Strength of Orthoenstatite Single Crystals at Mantle Pressure and Temperature and Comparison with Olivine

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Highlights

Orthoenstatite single-crystal plasticity is investigated at mantle *P* and *T* conditions

Rheological laws for [001] dislocation slip in (100) and (010) planes are quantified

OPx [001](100) slip system is weaker than [001](010) slip system at mantle conditions

Olivine slip systems are weaker than OPx slip systems at most mantle conditions

Olivine and OPx weak slip systems have comparable strength in the shallow lithosphere

Abstract

Oriented single crystals of orthopyroxenes (OPx) were deformed in axisymmetric compression in the D-DIA at pressure and temperature in excess of 3 GPa and 1040°C. Two crystal orientations were tested with the compression axis parallel to either $[101]_c$ crystallographic direction, to investigate $[001](100)$ dislocation slip-system strength, or $[011]_c$ direction to investigate $[001](010)$ slip-system strength. These slip systems are the most active in orthopyroxenes. Applied differential stresses and specimen strain rates were measured in situ by synchrotron X-ray diffraction and radiography. We used these data and comparison with previously reported low-pressure flow laws for protoenstatite and orthoenstatite to determine the power law parameters for the deformation of orthoenstatite crystals, which characterize OPx dislocation slip-system strengths. Applying these laws at reasonable mantle stresses along oceanic and continental geotherms indicates that OPx $[001](100)$ slip system is weaker than OPx $[001](010)$ slip system to ~260 km depth where the strengths converge. It also indicates that both OPx slip systems are significantly stronger than olivine slip systems throughout the upper mantle, except in the upper most mantle, in the lithosphere, where OPx $[001](100)$ slip system may be as weak or even weaker than olivine $[100](010)$ easy slip system.

1. Introduction

Thermal convection of ductile peridotites in the Earth's upper mantle drives plate tectonics. Orthopyroxenes (OPx) are the second most abundant constituent of peridotite in the top 200 km, with volume fraction in excess of 15% (Green and Ringwood, 1963; Frost, 2008). They are also major constituents of the mantles of planetary bodies with enstatite-chondrite origins, such as Mercury (Ebel and Alexander, 2011). $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3$ orthoenstatite (*Pbca* space group), commonly called enstatite, is a good representative of Earth's mantle orthopyroxenes; yet, its high-temperature plasticity is still poorly constrained. This is because at low temperature (T) the stable phase is clinoenstatite (Presnall, 1995; Figure 1), while at $T > 1000^\circ\text{C}$ and pressure (P) lower than typically 1.0 GPa it transforms into protoenstatite, an unquenchable orthorhombic polymorph (*Pbcn* space group) which has similar b and c axes but an a axis almost twice as short as orthopyroxene (0.93 nm instead of 1.82 nm for the Mg end member). High shear stress on (100) plane also promotes the ortho-clinoenstatite transition, rarely observed in naturally deformed rocks, which renders difficult studying enstatite rheology at moderate temperature, even at high pressure (Raleigh et al., 1971; Coe and Kirby, 1975). Here, we present new experimental data on the high-temperature deformation of orthoenstatite single crystals, obtained in the *Pbca* stability field. These data allow estimating the effect of pressure on enstatite rheology in the dislocation creep regime and comparing orthopyroxenes and olivine strength at mantle conditions.

Dislocation creep was identified in early studies has an important deformation mechanism at high temperature in dry and wet enstatite (Raleigh et al., 1971; Kohlstedt and Vander Sande, 1973; Ross and Nielsen, 1977). This has been confirmed by further studies (Van Duysen et al., 1985; Nazé et al., 1987) which identified [001](100) as the easiest slip system, together with two other slip systems: [001](010) and [010](100). Dissociation of [001] edge dislocations in (100) plane, according to the reaction $[001] \rightarrow 1/6[001] + 5/6[001]$, is also reported in association with the ortho-clinoenstatite transformation at moderate to low temperature; glide of the strong $5/6[001]$ partial dislocation generates then the "untwinning" of one orthorhombic unit cell into two monoclinic unit cells. Dissociation of [001] dislocation has also been recently observed in naturally deformed crystals, in association with subgrain boundary formation

(Kogure et al., 2014). Bruijn and Skemer (2014) estimated recently that, in the upper mantle, orthopyroxenes with grain size larger than ~150-500 μm deform in the dislocation creep regime.

The strength contrast between olivine and orthoenstatite has significant implications for peridotite deformation and, hence, for mantle convection. However, experimental studies of olivine + enstatite aggregate plasticity, which are beyond the scope of this article, lead to confusing results (see Supplementary material for details). One approach to simplify the problem, and constrain olivine and orthoenstatite strengths in the dislocation creep regime, is to investigate the plasticity of oriented single crystals. Deforming crystals in specific crystallographic orientations allows activating one or several specific dislocation slip systems, and quantifying their individual plastic responses. The high-temperature rheology of olivine single crystals has been extensively studied (e.g., Mackwell et al, 1985; Bai et al., 1991; Raterron et al., 2012; Girard et al., 2013). In contrast, little work has been done on the rheology of orthopyroxene single crystals. Schloessin and Ranalli (1988) deformed protoenstatite single crystals by three-point bending at 1 atm and 1050°C, which activated the [001](100) slip system; but their work was focused on demonstrating the feasibility of the techniques. Mackwell (1991) reports the investigation of protoenstatite single-crystal rheology at 1 atm. The crystals were axially deformed at temperature in excess of 1300°C, with the compression axis at 45° angle from both [100] and [001] directions (along the so-called [101]_c crystallographic direction), which promotes the activation of the easiest [001](100) slip system alone with a maximum Schmid factor ($S=0.5$). Mackwell observed that they deformed by dislocation creep and, from comparison with olivine single-crystal rheology, inferred that enstatite is likely stronger than olivine under mantle conditions. Although these results on protoenstatite crystals do not directly apply to mantle *Pbca* enstatite crystals, they provided a first quantification of [001](100) slip system strength at high temperature in an orthorhombic enstatite crystal. Interestingly, Mackwell (1991) observed that creep is insensitive to oxygen fugacity despite the presence of iron, unlike that of olivine single crystals (Bai et al. 1991). He also determined a stress exponent of $n = 3.8 \pm 0.5$, similar to that of olivine single crystals ($n = 3.5 \pm 0.1$, Bai et al., 1991). More recently, Ohuchi *et al.* (2011) carried out shear deformation experiments in a Griggs apparatus on oriented orthoenstatite single crystals in contact with polycrystalline olivine ($P = 1.3$ GPa and

