Plastic deformation of dry fine-grained olivine aggregates under high pressures

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Abstract

This study investigates the effect of pressure on diffusion creep of dry San Carlos and synthetic (prepared by sol-gel method) olivine. We prepared dry (water content < 9 ppm wt) fine-grained (< 1 \( \mu \text{m} \) grain-size) olivine and deformed the samples (both San Carlos and sol-gel olivine in the same assembly) in the same sample assembly under high-pressure (\( P = 2.9–8.8 \text{ GPa} \)) and modest temperatures (\( T = 980–1250 \text{ K} \)) at a fixed strain-rate. Evolution of strength was studied using the radial X-ray diffraction from various diffraction planes. We found that San Carlos and sol-gel olivine show similar rheological behaviour (when normalized to the same grain-size). Stress estimated by the radial X-ray diffraction increases with time and initially shows similar values for all diffraction planes. In many cases, stress values start to depend on the diffraction planes in the later stage and time dependence becomes minor. The micro-structural observations show that grain-size increases during an experiment. The results are interpreted using a theory of radial X-ray diffraction and the theoretical models of diffusion and dislocation creep. We conclude that the initial stage of deformation is by diffusion creep, but deformation in the later stage is by dislocation creep. For dislocation creep, our results are in reasonable agreement with previous low temperature dislocation creep results after a correction of temperature effect. For diffusion creep, we obtain an activation volume of 7.0 ± 2.4 \( \text{cm}^3/\text{mol} \) that is substantially smaller than the values reported on dislocation creep but agrees well with the results on grain-growth. By comparing the present results on dry olivine with the previous results on wet (water-saturated) olivine, we found that water enhances diffusion creep but only modestly in comparison to dislocation creep. The difference in the pressure and water content dependence between diffusion and dislocation creep has an important influence on the dominant deformation mechanisms of olivine in the upper mantle.
Plastic deformation of minerals such as olivine occurs either by dislocation or diffusion creep in most parts of the upper mantle (e.g., Karato et al., 1986; Karato and Wu, 1993; Hirth and Kohlstedt, 1995a,b; Mei and Kohlstedt 2000a,b). Because some geophysically relevant questions (e.g., seismic anisotropy, shear localization) are sensitive to deformation mechanisms, it is important to explore the dominant deformation mechanisms in Earth’s upper mantle and understand how pressure might modulate it. The rate of deformation (\( \dot{\varepsilon} \)) is dependent on pressure (\( P \)) and temperature (\( T \)) as

\[
\dot{\varepsilon} = A \cdot \sigma^n \cdot d^{-m} \cdot \exp\left( -\frac{E^* + PV^*}{RT} \right)
\]

(1),

where \( A \) is a constant, \( \sigma \) is deviatoric stress, \( d \) is grain size, \( R \) is the gas constant, \( E^* \) is activation energy, \( V^* \) is activation volume, \( n \) is the stress exponent and \( m \) is the grain size exponent and both \( n \) and \( m \) depend on deformation mechanism (e.g., (Karato, 2008)).

Among the parameters in the flow law relation (Eq. (1)), \( A, n, m \) and \( E^* \) are relatively easy to measure and reasonably well constrained for olivine for both diffusion and dislocation creep at least under low-pressure conditions. In contrast, the activation volume (\( V^* \)) that represents the pressure effects on deformation is difficult to measure, and most previous studies on \( V^* \) were on dislocation creep (e.g., Dixon and Durham, 2018; Kawazoe et al., 2009; Li et al., 2006). In the case of diffusion creep, not many studies were done to estimate \( V^* \) because of the challenge in controlling grain size. In most previous studies on deformation in the deep upper mantle, the activation volume of diffusion creep was assumed (e.g., Hirth and Kohlstedt, 2003; Karato and Wu, 1993), and in such a case, the validity of such an assumption needs to be evaluated. An exception is Mei and Kohlstedt (2000a), who reported \( V^* \sim 15 \pm 5 \text{ cm}^3/\text{mol} \) based on...
low-pressure data up to 0.45 GPa. However, the validity of their estimated uncertainties is uncertain due to the low-pressure range used in their study. Among the reports based on the higher pressure data, Nishihara et al. (2014) reported $V^*$ of 8.2±0.9 cm$^3$/mol for dry olivine in the diffusion creep regime, using modestly small grain size samples based on the data from $P=3.0-5.4$ GPa. However, under their experimental conditions, samples deformed in the mixed regime and the estimated creep law parameters have large uncertainties. Another is Silber et al. (2022) where they used natural San Carlos as well as synthetic fine-grained aggregates (~0.2-0.7 μm grain-size) and determined $V^*$ of 2.5 ± 0.6 cm$^3$/mol for diffusion creep under the “wet” (water-rich) conditions ($P=3-10$ GPa). In this paper, we report the activation volume of natural and synthetic olivine samples made from San Carlos olivine or from sol-gel method, extending the previous study (Silber et al., 2022) to “dry” conditions.

A key to this work is the preparation of fine-grained specimens, minimizing grain-growth during deformation experiments, and the use of the in-situ radial X-ray diffraction with a help of a theory (Karato, 2009) to infer the operating mechanisms of deformation. In the next section, we describe the experimental procedure, including the sample preparation and characterization. And in a later section, we summarize the experimental observations and present a flow law for diffusion creep under dry conditions. In the final section we will discuss some implications of the present results.

