

## Research report for the long-term ERI visit during 2019/02/01 to 2020/01/31

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Diopside ( $\text{CaMgSi}_2\text{O}_6$ ) is one of the major rock-forming minerals in the lower crust and upper mantle, where deformation occurs by aseismic creep. Earlier experimentally determined flow law parameters of diffusion creep of polycrystalline diopside by different groups (Bystricky & Mackwell, 2001; Dimanov et al., 2003, 2007; Dimanov & Dresen, 2005; Hier-Majumder et al., 2005) show many discrepancies. For example, the  $Q$  value varies from 364 to 760 kJ/mol in addition to large differences in the  $A$  value. Variation in composition (e.g. impurity content) in the initial source material can affect the diffusional properties of their diopside samples by altering the point defect concentration and the state of chemical bonding. Furthermore, initial grain-size distribution and the method for grain size measurements are different in the earlier studies, which can generate contrasting results of strength due to grain size sensitivity of diffusion creep (e.g. Hansen et al., 2011). In addition, there are variations in the process of sample preparation (e.g. dry or wet milling, hot-pressing conditions, chemical environment etc.) among different studies. In order to constrain a robust diffusion creep flow law for diopside, I have carried out high-temperature uniaxial creep experiments with reagent derived highly dense, fine-grained Fe-free polycrystalline diopside aggregates (+ forsterite / anorthite) with homogeneous microstructure. I was able to develop such high-quality samples for rock deformation by mixing high-purity nanosized chemical compounds in appropriate proportion and utilizing vacuum Spark Plasma Sintering (SPS) technique.

I have conducted uniaxial compression experiments on fine-grained diopside with either 4 or 10 vol% forsterite and 10 vol% anorthite. I changed the average grain size in the diopside with forsterite aggregate from 0.43 to 4.07  $\mu\text{m}$  to reveal the grain size sensitivity of the creep rate. The secondary mineral phases were added to vary the chemical environment and to stabilize the microstructure through grain boundary pinning during the creep tests. The Fo fraction was changed to vary the initial grain size for robust grain size exponent measurement. In the first case, the Di (Fo) aggregate was prepared by mixing nanosized powder of  $\text{Mg}(\text{OH})_2$  (average particle size of 50 nm, purity of 99.98%), colloidal  $\text{SiO}_2$  (average particle size of 30 nm, purity of 99.9%) and  $\text{CaCO}_3$  in appropriate molar proportion. In the second case, Di (An) aggregate was developed by mixing  $\text{SiO}_2$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$  (average particle size of 0.1  $\mu\text{m}$ , purity of 99.9%) and  $\text{Al}(\text{OH})_3$  (average particle size of 0.75  $\mu\text{m}$ , purity of 99.6%). SPS is a very efficient method to synthesize fine-grained, dense (>99 %) aggregates with little grain growth during sintering (Guignard et al., 2011; Koizumi et al.,

2020).

Mechanical data were obtained at a stepped load for a temperature range of 1050 to 1170 °C. The observed strain rates are best explained by stress and grain size exponent values of 1 and 2, respectively, and activation energy of ~720 kJ/mol, which indicates lattice diffusion creep. The flow law for Di (Fo) is as follows,  $\dot{\epsilon}_{\text{diff}} = 8.01 \times 10^{19} \mu\text{m}^2/\text{MPa}/\text{sec} \cdot (\sigma/d^2) \cdot \exp\left(-\frac{720 \text{ kJ/mol}}{RT}\right)$ . Anorthite bearing aggregate is ~3 times weaker than forsterite-bearing aggregate, probably due to the presence of aluminium. Since both of our diopside samples in the Arrhenius plot have the same activation energy, the difference in strength (~3 times) between Di (Fo) and Di (An) is explained by the difference in the  $A$  value. Therefore, the  $A$  value for Di (An), which is larger by a factor of ~3 relative to the value for Di (Fo), might be explained by increasing point defect due to Al dissolution into diopside.

I have compared previously reported diffusion creep rates of diopside in nondimensional stress and strain-rate space, constructed based on the above-mentioned diffusion creep law. It demonstrates that we can summarize all the previously obtained experimental results from different groups based on similar strain rate dependencies on stress, grain size and temperature as my new mechanical data. It is indicative of the operation of the same underlying creep mechanism, i.e. lattice diffusion creep in this case. The similar creep strengths of synthetic Fe-free aggregates in comparison to the naturally-derived Fe-bearing aggregates show that Fe has no significant effect in controlling the rate of diopside diffusion creep. The  $Q$  value determined in this study is higher than its typical value for silicate minerals (300-600 kJ/mol) (Rybacki & Dresen, 2000; Bruijn & Skemer 2014; Nakakoji et al., 2018). It is interesting to note that such a high  $Q$  value is comparable to the high activation energy reported for dislocation creep ( $760 \pm 40$  to  $719 \pm 34$  kJ/mol) in diopside (Bystricky & Mackwell, 2001; Dimanov et al., 2003). The dislocation creep is rate controlled by diffusion in the lattice (i.e. climb-control), such that essentially the same  $Q$  value for lattice diffusion and dislocation creep is well supported from the micro-processes of both the creep mechanisms.

This work has already been published. Therefore, the necessary references, creep-data and figures can be obtained from the published manuscript.

**Ghosh, S., Koizumi, S., Hiraga, T. (2020): Diffusion creep of diopside. Journal of Geophysical Research: Solid Earth. DOI: [10.1029/2020JB019855](https://doi.org/10.1029/2020JB019855).**