$T = 700^{\circ}\text{--}1100^{\circ}\text{C}$). They investigated the activity of [001](100) and [001](010) dislocation slip systems. However, in their experiments shear strain and differential stress were not measured, but constrained after the runs by quantifying the rotation of a strain marker in the run products and measurement of dislocation density in adjacent olivine, which does not allow determination of whether steady-state conditions of deformation were achieved. Also, their data for [001](100) slip system were obtained after specimens had almost entirely transformed into low clinoenstatite; so the corresponding rheological laws characterize creep in clinoenstatite and not orthoenstatite. Nevertheless, Ohuchi et al. (2011) report a first rheological law quantifying the activity of [001](010) slip system in mantle (*Pbca*) orthoenstatite. From comparison of their flow law with that of olivine single crystals, as well as comparison of the single-crystal strain with that of the adjacent polycrystalline olivine, they conclude that orthoenstatite is significantly weaker than olivine at lithospheric conditions. This result contradicts Mackwell (1991) and is also inconsistent with estimates based on field observations of orthopyroxene versus olivine strength contrast (e.g., Tikoff et al., 2010). There is clearly a need for more experiments on orthoenstatite rheology to better constrain mantle deformation.

2. Experimental methods and run-product microstructures

2.1. Starting materials

Cylindrical specimens, ~ 1.2 mm in diameter, were cored from gem-quality enstatite crystals from Tanzania ($\text{En}_{84.9}\text{Fs}_{14.7}\text{Wo}_{0.4}$, Supplementary material, Table S1), then polished on both ends to a final length of 1 to 2 mm. Two crystallographic orientations were chosen – verified to within $\pm 5^{\circ}$ by transmission electron microscopy (TEM) – with the axis of the cylinder (the compression axis) along either the $[101]_c$ direction mentioned above, or $[011]_c$ direction which is at 45° angle from both $[010]$ and $[001]$ directions and promotes the activation of [001](010) dislocation slip system with $S=0.5$. In order to compare enstatite strength with that of olivine, oriented olivine specimens were prepared in a similar way from gem-quality San Carlos olivine crystals, with their axis along either $[110]_c$ direction or $[011]_c$ direction which promote respectively $[100](010)$ or $[001](010)$ easy slip systems. In some of our experiments, enstatite crystals were deformed together with enstatite aggregates sintered from powders at

the onset of the runs. The starting powders (grain size ranging from 1 to 5 μm), were prepared from Tanzanian crystals and a crystal of enstatite ($\text{En}_{76.8}\text{Fs}_{22.6}\text{Wo}_{0.6}$, Table S1) from Bamble, Norway (details in Supplementary material). In order to control silica activity during the runs, the enstatite crystals were enrobed with a thin layer ($\sim 20\text{ }\mu\text{m}$) of San Carlos olivine powder prior to loading into the high-pressure cell. Similarly, olivine crystals were enrobed with a thin layer of enstatite powder.

2.2. Water content

Water contents were measured in the starting material and selected run products by collecting unpolarized infra-red absorbance spectra using the Nicolet Magna 560 FTIR spectrophotometer with NicPlan microscope at Texas A&M University (details in Supplementary material). Figure 2 shows the absorbance spectra for the starting material and the single-crystal products of runs EN020 and EN022. The starting material is almost dry, as showed by the quasi absence of OH band in the corresponding spectrum. Run-product hydroxyl contents (C_{OH}) were calculated using the Paterson (1982)'s calibration leading to values of 380 and 780 ppm H/Si for the sample from run EN020, and 340 ppm H/Si for the sample from run EN022. See Supplementary material for details regarding the observed hydroxyls bands. The observed differences in run-products hydroxyls contents fall within the uncertainty on the measurements (unpolarized IR beam on non-oriented crystals). Although significant, these values are much lower than saturation concentrations, which in orthoenstatite are in excess of 1,800 and 20,600 ppm H/Si at 1100°C and 1.5 GPa, respectively in Al undersaturated and saturated crystals (Rauch & Keppler, 2002; Mierdel et al, 2007), and in all crystals higher than 9,000 ppm H/Si at 1150°C and 8 GPa (Stalder et al., 2015). Whether the small amount of hydroxyls detected in our specimens has a significant weakening effect on enstatite crystals (as it has on olivine crystals, see below) is unknown.