Methods

Sample preparation
To address potential difference in strength between San Carlos olivine (Mg_{0.91}, 
Fe_{0.09})_2SiO_4, and synthetic olivine (solgel), two sets of samples were prepared. Following Karato et al. (1986) we prepared fine-grained aggregates of San Carlos (SC) olivine. We selected pristine San Carlos olivine crystals which were initially manually pulverized. Pulverized powder was further ground in a ball mill for at least 24 hours. The ultrafine powder was extracted via sedimentation technique. Separated ultrafine powder had an average grain-sizes between 100-200 nm.

The ultrafine powder was then mixed with 1 wt% orthopyroxene (opx) to control the silica activity. The grain growth mitigation was achieved by adding up to 5 wt% nano-size (0.013 μm) alumina. The prepared mixture was baked at 1273 K in a controlled oxygen fugacity gas furnace (f_{O_2} \sim 10^{-7} \cdot 10^{-8} (Pa)) and then loaded into the Ni capsule. These densely packed samples were subsequently hot-pressed at 3 GPa and 1073 K for one hour.

The preparation of solution gelation (solgel) samples was done following the method described by Faul and Jackson (2007). Specifically, dissolution of magnesium and iron nitrates was carried out in ethanol and homogenized with tetraethyl orthosilicate. To remove ethanol from the mixture, the solution was heated on a hot plate at 30° C for several days. During the heating, the gelation was initiated by introducing small amount of nitric acid (HNO_3) to the solution which was continuously stirred in a beaker with a magnetic agitator.

The final synthesis and drying of olivine with composition (Fe_{0.1},Mg_{0.9})_2SiO_4 was done by baking at high temperature (1273 K) under the oxygen fugacity using CO_2 and H_2 gas mixture (f_{O_2} \sim 10^{-7} \cdot 10^{-8} (Pa)). Finally, the synthesized crystalline material was milled again and sintered as in the case of San Carlos olivine. Following this step, the samples of desired length and width
(1.3 × 1.0 mm) were core drilled and dried again under controlled $f_{O_2}$ to remove any water absorbed from the environment.

**Grain size, water content measurements and sample assembly**

We measured the initial grain sizes of hot-pressed samples using a scanning electron microscope (SEM) (FEI/Philips XL30 ESEM-FEG). As in our previous work, we encountered difficulties in reliably measuring the grain size on polished and acid etched samples due to the overall ultrafine grain size in our prepared polycrystalline aggregates where the grain boundaries could not be resolved with desired clarity. To overcome that obstacle, grain size analysis was performed on fractured sample surfaces (Figure 1) (the same technique was used by Silber et al. (2022)). This approach was validated by simultaneously conducting the grain size analysis on perfectly polished and acid etched samples and on the same, but fractured samples, originating from a secondary olivine with substantially larger grain sizes (> 1 μm). The grain size distribution was determined using the intercept method and multiplying the obtained values by the conversion factor of 1.5 (e.g., Abrams, 1971; Cahn and Fullman, 1956) (Figure 2). Grain-size was also measured from all samples after deformation experiments. The typical starting grain size for solgel olivine was estimated to be in the range of ~0.15 - 0.25 μm. In the case of San Carlos olivine samples, the observed grain size was somewhat larger (~0.20 - 0.50 μm).

The water content was determined for representative samples to ensure that the water content is small enough to observe “dry” behavior in plastic deformation. The measurement of each representative sample set was conducted using Fourier Transform Infrared Spectroscopy (FTIR) using Excalibur FTS 3000 with UMA 600 Microscope. For this analysis, representative samples were sequentially finely polished. Polished samples were prepared to thickness of ~100
μm and scanned using 50 × 50 μm aperture. The collected spectra were analyzed between 3000 and 3700 cm\(^{-1}\), corresponding to absorption bands generally associated with hydrogen in olivine. The linear function was employed in background correction specifically for the purpose of repeatability. The corrected and integrated infrared spectra was used to calculate hydroxyl concentration Paterson (1982).

FTIR analysis of selected samples showed a small amount of water well below 9 ppm wt, presumably acquired by samples during high-pressure experiments. After deformation, the samples were analyzed again to confirm that water content did not change appreciably during the deformation experiment (Figure 3).

The cell design and geometry followed the procedure established by Girard et al. (2020) and used in Silber et al. (2022). In this arrangement, both San Carlos and solgel samples were emplaced symmetrically relative to the center of the cell, separated by pyrope and platinum disc strain markers. Therefore, the pressure and temperature (and the macroscopic stress) conditions are nearly identical for these two samples.

**Experimental procedure and uncertainty estimates**

In total, four deformation experiments were performed at the 6-BM B white X-ray beamline at Advanced Photon Source (APS) in Argonne National Laboratory using a D-DIA apparatus (e.g., Wang et al., 2003) (the experimental procedure is the same as in Silber et al. (2022).

Prior to each deformation experiment in D-DIA, the X-ray beam calibration was conducted while the sample assembly is under (nearly) hydrostatic condition. Diffraction data
was collected from the samples before uniaxial stress was applied and used as a reference in order to calculate the differential stress during deformation (deviatoric stress during this stage was kept minimum by retracting the differential rams). Also, pressure and temperature of each run were estimated from the X-ray diffraction data on platinum and pyrope before deformation. For equation of state (EOS) of platinum, we used the results reported by (Matsui et al., 2009; Zha et al., 2008) and for pyrope (Hu et al., 2016; Zou et al., 2012; Fan et al., 2017).

