in this study

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Assembly type</th>
<th>Confining Pressure (MPa)</th>
<th>Temperature (°C)</th>
<th>Strain Rate (s⁻¹)</th>
<th>Strain (%)</th>
<th>Strength (MPa)</th>
<th>Grain size (µm)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-69</td>
<td>SSA</td>
<td>1500</td>
<td>850</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>15</td>
<td>Hydrostatic grain growth experiment on stacked sample of natural magnesite and dolomite.</td>
</tr>
<tr>
<td>Z-70</td>
<td>SSA</td>
<td>1500</td>
<td>900</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16</td>
<td>Hydrostatic grain growth experiment on magnesite.</td>
</tr>
<tr>
<td>Z-71</td>
<td>SSA</td>
<td>1500</td>
<td>850</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16</td>
<td>Hydrostatic grain growth experiment on magnesite, starting grain size d = 3 µm</td>
</tr>
<tr>
<td>Z-72</td>
<td>SSA</td>
<td>1500</td>
<td>850</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>14</td>
<td>Hydrostatic grain growth experiment on magnesite. Used cored samples for D-DIA 16 µm experiments.</td>
</tr>
<tr>
<td>Z-73</td>
<td>SSA</td>
<td>900</td>
<td>500</td>
<td>1.6 * 10⁻⁵</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>Fine-grained magnesite, low temperature plasticity. TC failed at conditions after 3 hours</td>
</tr>
<tr>
<td>Z-74</td>
<td>SSA</td>
<td>900</td>
<td>500</td>
<td>1.6 * 10⁻⁵</td>
<td>14</td>
<td>2400</td>
<td>3</td>
<td>Fine-grained magnesite, low temperature plasticity. Successful experiment</td>
</tr>
<tr>
<td>Z-75</td>
<td>SSA</td>
<td>900</td>
<td>500</td>
<td>1.6 * 10⁻⁵</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>TC failed at conditions</td>
</tr>
<tr>
<td>Z-76</td>
<td>SSA</td>
<td>900</td>
<td>500</td>
<td>1.6 * 10⁻⁵</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>TC failed at ~500 MPa</td>
</tr>
<tr>
<td>Z-77</td>
<td>SSA</td>
<td>900</td>
<td>500</td>
<td>1.6 * 10⁻⁵</td>
<td>14</td>
<td>1600</td>
<td>16</td>
<td>Grains hydrostatically grew to 16 µm and then a single-step deformation was performed, successful</td>
</tr>
<tr>
<td>Z-79</td>
<td>MSC</td>
<td>350</td>
<td>700</td>
<td>1.6 * 10⁻⁵</td>
<td>10</td>
<td>-</td>
<td>Crushed sample at the beginning of the</td>
<td></td>
</tr>
</tbody>
</table>
Table A1. List of all experiments performed in this study (Continued)

| Z-82   | MSC  | 350 | 700 | $1.6 \times 10^{-5}$ | - | - | 3 | experiment, incorrect data |
| Z-83   | MSC  | 350 | 700 | $1.6 \times 10^{-5}$ | - | - | 3 | TC failed |
| Z-84   | MSC  | 350 | 730 | $1.6 \times 10^{-5}$ | - | - | 3 | TC failed |
| Z-86   | MSC  | 350 | 700 | $1.6 \times 10^{-5}$ | 27 | 207 237 172 27 | 3.1 4.7 6.6 | Grain growth stepping experiment for 1, 6, and 24 hours. After annealing for 24 hours, the microstructures evolved causing the weakening during the last step, successful |
| Z-89   | MSC  | 350 | 700 | $1.6 \times 10^{-5}$ | - | - | 3 | TC failed |
| Z-93   | MSC  | 350 | 700 | $1.6 \times 10^{-5}$ | - | - | 3 | TC failed |
| Z-95   | MSC  | 350 | 750 | $1.6 \times 10^{-5}$ | 7 | 374 | 3 | The sample did not match expected results, so no further investigation was done. |
| Z-97   | MSC  | 350 | 800 | $1.6 \times 10^{-5}$ | 23 | 151 275 185 | 3.1 5.4 7.5 | Grain size stepping experiment for 1, 6, and 24 hours annealing periods. Microstructures evolved during the 24 hour annealing period causing a strength weakening during the last deformation step. |
| Z-101  | SSA  | 350 | 700 | $1.6 \times 10^{-5}$ | 7 | 82 | 6.6 | The sample did not match expected results, so no further investigation was done. |
| Z-102  | SSA  | 350 | 700 | $1.6 \times 10^{-5}$ | 8 | 255 | 6.4 | Grains were annealed for 6 hours ($d = 6.4 \mu m$) and then a single deformation step was completed, successful |
| Z-107  | SSA  | 350 | 700 | $1.6 \times 10^{-5}$ | 8 | 305 | Grains were annealed for 1 hour ($d = 3.2 \mu m$) and |