2.3. Deformation protocol and analytical techniques

Deformation experiments were performed in the Deformation-DIA apparatus (D-DIA, Wang *et al.*, 2003) at the X17B2 beamline of the National Synchrotron Light Source (Upton, NY, USA), at P ranging from 3.0 to 6.6 GPa, T in the range 1044°–1377°C (Table 1). The explored P - T

conditions fall within the dashed rectangle in Figure 1, within the *Pbca* enstatite stability field. The assembly and protocols used here have been described elsewhere (e.g., Raterron et al., 2013; Supplementary material), and are summarized below.

We used a boron-epoxy pressure medium and, to compress the D-DIA cells, tungsten carbide anvils opaque to the X rays or transparent sintered diamond anvils. In each cell, two specimens placed in series within a BN sleeve were compressed in-between two alumina pistons. They were separated from each other and from the pistons by Re foils, which allow measuring specimen length on the collected X-ray radiographs (see below). Temperature was measured with two W3%Re-W25%Re thermocouples or, when thermocouples failed, was estimated using previously calibrated temperature-vs-power curves. The cell assembly was first compressed to the target pressure, then maintained at 1200°C and hydrostatic conditions for ~1 hour, to ensure restoration of the cold-compression damages before deformation at run conditions. At the end of the runs, specimens were quenched by switching off the furnace power, and the cell was decompressed within typically 2-3 hours.

The applied differential stress (σ) and specimen strain rates ($\dot{\epsilon}$) (Figure 3) were measured in situ by X-ray diffraction and imaging (radiography), respectively, using now classical techniques which have been described in details elsewhere (Vaughan et al., 2000; Chen et al., 2004; Raterron and Merkel, 2009; Supplementary material).

2.4. Enstatite run-product microstructures

The enstatite crystals retrieved after the experiments were still single crystals, as observed by light microscopy in between crossed Nicols in the sections prepared from the centers of the run products for FTIR and TEM measurements (supplemental Figure S1). A representative deformed [101]_c enstatite crystal was investigated by transmission electron microscopy (TEM). The aim of this investigation, carried out using the Philips CM30 microscope at the Université de Lille, was to verify that enstatite [101]_c crystals did not transform into clinoenstatite during the runs, i.e. that specimen untwinning (see introduction) was absent or limited during high-temperature deformation. Figure 4.a shows the typical microstructure observed in the [101]_c enstatite crystal which experienced more than 20% strain at pressure $P \sim 4.5$ GPa and $T \sim 1320^\circ\text{C}$, and a final differential stress σ of ~ 1.2 GPa (run EN009, Table 1).

Numerous [001] dislocations are visible, which attest that the [001](100) slip system was active during the run. Many dislocations are dissociated into two partials in (100) plane. However, the extent of the stacking faults in-between the partials is very limited, in many cases less than ~50 nm in width. Such small stacking faults could not have accommodated the large strain experienced by the specimen at high temperature. Therefore, we interpret the dissociations and associated stacking faults as cold deformation features resulting from specimen decompression at room temperature. Decompression in the D-DIA induces limited strain on the specimens. Small, somewhat aligned, sessile dislocation loops are also occasionally observed in the specimen (Figure 4.a). Such loops are usually interpreted as resulting from dislocation dipole annihilation by climb, which suggests that climb assisted dislocation glide during deformation. Also, some curved segments of edge or mixed dislocation lines exhibit little or no dissociation (Figure 4.b), which is another indication of climb since dislocations in climb configuration cannot easily dissociate into partials.

We conclude that most of the high-temperature strain in [101]_c enstatite crystals was accommodated by [001] dislocation glide in (100) plane, likely assisted by dislocation climb, and that the observed limited untwinning occurred during decompression and is not representative of enstatite high-*T* deformation. Therefore, the high-temperature rheological data obtained here for enstatite [101]_c crystals are representative of [001](100) slip-system activity.

3. Rheological results and analysis

3.1. Rheological data

Deformation data, with controlled steady-state strain rates $\dot{\epsilon}$ ranging from 2.8×10^{-6} to $6.3 \times 10^{-5} \text{ s}^{-1}$ and differential stresses (σ) in the range 130 - 1870 MPa, collected using the methods described above, are reported in Table 1. The average temperature of each (top or bottom) specimen in the compression column is calculated based on sample position, temperature at the center of the assembly and temperature gradients reported for this assembly (Raterron et al., 2013). Pressure and differential stress measured in both top and bottom alumina pistons are also reported and are usually consistent with each other within uncertainties, although significant differences are occasionally observed. These are likely due to

pressure gradients within the cell which are notable at the lowest explored temperature (~1050°C, run EN021). When analyzing the data (see below), we use the reported mean P and σ values, together with each specimen average temperature. We observed that steady-state conditions were achieved faster (for lower strain) when deforming single crystals than when deforming aggregates. This is not surprising since there are fewer deformation mechanisms in oriented single crystals than in aggregates, so equilibrium microstructures are expected to be achieved at lower strain in single crystals than in polycrystals. All steady-state strain rates reported here were obtained over specimen strain in excess of typically 3% and up to ~10% (e.g., Figure 3), except for the slowest single-crystal strain rates ($\leq 6 \times 10^{-6} \text{ s}^{-1}$) which were obtained over ~1% to 2% strain. We focus below on the data obtain for the single crystals. Data regarding polycrystalline enstatite will be the topic of a forthcoming article.

Enstatite [101]_c crystals and San Carlos olivine crystals exhibit comparable strength, i.e., comparable strain rates at given stress (Table 1, runs EN009, and EN011), while enstatite [011]_c crystals are most often stronger (Table 1, runs EN019 and EN021). A detailed analysis of these observations is given below.