The errors in pressure estimate result from the uncertainties of the molar volume of a sample by X-ray diffraction and from temperature uncertainties in the equation of state including thermal expansion. Consequently, we can take advantage of the fact that $P$-estimates from the molar volume also depend on $T$ and by using EOS’s of two materials we can determine both $P$ and $T$. The uncertainties in the pressure estimate are $\sim 0.5$ GPa, and for temperature it is $\sim 50$ K.

In contrast to a case of dislocation creep, annealing was kept to a minimum to minimize grain growth. The deformation, achieved by advancing vertically positioned opposite anvils at uniform rate, was initiated 15 min after the target temperature was reached for each experiment (time needed to collect high $P$-$T$ spectra).

The collection of X-ray diffraction spectra during deformation experiments was conducted in equal intervals (every 3 minutes). The strain of both San Carlos and solgel sample was determined from the X-ray radiography images of strain markers, collected during the deformation, between each X-ray diffraction.

The uncertainty in strain (and strain-rate) determined from the radiographic images in our experiments ranges up to 10% and depends on the pixel size of the image relative to the sample thickness, the quality of the image, processing software and total strain. Strain-rates were between $0.2-9.5 \times 10^{-6}$ s$^{-1}$ (Table 2).
Stress was derived from the radial X-ray diffraction performed on each sample. This was done at the same time intervals as strain data collection. The lattice strain, obtained from the diffracted and azimuthally collected X-rays, was used in calculation of the differential stress $\sigma_{hk}$ for the particular (hkl) reflection in crystals during deformation. This approach is based on Singh et al. (1998):

$$d_{hkl}(\psi) \propto d_{hkl}^0 \left[1 + \frac{\sigma_u}{6M} (1 - 3\cos^2 \psi) \right]$$ (2),

where $d_{hkl}$ the $d$-spacing for the lattice plan (hkl) during deformation, $d_{hkl}^0$ is the $d$-spacing under the hydrostatic conditions for the lattice plan (hkl), $M$ is the Voigt-Reuss-Hill average of shear modulus, $\psi$ is the azimuthal angle, and $\sigma_u$ is the uniaxial stress applied on the material that we want to estimate. Stress is estimated by fitting the $d_{hkl}(\psi)$.

We used Plot85 in initial analysis (Dixon and Durham, 2018; Li et al., 2004; Li et al., 2006; Vaughan et al., 2000). To determine stress in olivine, we used the best-observed diffraction peaks obtained from (130), (131) and (112) planes. The errors in stress were calculated using the same methodology as in Silber et al. (2022).

Results

Microstructure and grain sizes

Figures 1 & 2 show the SEM images of representative samples, before and after deformation experiments. The average initial and final grain sizes estimated from the intercepts measurements are given in Table 1. Pressures, temperatures, and corresponding uncertainties for each experiment are also shown in Table 1. We followed the methodology of grain size quantification given by Silber et al. (2022). They showed that for samples with ultrafine grain
sizes (~0.1-1 μm), it is preferential to quantify the grain sizes from fractured surfaces. That is clear from Figures 1 and 2, as this approach permits the sub-0.1 μm grains to be preserved and quantified. A typical SEM preparation method using polishing and acid etching to expose grain boundaries generally leads to obliteration of the smallest grains in etched samples and hence would not be represented in general grain size distribution (i.e., Figure 2).

It can be seen from Figure 2 that appreciable grain growth occurred despite the presence of OPX and pinning with nano-size alumina. However, the final grain sizes, in experiments with the greatest grain growth, did not exceed 1 micron. Grain sizes in all samples follow nearly log-normal distribution and grain boundaries exhibit typical ~120° angles.

**Water content in the samples**

Although we did not add any water in our experiments, some water may come from the sample assembly during high-pressure experiments (see e.g., Karato, 1989). Therefore, to mitigate potential water diffusion from the cell assembly components, boron epoxy cube, boron nitride sleeves, alumina pistons as well as sample were baked in the oven for 24 h prior to the deformation experiments. We measured the water content of our sample before and after a deformation experiment.

We estimated water content by FTIR. The representative FTIR spectra of initial and recovered San Carlos olivine and solgel samples are shown in Figure 3. The observed initial water content in samples hot-pressed at 3 GPa and subsequently dried under controlled fugacity, is low (less than ~5 ppm wt) almost below the detectability limit. However, we observed higher water content after deformation experiments < 9 ppm wt) which suggests some absorption of water from the ambient air in the range of 3600 – 3400 cm\(^{-1}\). These values of water content are less than the threshold water content to see “dry” behavior.
The stress, calculated from X-ray diffraction peaks during the deformation experiments, is plotted as a function of strain for each experiment for both San Carlos olivine and solgel olivine samples (Figure 4a-h). All our experiments were deformed at a fixed strain rate to the total strains of ~ 4 – 15% (Figure 4a-h).

In all experiments, we observed hardening in the initial stage. Also in this stage, the (hkl) dependence of stress is negligible or very small. However, at a certain time (strain), (hkl) dependence of stress becomes stronger. And after this stage where large (hkl) dependence is observed, stress level becomes nearly independent of time (strain). Figure 4c,d is an exception, where transition to nearly independent time-stress relationship is not observed due to the early termination of the experimental run.

The figure also shows results for San Carlos olivine and sol-gel olivine. When grain-size is similar, creep strength of these two olivine samples is similar, although strength is different for different grain-size (see a discussion in the later section). The mechanical data also shows that the stress level is sensitive to pressure. At higher pressures, stress (for a given temperature and strain-rate) becomes larger.