Table A1. List of all experiments performed in this study (Continued)

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>Location</th>
<th>Pressure</th>
<th>Grain Size</th>
<th>Deformation Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAG_005</td>
<td>Durham</td>
<td>2400</td>
<td>Fine</td>
<td>29</td>
<td>coarse; 3.2 stacked magnesite/dolomite experiment</td>
</tr>
<tr>
<td>MAG_007</td>
<td>Durham</td>
<td>2400</td>
<td>Fine</td>
<td>3</td>
<td>Pressure stepping experiment at 2.4, 5, and 7.4 GPa, successful results</td>
</tr>
<tr>
<td>MAG_011</td>
<td>Durham</td>
<td>5000</td>
<td>Fine</td>
<td>80</td>
<td>Stacked samples of d = 3, and 16 µm, successful experiment</td>
</tr>
<tr>
<td>MAG_013</td>
<td>Durham</td>
<td>8000</td>
<td>Fine</td>
<td>80</td>
<td>Pressure experiment with d = 80 and 3 µm, not used in study</td>
</tr>
<tr>
<td>MAG_015</td>
<td>Durham</td>
<td>2400</td>
<td>Fine</td>
<td>16</td>
<td>Stacked samples of d = 16 µm and d = 3 µm, successful experiment</td>
</tr>
<tr>
<td>MAG_017</td>
<td>Durham</td>
<td>8000</td>
<td>Fine</td>
<td>80</td>
<td>High pressure experiment, successful data</td>
</tr>
</tbody>
</table>
The following appendix contains strain vs. time data that was collected at Argonne National Laboratory, and was not included in the text of this thesis.

Figure A1. Experiments were performed on $d = 3 \text{ } \mu m$ and $d = 80 \text{ } \mu m$ cylinders of magnesite at $T = 500^\circ \text{C}$ and $P = 8.0 \text{ GPa}$ using the D-DIA. The cylinders are stacked, so strain can be observed under identical conditions. Both magnesite grain sizes deformed by the same strain.
APPENDIX C
GRAIN BOUNDARY TRACINGS

The following appendix shows two examples of magnesite grains that were traced using Adobe Illustrator and then measured using Image SXM software. The first figure is showing magnesite deforming at low temperatures \( T = 500 \, ^\circ \text{C} \) and the second figure is showing magnesite deforming at high temperatures \( T = 700 \, ^\circ \text{C} \).
Figure 1C. Examples of grain tracings used to calculate the average grain size of each deformed sample. (Top) undeformed sample with grain size of 16 µm (Bottom) post deformation sample at $T = 500 ^\circ C$ and $P = 5.0$ GPa.
Figure 1C. Examples of grain tracings used to calculate the average grain size of each deformed sample. (Top) undeformed sample with grain size of 16 µm (Bottom) post deformation sample at \( T = 500 \) °C and \( P = 5.0 \) GPa.
APPENDIX D
SEM IMAGES

The following appendix is SEM images that were not used in the microstructural analysis in this study.
Figure 1D. SEM scale BSE image of magnesite deformed at $T = 500$ °C and $P = 5.0$ GPa. Grains are mechanically twinned and grains average $d = 16 \mu m$ in diameter.
Figure 2D. SEM scale BSE image of magnesite deformed at $T = 700$ °C and $P = 300$ MPa. Grains were annealed and left to become extensively rounded. Pore spaces are observed around the grain boundaries as well as within the magnesite aggregate grains.