Table 1 data were analyzed using the classical high-temperature power creep law:

$$\dot{\epsilon} = A \sigma^n fO_2^m \exp - \frac{E^* + PV^*}{RT} \quad (1),$$

where $\dot{\epsilon}$ is the strain rate, A is a pre-exponential factor, $\sigma = \sigma_1 - \sigma_3$ the differential stress with σ_1 the principal stress, n and m are constants, fO_2 is the oxygen fugacity, E^* the activation energy, V^* the activation volume, and R the gas constant. Since protoenstatite [101]_c crystal plasticity is insensitive to fO_2 (Mackwell, 1991), our experiments were not designed to measure an fO_2 effect; we thus assume in the following $m = 0$ for both enstatite [101]_c and [011]_c crystals. Estimates for A , n , E^* and V^* parameters for enstatite crystal rheological laws were extracted from the data using the protocols detailed below. They are reported in Table 2, together with previous estimates of Equation (1) parameters for San Carlos olivine crystals.

3.2. Quantification of the activation volume V^*

V^* was calculated by comparing the strain rates we obtained experimentally with strain rates expected at low pressure for similar crystals in similar orientations. For this calculation, we followed the method described in details by Raterron et al. (2012), assuming:

$$\dot{\epsilon}_{(P,T,\sigma)} = \dot{\epsilon}_{(P_o,T,\sigma)} \exp\left(-\frac{PV^*}{RT}\right) \quad (2),$$

where $\dot{\epsilon}_{(P,T,\sigma)}$ is the strain rate measured at our experimental P , and T and σ conditions.

$\dot{\epsilon}_{(P_o,T,\sigma)}$ is calculated using Equation (1) with $m=0$ and the A^* , n , and E^* parameters reported by previous authors for deformation at pressure $P_o < P$, and assuming our experimental T and σ values. V^* values are quantified from the corresponding slopes on $\ln(\dot{\epsilon})$ versus P/RT plots, as illustrated on Figure 5 on $\log_{10}(\dot{\epsilon})$ versus P/RT plots for convenience. For this plot, uncertainties on P and T are accounted for along the x axis by plotting P/RT minimum and maximum values within uncertainties. The uncertainty $\delta\sigma$ on σ , which is significant in high-pressure experiments (Table 1), is accounted for on the y axis by plotting two low- P strain rates for each experimental condition, using either the minimum or maximum stress values: $\sigma_{\min} = \sigma - \delta\sigma$ or $\sigma_{\max} = \sigma + \delta\sigma$. Maximum $V_{\max}^*$ and minimum $V_{\min}^*$ arise from the resulting two slopes, leading to an average $V_i^* = 1/2(V_{\max}^* + V_{\min}^*)$ with uncertainty $\delta V_i^* = 1/2(V_{\max}^* - V_{\min}^*)$. The final V^* and its uncertainty for a given crystal orientation is the weighted mean of all obtained $V_i^* \pm \delta V_i^*$ values.

For enstatite $[101]_c$ crystals, we used for comparison the rheological law obtained at $P_o = 1$ atm reported by Mackwell (1991), for protoenstatite crystals deformed in the same orientation. These later data are the only available for glide of $[001](100)$ dislocations in an orthorhombic enstatite structure. Protoenstatite and orthoenstatite have almost identical structure in the (100) plane along the $[001]$ direction, which makes this comparison pertinent. Figure 5.a shows $\log_{10}(\dot{\epsilon})$ versus P/RT for these specimens. From the slopes in Figure 5.a, we obtained the mean $V^* = 13.6 \pm 3.9 \text{ cm}^3/\text{mol}$ characterizing the effect of pressure on $[001](100)$ slip system activity.

For enstatite [011]_c crystals, within which the (010)[001] slip system is activated, we used the rheological law reported for orthoenstatite at $P_0 = 1.3$ GPa by Ohuchi et al (2011), for simple shear deformation in (010) plane in the [001] direction. With $\dot{\gamma}$ and τ the simple shear strain rate and stress, we have [011]_c crystal compression strain rate $\dot{\epsilon} = 1/2 \dot{\gamma}$ and the differential stress $\sigma = 2\tau$. Figure 5.b shows $\log_{10}(\dot{\epsilon})$ versus P/RT for [011]_c crystals, leading to the mean $V^* = 8.3 \pm 3.8$ cm³/mol for enstatite [001](010) slip system.

3.3. Quantification of the stress exponent n

A recurrent issue in high-pressure deformation experiments is the large uncertainty on stress which results from i) large heterogeneities in the stress field within polycrystalline materials with strong elastic and plastic anisotropy, and ii) uncertainties in the measurements of small d -spacing variations (above and Supplementary material). This prevents quantifying the n parameter in Equation (1) using classic $\ln(\dot{\epsilon})$ versus $\ln(\sigma)$ plots. Following the method proposed by Bollinger et al. (2015), we thus quantified enstatite crystal stress exponent n_{En} by comparison with San Carlos olivine stress exponent n_{Ol} , which value of 3.5 has been accurately quantified in low- P experiments with accurate stress measurements (Bai et al., 1991). This value is also accepted by the community as representative of San Carlos olivine deformation at mantle conditions. In experiments where enstatite and olivine crystals are stacked atop each other in the compression column, both crystals experience the same differential stress. For a given stress and strain rate increment, we have:

$$n_{En} = n_{Ol} \times \left(\ln \frac{\dot{\epsilon}_{En}^i}{\dot{\epsilon}_{En}^{ii}} / \ln \frac{\dot{\epsilon}_{Ol}^i}{\dot{\epsilon}_{Ol}^{ii}} \right) \quad (3),$$

where $\dot{\epsilon}_{En}^i$ and $\dot{\epsilon}_{En}^{ii}$ are enstatite strain rates measured respectively before and after the stress increment (i.e., consecutive strain rates), and $\dot{\epsilon}_{Ol}^i$ and $\dot{\epsilon}_{Ol}^{ii}$ are those for olivine.