Discussion

Deformation mechanisms

The flow law for high-temperature creep can generally be given by equation (1). For diffusion creep, \( n=1 \) and \( m=2-3 \), whereas for dislocation creep \( n=3-5 \) and \( m=0 \) (Karato, 2008). Therefore a common way to infer the operation of diffusion creep in an experimental study is to
determine $n$ and $m$ to show $n=1$ and $m=2-3$ (e.g., (Karato, 2008; Karato et al., 1986; Mei and Kohlstedt, 2000a; Mei and Kohlstedt, 2000b)).

However, estimating these parameters under high-pressure deformation experiments is challenging. Unlike low-pressure experiments (using the Paterson apparatus), a sample is surrounded by several solid materials in the high-pressure deformation experiments ($P>3$ GPa) (e.g., (Wang et al., 2003; Yamazaki and Karato, 2001)). Consequently, when strain-rate is modified, various portions of a sample assembly are gradually deformed leading to a slow redistribution of stress/strain in a sample assembly. Therefore the strain-rate of a sample does not change to a new strain-rate immediately, and this makes it difficult to determine the stress exponent (a detailed analysis was made to estimate $n$ for such a case is given by (Silber et al., 2022)).

We use the following methods to infer the operation of diffusion creep following our previous study (also see Silber et al., 2022): (i) a comparison of the strength of a polycrystalline sample with the estimated strength of relatively coarse-grained specimens corresponding to dislocation creep, (ii) a comparison of measured strength with strength calculated from a theoretical model of diffusion creep and measured diffusion coefficients, (iii) the diffraction plane (hkl) dependence of stress, and (iv) the analysis of time hardening using grain-growth kinetics constrained by the initial and the final grain-sizes.

(i) Let us take a case of SAN515 (initial grain-size ~0.2 micron, the final grain-size ~0.8 micron) where deformation experiment was conducted at $P=5.9$ GPa, $T=1080$ K and strain-rate is $10^{-5}$ s$^{-1}$. The measured stresses in the initial parts of SAN515 (i.e., at 1 % strain) is ~400 MPa that would correspond to a grain-size of ~0.3 μm. Based on the report by (Kawazoe et al., 2009) on dry dislocation creep of olivine (~5 μm grain-size), we can
also calculate the stress of a sample at the same P, T and strain-rate if deformation were
by dislocation creep. The stress will be ~30-50 GPa (a large uncertainty is caused by the
(hkl) dependence of stress) at P=5.9 GPa, T=1080 K and strain-rate of 10^{-5} s^{-1} that is
much higher than the observed stress (~400 MPa). This large difference indicates that the
samples in our experiments deformed (at least initially) by grain-size sensitive (diffusion)
creep because of a much smaller grain-size (~0.3 micron) than grain-size in (Kawazoe et
al., 2009)’s samples (~5 μm).

(ii) Using our mechanical results in Table 3, we calculated grain-boundary diffusion
coefficient δD for each experiment (assuming coble creep) and compared our estimates
with the Si and Mg grain-boundary diffusion coefficients in olivine reported in previous
studies (e.g., Fei et al., 2018; Fei et al., 2016). The diffusion coefficient calculated using
our creep data are well within one order of magnitude of the value estimated from
previous studies. We conclude that our results are in reasonable agreement with previous
reported diffusion coefficients (e.g., 2018; Fei et al., 2016).

(iii) A remarkable observation is that in most of the initial part of our experiments where
grain-size is small, the (hkl) dependence of stress is weak, whereas the (hkl) dependence
becomes large in the later stage where grain-size is larger (see Fig. 1). The (hkl)
dependence of stress provides an important clue on the deformation mechanism if one
uses a theory by (Karato, 2009). In a synchrotron deformation experiment, stress acting
on a sample is calculated from the lattice strain (equation (2)). As equation (2) indicates,
one can determine the lattice strain for different diffraction planes (hkl). The results often
show that stresses estimated for different (hkl) differ substantially (e.g., (Weidner et al.,
2004)). (Karato, 2009) showed that the (hkl) dependence of stress is caused mostly by
plastic anisotropy. And plastic anisotropy is strong for dislocation creep while it is weak
(or nearly zero) for diffusion (creep) (e.g., (Dohmen et al., 2002; Durham and Goetze,
1977; Houlier et al., 1990; Houlier et al., 1988; Jaoul et al., 1981)). Therefore, the
absence of (hkl) dependence (absence of plastic anisotropy) in the initial part of our
experiments is a strong indication of the operation of diffusion creep, and the gradual
transition to a marked (hkl) dependence in the later stage can be attributed to a transition
to dislocation creep by grain-growth.

(iv) Those analyses strongly suggest that most of the initial stage of deformation is by grain-
size dependent diffusion creep. A complication is that because the strength in the
diffusion regime depends on grain-size that changes with time, the flow law must be
estimated based on the estimated grain-size at any point in the data. A simple way to
estimate grain-size during deformation is to interpolate the measured initial and final
grain-size assuming a relation for grain-growth (e.g., Chapter 13 of (Karato, 2008)),

\[ d^{n_g}(t) = d^{n_g}(0) = kt \]  (3)

where \( d \) is grain-size, \( n_g \) is a grain-size exponent (=2-4 for most cases), \( t \) is time and \( k \) is a rate
constant that depends on temperature and pressure (and water content etc. (e.g., (Karato, 1989))).
Given the initial and the final grain-size, one can calculate \( k \) for a given condition (assuming a
few values of \( n_g \)), and consequently estimate the grain-size at any time during an experiment.
Therefore, one can determine the flow law corresponding to diffusion creep from the time-
dependent stress for a given run.
The values of $k$ determined from the present study ($10^{18.3} \text{ m}^2 \text{s}^{-1}$) are substantially lower than the value extrapolated from Karato (1989) ($10^{15.6} \text{ m}^2 \text{s}^{-1}$)). This is likely due to the pinning effects by $\text{Al}_2\text{O}_3$. We also calculated $K$ for $ng=3$ $K=10^{-22.7(+/-1.6)} \text{ m}^3/\text{s}$ and $ng=4$, $K=10^{-29.3(+/-1.6)} \text{ m}^4/\text{s}$. Because grain-growth kinetics is so slow, different values of $n_g$ do not make much difference in estimated grain-size during deformation.