Four values of [101]_c crystal stress exponent were extracted from our data. Assuming in Equation 3 the exponent $n = 3.5$ for olivine, we obtain $n = 2.98, 2.76, 4.02$, and 4.07 , from the four stress increments in runs EN009 and EN011. This leads to the mean $n = 3.5 \pm 0.7$ for enstatite [101]_c crystals, a value which characterizes [001](100) slip system. This value is in good agreement with the value of $n = 3.8 \pm 0.5$ reported for protoenstatite by Mackwell (1991). We

thus conclude that $[101]_c$ enstatite crystals exhibit within uncertainty the same stress sensitivity than that of San Carlos olivine crystals.

Similarly, three values for enstatite $[011]_c$ crystal stress exponent ($n = 3.61, 5.79$, and 2.88) were obtained from three stress increments carried out during run En019 and En021, assuming that enstatite $[101]_c$ crystal stress exponent is $n = 3.5$ (see above). This leads to the mean $n = 4.1 \pm 1.5$ for enstatite $[011]_c$ crystals. Despite the large uncertainty, we have confidence in our measurement since Ohuchi et al. (2014) report a similar value (4.2 ± 0.3) for $[001](010)$ slip system. The high stress sensitivity of enstatite $[011]_c$ crystals is illustrated on Figure 3, where changes in the differential stress affect more $[011]_c$ crystal strain rate than $[101]_c$ crystal strain rate. We thus conclude that enstatite $[011]_c$ crystals are more sensitive to stress variations than both olivine crystals and enstatite $[101]_c$ crystals.

The n values reported here for both enstatite $[101]_c$ and $[011]_c$ crystals, obtained by direct and indirect comparison with olivine crystals stress sensitivity, are consistent within uncertainties with all experimental data reported in Table 1. This is illustrated in Figure 6 which shows $\log_{10}(\dot{\epsilon})$ versus $\log_{10}(\sigma)$ plots for both crystal orientations at reference $P = 5$ GPa and $T = 1400^\circ\text{C}$. For these plots, the P correction was calculated using the V^* values obtained above, while the T correction was operated using the E^* values obtained in the next section (see Table 2). Note, however, that because of the large uncertainties on experimental stress, which propagate onto the corrected strain rates, accurate estimates of crystal stress sensitivities cannot be directly extracted from such a plots.

3.4. Quantification of activation energy E^* and A parameters

To complete the determination of enstatite crystal rheological law (Equation 1), one needs to quantify the activation energy E^* and pre-exponential factor A for each crystal orientation. These two parameters are strongly coupled, once the activation volume V^* and stress exponent n are known, which is the case here (see above). They can thus be extracted together from the high-pressure data by minimizing the standard deviation in *Calculated stress* versus *Measured stress* plots, as well as that in *Calculated strain rate* versus *Measured strain rate* plots. This is illustrated in Figure 7, where the *Calculated stresses* are obtained from the

Measured strain rate at experimental conditions (Table 1) – using in Equation 1 the V^* and n parameters obtained above (see Table 2), and assuming different sets of A and E^* parameters – and where the *Calculated strain rates* are obtained from the *Measured stresses* using the same set of rheological law parameters. For these plots, the uncertainties on calculated parameters (either stress or strain rate) are obtained by propagating through Equation 1 the uncertainties on experimental values (i.e., on either strain rate or stress).

For enstatite $[101]_c$ crystals, the best-fitting set of parameters is $A = 5.20 \times 10^{-6} \text{ MPa}^{-n} \text{ s}^{-1}$ and $E^* = 225 \pm 50 \text{ kJ/mol}$. Uncertainty on E^* was estimated by varying E^* and adjusting A to keep a reasonable correlation between calculated and measured stresses, with a fitted slope of 1, until the calculated strain rate values step out of the observed experimental range with relative errors exceeding 20%. The A parameter is extremely sensitive to small variations of E^* (lever arm effect to infinite temperature), so its uncertainty is not relevant. Note that, despite the large scatter in the experimental points, most of them are accounted for within uncertainties using the flow laws parameters reported in Table 2. The obtained E^* value is significantly lower than the one reported by Mackwell (1991) for protoenstatite $[101]_c$ crystals ($820 \pm 80 \text{ kJ/mol}$). Fitting our data with Mackwell's E^* value leads to a very poor correlation between calculated and measured stresses, and to calculated strain rates two order of magnitude higher than the measured ones, i.e. our data cannot be fitted using Mackwell's activation energy in Equation 1. This discrepancy is illustrated in supplementary Figure S2.a, where Mackwell's data obtained at low P and our high- P data points are plotted on $\log_{10}(\dot{\epsilon})$ versus $1/RT$ plots at reference pressure and stress, and clearly exhibit different slopes. Possible explanation of this discrepancy are discussed below (Section 4).

For enstatite $[011]_c$ crystals, the best set of parameters is $A = 1.83 \text{ MPa}^{-n} \text{ s}^{-1}$ and $E^* = 450 \pm 30 \text{ kJ/mol}$, which characterizes $[001](010)$ slip system activity. Despite fewer data points than in the previous case, we obtained a very good correlation between experimental and calculated values. Ohuchi et al. (2011) report an activation enthalpy of $114 \pm 18 \text{ kJ/mol}$ at $P_o = 1.3 \text{ GPa}$ for $[001](010)$ slip system. Taking into account the activation volume $V^* = 8.3 \text{ cm}^3/\text{mol}$ obtained here for this slip system (Table 2), i.e. subtracting the $P_o V^*$ contribution to the apparent activation enthalpy, Ohuchi et al. (2011)'s value leads to an activation energy of 103 kJ/mol ,

much lower than the one obtained here (Figure S3.b). Our data cannot be fitted with such low activation energy, which question about the discrepancy between Ohuchi et al. (2011)'s and our value for [001](010) slip system activation energy (further discussion in Section 4).

4. Discussion and geological significance

We report here complete rheological laws, including for the first time pressure sensitivities, for orthoenstatite [001] dislocation slip in either (100) plane or (010) plane. Table 2 gives Equation 1 parameters for [101]_c and [011]_c crystals, characterizing respectively [001](100) and [001](010) dislocation slip systems. These result are critical to better understand the role of enstatite in the plasticity of upper mantle rocks in regime of deformation involving creep of dislocations, such as the dislocation creep regime or dislocation-assisted grain-boundary sliding regime (disGBS, Hirth and Kohlstedt, 1995; Hansen et al., 2011), and to input enstatite plastic properties into multiscale modeling for peridotite deformation (e.g., Raterron et al., 2014).

We compared our high-pressure data with previously reported low-pressure rheological laws (Figure 5). The conclusions drawn for orthoenstatite [001](100) slip system rely on the assumption that glide of [001] in (100) plane is comparable in both the protoenstatite and orthoenstatite structures. For all data, we also assumed that steady state condition of deformation were achieved during the experiments, an assumption not necessarily verified in Ohuchi et al.'s (2011) experiments (see introduction). Another possible differences between studies, is crystal hydroxyl contents (see section "Water content"). Although no data are available on the water effect on enstatite rheology (for olivine crystal: Mackwell and Kohlstedt, 1985; Girard et al., 2013), it is possible that different water (hydroxyl) contents result in different plastic responses. Finally, let us emphasize that Equation 1 parameters are correlated with one another, i.e. that the error on a given parameter can significantly affect the value of another parameter when reducing the data. These differences between crystals structures, hydroxyl contents, experimental measurements and data reduction methods, can result in significant differences in the obtained rheological parameters. With these reservations in mind, we discuss below our rheological results.

4.1 Reported flow law parameters

Our data show that pressure has a hardening effect on orthoenstatite dislocation slip systems, with apparent activation energies of $V^* = 13.6$ and $8.3 \text{ cm}^3/\text{mol}$ for [001](100) slip system and [001](010) slip system, respectively. These V^* values are reasonable when compared with those reported for other mantle silicates: San Carlos olivine slip-system V^* values are between 3 and $12 \text{ cm}^3/\text{mol}$ (Table 2), and a value of $V^* = 17 \text{ cm}^3/\text{mol}$ has been reported for diopside easiest slip system (Amiguet et al., 2009). Without atomistic modeling for orthoenstatite dislocation cores and associated mobility, it is speculative to discuss the physical meaning of the apparent activation volumes we obtained; these values, nonetheless, characterized empirically the effect of pressure on enstatite slip-system activities.

We obtained values of $n = 3.5$ and 4.1 for the stress exponent characterizing enstatite [001](100) and [001](010) slip systems, respectively. These values are in good agreement with those reported for these slip systems at low pressure in proto- and ortho-enstatite (Mackwell, 1991; Ohuchi et al., 2011). Dislocation creep at high temperature is often associated with the stress exponent $n \geq 3$ and up to 4.5, which is explained by the micromechanical model proposed by Weertman and Weertman (1975). In the framework of this model, exponent $n > 3$ characterize climb-controlled dislocation creep. The n values obtained here fall in the range of values expected from the Weertman's model and are consistent with the present experimental set up, where crystal strain is mostly accommodated by dislocation glide. It is likely that dislocation climb have contributed to accommodating some strain in $[101]_c$ crystals (see section *[101]_c enstatite run-products microstructures*), as well as in $[011]_c$ crystals which exhibits a stress exponent $n > 4$.

The values obtained here at high pressure for the activation energy - $E^* = 225$ and 450 kJ/mol for respectively [001](100) and [001](010) slip system - differ significantly from the values previously obtained at low pressure for these slip systems in proto- and ortho-enstatite. Slip system activation energy is generally associated with the controlling deformation mechanism; different activation energies suggest that different mechanisms may control deformation at low pressure and high pressure. In the case of high-temperature dislocation creep in olivine crystals, it has been shown that several mechanisms, either in parallel or series,

contribute to a given slip-system plastic response; which requires using combinations of rheological laws in the form of Equation 1 to account for experimental observations (Bai et al., 1991, and Table 2). Therefore, using here a single Equation 1 may be an oversimplification resulting in variations with pressure in the apparent E^* . Other possible explanations for the discrepancy are: i) changes with pressure in the geometry of the dislocation cores which can affect the lattice friction dislocations have to overcome in their motions, hence the activation energy; along this line it is worth recalling that orthopyroxenes elastic moduli exhibit a highly anomalous non-linear pressure dependence (Webb and Jackson, 1993). ii) Different minor-element or proton (hydroxyl) concentrations in the crystals investigated in different studies; and iii) as mentioned above, propagation of errors among flow-law parameters in data reduction. We conclude that the activation energies reported here are apparent activation energies characterizing enstatite dislocation slip systems plastic response in the framework of the present single-Equation 1 flow laws.