An issue in this approach is that, in most cases, the final stage of deformation occurs by dislocation creep. In dislocation creep, grain-size could be controlled by the stress when dynamic recrystallization is extensive (e.g., Karato et al., 1980). If this is the case, then the final grain-size is not determined by grain-growth. To check this point, we compare the final grain-size from the stress using the experimental data by van der Wal et al. (1993). We found that the grain-size estimated from this relation is substantially smaller than the observed value suggesting that dynamic recrystallization does not occur much. This is likely due to the low temperature, low water content and small strain (for the temperature, water content and strain dependence of dynamic recrystallization, see Zhang et al., 2000).

**Activation volume for diffusion creep**

We estimate activation volume for diffusion creep based on the data at different pressures. We select data corresponding to diffusion creep based on the criteria discussed above. However, since rheological behavior in diffusion creep also depends on grain-size (and temperature), we need to compare the results at different pressures for the same grain-size and temperature (normalization). We compare strain-rate at different pressures at a common stress (50 MPa), a common grain-size (1 micron), and a common temperature (1100 K) using equation (1) ($n = 1$) assuming $m = 2$ or 3. Also, in normalizing with respect to temperature, we used $E^* =$
295 or 375 kJ/mol, which represents the most common range of activation energy values in
published literature.

The experimental stress and strain-rate, along with calculated grain sizes, required for
normalization are given in Table 2. The values of stress and strain reported in Table 2 were
taken at a point on the stress/strain curve before diffusion creep terminated. The reasoning is
that rheological data (strain-rate, stress) for diffusion creep are evolving (because of concurrent
grain-growth). We chose the data within a regime where (hkl) dependence is nearly zero and
time-hardening is present. As we showed before, the data in that regime follows the creep law
(Eq. (1)), and therefore as far as the data follows that equation, choice of data does not affect our
analysis.

To calculate activation volume from our data, we need to compare data at different
pressures at a common stress, grain-size and temperature ($T_0, d_0, \sigma_0$, are the normalization
temperature ($T_0 = 1100$ K), normalization grain size ($d_0 = 1$ μm), normalization stress ($\sigma_0 = 50$
MPa)). Figure 6 shows plots of normalize strain-rate as a function of pressure.

We calculate the activation volume using the following relationship:

$$V^* = -RT \frac{3 \log \dot{\varepsilon}(T, d, \sigma)}{\partial P}$$

where $\dot{\varepsilon}(T_0, d_0, \sigma_0)$ is the normalized strain rate and $T_0, d_0, \sigma_0$ are the normalization temperature
($T_0 = 1100$ K), normalization grain size ($d_0 = 1$ μm), normalization stress ($\sigma_0 = 50$ MPa),
respectively.
The results are summarized in Table 3. Using the data both San Carlos and solgel olivine, we calculated $V^*$. Because we normalize the data to common grain-size and temperature (and a common stress), the estimated activation volume ($V^*$) depends on the aviation energy ($E^*$) and range from 4.4 to .9.4 cm$^3$/mol. This activation volume is close to the activation volume for grain-growth (~5.0-5.2 cm$^3$/mol) (Zhang and Karato, 2021). The activation volume for (dry) diffusion creep is substantially smaller than the activation volume for dry dislocation creep ($V^* \sim$15 cm$^3$/mol (Kawazoe et al., 2009)).

A comparison between San Carlos and solgel olivine

Let us now compare the rheological results for San Carlos and sol-gel olivine (in the diffusion creep regime). As seen in Figure 5, in a case where grain-size is similar, diffusion creep behavior of San Carlos olivine is nearly identical to that of sol-gel olivine (SAN 514). When grain-size is different, rheological behavior is different, but the results can be attributed to the difference in grain-size. Therefore, we conclude that in the diffusion creep regime, the rheological behavior of San Carlos olivine and sol-gel olivine is similar.

This is in contrast to the result by (e.g., Faul and Jackson, 2007) where a large difference in diffusion creep behavior between San Carlos and sol-gel olivine was reported. Their sol-gel olivine shows much larger creep strength (a factor of ~100 or more) than San Carlos olivine reported by Hirth and Kohlstedt (1995). Our results on diffusion creep in San Carlos olivine are not far from those reported by Mei and Kohlstedt (2000a) and Hirth and Kohlstedt (2003) when compared at the same temperature and pressure and grain-size. In contrast, our results for sol-gel olivine show much weaker strength than Faul and Jackson (2007) (at the same condition). The cause of this large discrepancy is unclear. Because the temperature we used is substantially lower...
than the solidus, we do not expect any effects of partial melting which might have played role in Faul and Jackson (2007) conclusions.