The flow laws reported here (Table 2), thus provide first-order estimates of slip-system activities as function of pressure, temperature and stress; they are applied below to investigate the relative activities of orthopyroxenes and olivine slip systems in different geodynamical contexts.

4.2. Extrapolation to Mantle conditions

Figure 8 shows the relative activity of orthopyroxenes (OPx) and olivine slip systems along continental and 20-Ma oceanic geotherms (see Raterron et al., 2012, their Fig. 2.a). The figures are limited to 300-km depth since deeper in the mantle orthoenstatite transforms into high- P clinoenstatite (Figure 1). The activated slip systems in each mineral and crystal orientation are listed in Table 2. The proxy for slip-system activity is here the relative crystal strain rate, as obtained using Table 2 flow-law parameters normalized by that of olivine $[110]_c$ crystal strain rate which characterizes olivine easiest slip system at low pressure. To calculate olivine-crystal strain rates, we assumed an oxygen fugacity of FQM-2, i.e. two order of magnitudes below the fayalite-quartz-magnetite buffer fO_2 , which is a reasonable average value for the upper mantle (a review in Herd, 2008). In Figures 8 a-d we use the previously-reported dry olivine flow laws (Bai et al., 1991; Raterron et al., 2009, 2012), while OPx flow laws are from the present study

(Table 2). The strain rates in Figures 8.a and 8.b were obtained assuming a constant differential stress of 1 MPa, which is a reasonable value in the mid upper mantle (Bürgmann and Dresen, 2008); higher stresses up to 100 MPa are estimated at moderate temperature ($\sim 900^\circ\text{C}$) in lithospheric shear zone. Increasing stress on Figure 8 only increases the relative strain rates of OPx $[011]_c$ crystal (Figures 8.c and 8d), since all other crystals share the same stress sensitivity in Equation 1. Finally, wet olivine crystals are weaker than dry crystals, respectively by factors of ~ 1.5 , 2.5 and 2.0 on differential stress when deformed along $[110]_c$, $[011]_c$ and $[101]_c$ directions (Mackwell et al., 1985; Girard et al., 2013). These weakening factors translate respectively into factors of ~ 4 , 25 and 11 on crystal strain rates, accounting for olivine stress exponent $n = 3.5$. This effect weakens olivine crystal with respect to enstatite crystals, as illustrated in the supplementary material (Figures S3.a and S3.b).

In most upper mantle geodynamical contexts (oceanic, continental, with dry or wet olivine, low or high stress regime) olivine crystals are weaker than enstatite crystals, except at depth shallower than 80 km and 60 km in respectively the continental and oceanic lithosphere. Indeed, in the uppermost mantle, enstatite $[101]_c$ crystals may become as weak or weaker than olivine $[110]_c$ crystals. We thus conclude that in the upper mantle, olivine slip systems are weaker than OPx slip systems, by one or two order of magnitude on the strain rate, except in the shallow lithosphere where enstatite $[001](100)$ slip system may be as weak or weaker than olivine easy $[100](010)$ slip system. Figures 8.a and 8.b also show that, at reasonable stress conditions (i.e., at $\sigma = 1$ MPa), $[001](100)$ slip is weaker than $[001](010)$ slip system in OPx, to ~ 260 km depth (see also Figures S3 a,b). At that depth, both OPx slip systems exhibit comparable activities, which should translate into weaker CPO in the deformed rocks. Although orthopyroxenes crystals do not exhibit strong elastic anisotropies (Mainprice et al., 2000), this may contribute to the seismic anisotropy attenuation observed in the mid and deep upper mantle (Gung et al., 2003). Interestingly, at about 60 - 70 km depth under young oceans, i.e., at temperature circa 1200°C , all olivine slip systems and OPx easy $[001](100)$ system exhibit activities within one order of magnitude. This possibly weakens the rocks and may produce a locally weak seismic anisotropy, which may contribute to that expected at ~ 70 km depth beneath oceans at the lithosphere-asthenosphere boundary (e.g., Rychert and Shearer, 2009).

4.3. Comparison with naturally deformed orthopyroxenes

Our results are consistent with the classical microstructures observed in naturally deformed orthopyroxenites (e.g., Christensen and Lundquist, 1982; Skemer et al., 2006; Xu et al., 2006; Tommasi et al., 2008) and orthopyroxenite dikes within a host dunite (Tikoff et al., 2011). These microstructures show that i) orthopyroxenes exhibit crystal preferred orientations, with [100] crystallographic axis subnormal to the foliation and the [001] axis subparallel to lineation (so called Type-AC fabric, see Jung et al., 2010), consistent with an active [001](100) slip system, and ii) that olivine appears weaker than orthopyroxenes, which is expected in the dislocation creep regime given the high strength of OPx slip systems relative to that of olivine slip systems (Figure 8). Interestingly, Skemer et al. (2006) note that the OPx Type-AC fabric - that they observed in the Cima di Gagnome peridotite massif (central Alps) and attribute to a low-temperature ($\sim 800^{\circ}\text{C}$) deformation event - is “unusually strong” ; an observation in good agreement with our prediction of OPx [001](100) slip high activity at lithospheric conditions (Figure 8). Strong OPx Type-AC fabrics are also reported by Jung et al. (2010) in xenoliths from Spitsbergen, Svalbard, which also originated from a lithospheric deformation event at moderate temperature (850°C - 1000°C). These authors, however, report different OPX fabrics in the same xenoliths, notably the Type-BC fabric with [100] axis subnormal to the foliation and the [010] axis subparallel to lineation, which suggests a dominant [001](010) slip system and could be associated with high hydroxyls contents. If this observation is confirmed by further studies, it suggests a possible transition in OPx dominant slip system with increasing water content. Let us, thus, emphasize that the rheological laws reported here for orthopyroxenes apply to crystals with moderately low hydroxyl contents (typically < 800 ppm H/Si).