**A comparison with previous studies**

Our results on activation volume for diffusion creep are substantially smaller than the values reported before by Mei and Kohlstedt (2000a) (15 ± 5 cm$^3$/mol) from low pressure experiments ($P < 0.45$ GPa) and numerically derived estimates using a Markov chain Monte Carlo (MCMC) based on low-pressure data (i.e., Jain and Korenaga, 2020; 24 ± 7 cm$^3$/mol). We believe that the disagreement with previous experimental study (Mei and Kohlstedt, 2000) indicates that the uncertainties in the estimated $V^*$ by (Mei and Kohlstedt, 2000) at a low pressure range (0.1-0.45 GPa) are substantially larger than their estimate. Also a large discrepancy between our results and Jain and Korenaga, 2020 is due to the fact that their numerical calculations did not include data at high pressures. This comparison indicates the importance of high pressure studies on plastic deformation.

The results of our present study are compared with those by Silber et al. (2022) for water-saturated samples compared at the grain-size of 1 μm (m=3) and temperature of T=1100 K, stress of 50 MPa (**Figure 6**). Water-saturated samples deform faster than samples from the present study, and the pressure dependence is stronger for the samples from present than the water-saturated samples reported by Silber et al. (2022). The activation volume from the current study is 5.2 cm$^3$/mol as compared to $V^*$=1.9 cm$^3$/mol from Silber et al. (2022). The difference in $V^*$ between these two studies is partly due to the fact that in Silber et al. (2022) where samples were saturated with water, water content in olivine changes with pressure because the water solubility depends on pressure (e.g., Kohlstedt et al., 1996). In **Figure 6b**, we made a correction on the
pressure dependence of water content using the data by Kohlstedt et al. (1996). After this correction, $V^*$ from Silber et al. (2022) is $\sim 4$ cm$^3$/mol that is somewhat smaller than the present results on dry olivine.

Regarding the water effects, we use a flow law $\dot{\varepsilon} = A \cdot C_W^r \cdot \sigma^n \cdot d^{-m} \cdot \exp \left( -\frac{E^* + PV^*}{RT} \right)$, and use the results by Mei and Kohlstedt (2000) where they showed a correlation between “$r$” and $V^*$. $V^*$ is now determined to be $\sim 7$ cm$^3$/mol, and from Mei-Kohlstedt (2000) we estimated $r \sim 0.8$ that is substantially smaller than $r$ for dislocation creep ($r \sim 1.2$; Karato and Jung, 2003).

In Figure 7, we compare our data from this study with previously published dry diffusion creep data obtained at low pressure (e.g., Karato, 1986; Hirth and Kohlstedt, 1995; Mei and Kohlstedt, 2000). After normalization the results agree within error bars. We also plotted wet diffusion creep data and flow law by Silber et al., (2022) obtained at high pressure, and flow law by Mei and Kohlstedt (2000) obtained at low pressure. After normalization those are also in good agreement.

Nishihara et al. (2014) reported the results of deformation experiments of dry olivine where they identified both diffusion and dislocation creep at pressures at 3.1 - 5.4 GPa and temperature 1473 –1573 K yield activation volume of $8.2 \pm 0.9$ cm$^3$/mol and activation energy of $\sim 485$ kJ/mol. Although the activation volume they reported agree well with our results, the activation energy they estimated is much higher than those for diffusion and diffusion creep in olivine ($\sim 200$–$400$ kJ/mol; Andersson et al., 1989; Dohmen et al., 2002; Farver and Yund, 2000; Farver et al., 1994; Gardés and Heinrich, 2011; Gérard and Jaoul, 1989; Jaoul et al., 1980; Ryerson et al., 1989). We do not understand the cause for this discrepancy, but it is possible that...
the discrepancy is caused by the operation of both diffusion and dislocation creep under their experimental conditions.

On the other hand, there are some previous studies on diffusion in olivine single crystals and aggregates. For example, Fei et al. (2016) conducted Si-diffusion experiments on iron-free olivine aggregates and obtained the $V^*$ of $4.0 \pm 0.7 \text{ cm}^3/\text{mol}$ and $E^*$ of $220 \pm 30 \text{ kJ/mol}$. Smaller values of $V^*$ for forsterite ($\text{Fe}/(\text{Fe}+\text{Mg})=0$) than San Carlos olivine ($\text{Fe}/(\text{Fe}+\text{Mg})=0.1$) may be the influence of Fe.

Our results on dislocation creep regime may be compared with the previously reported results on the flow law of olivine aggregates in the dislocation creep regime under high pressures. When we compare our new results with the published results on the power-law dislocation creep including (Dixon and Durham, 2018; Karato and Jung, 2003; Kawazoe et al., 2009). In most previous studies cited above, deformation experiments were conducted at higher temperatures than our present study. When these results are extrapolated to the P-T conditions similar to ours, they predict substantially higher strength (stress) than we observed (e.g., using Karato and Jung 2003 dry flow law we obtain stress of roughly 100GPa) (except for Dixon and Durham (2018) where a low activation energy was assumed). This is likely due to the fact that dislocation creep in our experiments likely occurred in the Peierls creep regime because of low temperatures. Indeed a comparison with the results by (Mei et al., 2010) gives a better agreement.

Implications for plastic deformation in the whole upper mantle
As demonstrated before, important mechanisms of plastic deformation in most of the upper mantle are either power-law dislocation creep or diffusion creep (e.g., (Karato and Wu, 1993)). The relative importance of these two mechanisms can be estimated if all the flow law parameters (see equation (1)) are known. At the time when (Karato and Wu, 1993) was published, V* for diffusion creep was not available and therefore they estimated V* based on the experiments on diffusion-controlled dislocation recovery (Karato et al., 1993). Now with our new data from this study as well as (Silber et al., 2022), we now have experimentally constrained values of V* for diffusion creep for both water-saturated and dry conditions. In addition, we have a new result on the water content sensitivity of diffusion creep.

Therefore, we now have a complete data set for dry olivine rheology for both dislocation (Karato and Jung, 2003) and diffusion creep regime (this paper). The calculated deformation mechanism maps are shown in Figure 8 for 3, 12 GPa (at 1473 and 1673 K) for a range of water content (0 (dry), 10, 100 and 1000 ppm wt). The parameters we used are listed in Table 3. For simplicity, we assumed that m for diffusion creep is 3, n for dislocation creep is 3, and for diffusion creep is 1. And we assume that strain-rate is constant and $10^{-15} \text{s}^{-1}$.

We calculated strain-rates by these two mechanisms and determined the regime boundary (Figure 8). Because V* differ between the two deformation mechanisms, the regime boundary depends on pressure. Diffusion creep dominates over the power-law dislocation creep at relatively high pressures. One caveat in this exercise is that we did not take into account of the possible change in the rate-controlling slip system in the dislocation creep regime as suggested by (Masuti et al., 2019).

Acknowledgments
This research was supported by the National Science Foundation (EAR-1818792). RES thanks the Banting Postdoctoral Fellowship (Natural Sciences and Engineering Research Council of Canada) program administered by the Government of Canada for supporting this research. The author would like to also thank the facilities and staff of the Earth and Planetary Sciences department, at Yale University. Dr Zhenting Jiang for his help with the SEM analysis. The authors thank the beamline staff and scientists at 6-BM-B at APS. We also thank DOE and COMPRES for supporting in part our experimental efforts.

Data Availability

All data required to replicate this study are uploaded to a freely accessible repository, Harvard Dataverse, DOI: 10.7910/DVN/V98ETE (the dataset will be published upon acceptance of this paper – the private link (NOT for distribution) to the data set is here: https://dataverse.harvard.edu/privateurl.xhtml?token=dfc6afdf-1d6e-4025-b56c-93f4e869ba25).

Raw data were processed using Plot85, the open source software package developed by Stony Brook (http://www.mpi.stonybrook.edu/NSLS/X17B2/Support/Plot85/plot85.htm). The strain rates were measured from the time-stamped radiographic images using the open source software JImage, available at https://imagej.nih.gov/ij/download.html, and the proprietary software package Adobe Photoshop (www.adobe.com).
References


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Figure 6: Comparison between mechanical strength of water saturated olivine samples (Silber et al., 2022) and dry olivine samples at range of different pressures (normalized using $E^\ast=295\text{kJ/mol}$, $s=50\text{ MPa}$, $T=1100\text{ K}$, $d=1\mu\text{m}$ and $m=3$) a) comparison between Silber et al (2022) under saturated conditions without correcting for water concentration increasing with pressure, b) after applying the correction to Silber et al (2022) to account for the increase of water solubility with depth.
Figure 7: Comparison between “dry” and “wet” rheologies:

Strain-rates, obtained experimentally have been normalized to the same stress (100 MPa), temperature (1100 K) with $E^* = 295\text{kJ/mol}$, grain size (1micron) with $m = 3$, and pressure effect have been removed to only see the effect of water ($C_{\text{OH}}$) on the rheology. Data reported in this study are shown by the red square symbols. The rheological law obtained after our linear regression is shown in green dashline. Data from Silber et al., (2022) are shown by the blue square symbols and blue solid line. For comparison we also report Mei and Kohlstedt (2000) wet diffusion creep rheology (black solid line) assuming $r=0.75$ and $V^*=5\text{cm}^3/\text{mol}$. Additional data are plotted for comparison, Mei and Kohlstedt (2000) dry data (black symbol), Karato et al., (1986) dry data (red symbol) and Hirth and Kohlstedt (1995) samples with melt fraction <0.01 (purple symbol). The green shaded region represents water detectability limit of our FTIR measurements.
Figure 8: olivine deformation map under upper mantle pressure:

Stress versus grain size deformation map. The limit between diffusion and dislocation creep was calculated at T=1473K as well as 1673K and at pressure of 3GPa (left) and 12GPa (right), for m=3 (blue). The boundary between diffusion creep and dislocation creep region is represented by different shades of blue for different water content from “dry” (light blue) to 1000 ppm wt H2O (dark blue). The light blue region represents the range of grain size expected in the upper mantle and the green region represents the stress range expected in the upper mantle.
**List of Tables**

**Table 1**: Experimental conditions for each run and grain sizes for San Carlos and solgel samples. *The value of strain rate was determined on the Stress-Strain plot at the last point where diffusion creep operated (see Section 3.3).