Acknowledgements

This research was supported by the Consortium for Materials Properties Research in Earth Sciences (COMPRES) under NSF Cooperative Agreement EAR 06-49658, as well as the Agence Nationale de la Recherche (ANR) Grant BLAN08-2_343541 "Mantle Rheology". Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. The TEM national facility in Lille (France) is supported by the Conseil Regional du Nord-Pas-de-Calais, the European Regional Development Fund (ERDF), and the Institut National des Sciences de l'Univers (INSU, CNRS). Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. CH was supported by NSF grant EAR-1045820. The authors thank Steve Mackwell for providing them with details on the experiments he carried out on protoenstatite crystals. The original manuscript was improved in response to thoughtful suggestions by Ian Jackson and an anonymous reviewer.

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631 Figure 1: Part of the MgSiO_3 phase diagram (after Presnall, 1995) indicating the stability field of
632 five enstatite phases with their respective space groups. Low iron contents do not significantly
633 affect the field boundaries (e.g., Woodland, 1998). The grey line shows a classic continental
634 geotherm (Turcotte and Schubert, 2002). See text for further explanation.

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Figure 2: FTIR absorbance spectra of enstatite single-crystal starting material and products of run EN020 and EN022 (indicated). The starting material exhibits very low hydroxyl contents. Variable hydroxyl contents are detected in the run products: $C_{OH} = 340$ (EN022), and 380 and 780 (EN020) ppm H/Si. Although significant, these concentrations are low when compared to saturation concentrations at run conditions (see text for details).

Figure 3: Example of a strain vs time graph, here for an OPx [101]_c crystal (solid square) and an OPx [011]_c crystal (open diamonds) deformed together at constant $P \sim 5.3$ GPa and $T \sim 1320^\circ\text{C}$ during run EN019 (Table 1). Vertical dashed lines indicate changes in differential stress conditions; steady-state stress values are indicated. The numbers near the straight slopes indicate steady-state strain rates (in 10^{-6} s^{-1}).

Figure 4: Weak-beam dark-field TEM micrographs of an enstatite [101]_c crystal deformed to 20% strain at $P \sim 4.5$ GPa, $T \sim 1320^\circ\text{C}$ and final differential stress $\sigma \sim 1.2$ GPa (run EN009, Table 1). Numerous [001] dislocations are visible, many of them dissociated into two partials in (100) plane, as showed by the fringe patterns revealing stacking faults (i.e. enstatite “untwining”) in

663 between partials. A) The diffraction vector g is indicated. Note that stacking faults exhibit little
664 extensions. Small aligned sessile dislocation loops are occasionally observed (small arrows),
665 suggesting dipole annihilation by climb during deformation. B) Same orientation as above;
666 curved segments of edge or mixed dislocation lines exhibit little or no dissociation (small
667 arrows), suggesting a climb configuration.

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Figure 5: $\log_{10}(\dot{\epsilon})$ versus P/RT plots for a) enstatite $[101]_c$ crystals and b) enstatite $[011]_c$ crystals. P and T uncertainties are accounted for on the x axis by plotting for each high- P data point (Table 1) the minimum and maximum P/RT values within uncertainties. σ uncertainty is accounted for on the y axis by plotting the corresponding minimum and maximum strain rates calculated from previously reported low- P flow laws (authors and pressure indicated). A minimum slope (dashed line) and a maximum slope (plain lines), i.e. two values of V^* , are thus generated for each high- P data point, leading to the indicated weighted mean V^* .

Figure 6: $\log_{10}(\dot{\epsilon})$ versus $\log_{10}(\sigma)$ plots at reference pressure of 5 GPa and temperature of 1400°C for enstatite a) [101]_c crystals and b) [011]_c crystals. On these plots, experimental strain rates obtained at different P and T (Table 1) were corrected using in Equation 1 the V^* and E^* values reported in Table 2. The solid lines corresponds to the rheological laws using the parameters reported in Table 2 for enstatite crystals.

Figure 7: Calculated stress vs Measured stress plots (a and c), and $\log_{10}(\text{Calculated strain rate})$ vs $\log_{10}(\text{Measured strain rate})$ plots (b and d) for the indicated orthoenstatite crystals. Measured values and uncertainties are reported in Table 1. Calculated values with propagated uncertainties are obtained using the above V^* and n values (Table 2), and adjusting A and E^* to best fit both stress and strain-rate plots. The dashed lines, fitted to the data points, show on the stress plots the perfect correlation $y=1x$. On the strain-rate plots, they correspond to the best fit with slope 1.07 and 1.03 for $[101]_c$ and $[011]_c$ crystals, respectively.

Figure 8: Olivine (Ol) and OPx crystal relative strain rates as proxies for their activities along a 20-Ma oceanic and a continental geotherm, for the indicated differential stress σ . The activated slip systems in each mineral and crystal orientation (indicated) are listed in Table 2. Strain rates are normalized by that of [110]_c olivine, calculated at FQM-2 in dry conditions.

C)

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D)

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