<table>
<thead>
<tr>
<th>Deformation run</th>
<th>P (GPa)</th>
<th>T (K)</th>
<th>Sample</th>
<th>Initial grain size (μm)</th>
<th>Final grain size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAN 536</td>
<td>2.9 ± 0.3</td>
<td>1065 ± 33</td>
<td>San Carlos (K2090)</td>
<td>0.23 (0.15)</td>
<td>0.30 (0.24)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Solgel (K2091)</td>
<td>0.18 (0.12)</td>
<td>0.23 (0.15)</td>
</tr>
<tr>
<td>SAN 513</td>
<td>4.7 ± 0.9</td>
<td>980 ± 110</td>
<td>San Carlos (K1980)</td>
<td>0.17 (0.11)</td>
<td>0.18 (0.12)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Solgel (K2034)</td>
<td>0.17 (0.11)</td>
<td>0.17 (0.11)</td>
</tr>
<tr>
<td>SAN 515</td>
<td>5.9 ± 0.2</td>
<td>1080 ± 90</td>
<td>San Carlos (K2036)</td>
<td>0.21 (0.14)</td>
<td>0.78 (0.53)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Solgel (K2034)</td>
<td>0.17 (0.11)</td>
<td>0.53 (0.36)</td>
</tr>
<tr>
<td>SAN 514</td>
<td>8.8 ± 0.3</td>
<td>1249 ± 47</td>
<td>San Carlos (K1984)</td>
<td>0.39 (0.27)</td>
<td>0.98 (0.67)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Solgel (K1976)</td>
<td>0.38 (0.26)</td>
<td>0.98 (0.67)</td>
</tr>
</tbody>
</table>
Table 2: The mechanical data for diffusion creep used in the activation volume calculation. The stress value* and strain rate** were obtained from the point on time evolving stress/strain curve where diffusion creep is still operational before transition. The calculated grain size*** corresponds to time coordinate where stress and strain values were selected (see the main text for expanded discussion).

<table>
<thead>
<tr>
<th>Deformation run</th>
<th>Sample</th>
<th>Stress* (MPa)</th>
<th>Strain rate** x 10⁻⁶ (s⁻¹)</th>
<th>Calculated grain size*** (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAN 536</td>
<td>San Carlos (K2090)</td>
<td>110 ± 25</td>
<td>4.21 ± 0.21</td>
<td>0.24 (0.20)</td>
</tr>
<tr>
<td></td>
<td>Solgel (K2091)</td>
<td>55 ± 27</td>
<td>2.32 ± 0.12</td>
<td>0.18 (0.15)</td>
</tr>
<tr>
<td>SAN 513</td>
<td>San Carlos (K1980)</td>
<td>250 ± 21</td>
<td>0.49 ± 0.003</td>
<td>0.17 (0.12)</td>
</tr>
<tr>
<td></td>
<td>Solgel (K2034)</td>
<td>100 ± 13</td>
<td>0.2 ± 0.01</td>
<td>0.15 (0.10)</td>
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<tr>
<td>SAN 515</td>
<td>San Carlos (K2036)</td>
<td>510 ± 30</td>
<td>2.62 ± 0.17</td>
<td>0.35 (0.23)</td>
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<td></td>
<td>Solgel (K2034)</td>
<td>400 ± 16</td>
<td>1.74 ± 0.87</td>
<td>0.26 (0.17)</td>
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<tr>
<td>SAN 514</td>
<td>San Carlos (K1984)</td>
<td>950 ± 55</td>
<td>9.52 ± 0.48</td>
<td>0.63 (0.42)</td>
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<tr>
<td></td>
<td>Solgel (k1976)</td>
<td>940 ± 60</td>
<td>8.49 ± 0.42</td>
<td>0.62 (0.42)</td>
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</table>
Table 3: Activation volume and pre-exponential factor $A$ (s$^{-1}$ MPa$^{-n}$ μm$^m$) for different stress exponents and different activation energies. $A$ and error in $A$ are reported in log base 10.

<table>
<thead>
<tr>
<th>E* (kJ/mol)</th>
<th>m</th>
<th>T (K)</th>
<th>d (μm)</th>
<th>Stress (MPa)</th>
<th>log (A)</th>
<th>Error in log (A)</th>
<th>V* (cm$^3$/mol)</th>
<th>Error in V* (cm$^3$/mol)</th>
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<tr>
<td>295</td>
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<td>1100</td>
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<td>50</td>
<td>6.56E+00</td>
<td>6.43E+00</td>
<td>6.90E+00</td>
<td>9.00E-01</td>
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<td>3</td>
<td>1100</td>
<td>1</td>
<td>50</td>
<td>5.42E+00</td>
<td>4.89E+00</td>
<td>5.20E+00</td>
<td>4.00E-01</td>
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<td>1100</td>
<td>1</td>
<td>50</td>
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<td>1.16E+01</td>
<td>9.40E+00</td>
<td>2.30E+00</td>
</tr>
<tr>
<td>375</td>
<td>3</td>
<td>1100</td>
<td>1</td>
<td>50</td>
<td>9.93E+00</td>
<td>1.02E+01</td>
<td>7.70E+00</td>
<td>1.60E+00</td>
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</table>

**San Carlos**

**Normalization parameters**

**Calculated A and V**

<table>
<thead>
<tr>
<th>E* (kJ/mol)</th>
<th>m</th>
<th>T (K)</th>
<th>d (μm)</th>
<th>Stress (MPa)</th>
<th>log (A)</th>
<th>Error in log (A)</th>
<th>V* (cm$^3$/mol)</th>
<th>Error in V* (cm$^3$/mol)</th>
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<tr>
<td>295</td>
<td>2</td>
<td>1100</td>
<td>1</td>
<td>50</td>
<td>6.27E+00</td>
<td>6.18E+00</td>
<td>6.50E+00</td>
<td>9.00E-01</td>
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<tr>
<td>295</td>
<td>3</td>
<td>1100</td>
<td>1</td>
<td>50</td>
<td>4.94E+00</td>
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**Solgel**

**Normalization parameters**

**Calculated A and V**