Forsterite to wadsleyite phase transformation under shear stress and consequences for the Earth’s mantle transition zone

S. Demouchy\textsuperscript{a,}\textsuperscript{*}, D. Mainprice\textsuperscript{a}, A. Tommasi\textsuperscript{a}, H. Couvy\textsuperscript{b}, F. Barou\textsuperscript{a}, D.J. Frost\textsuperscript{c}, P. Cordier\textsuperscript{d}

\textsuperscript{a} Université Montpellier 2 & CNRS, UMR 5243, Géosciences Montpellier, Montpellier, France
\textsuperscript{b} Florida International University, Department of Mechanical and Materials Engineering, Center for the Study of Matter at Extreme Conditions, Miami, USA
\textsuperscript{c} Bayerisches Geoinstitut, University of Bayreuth, D-95440 Bayreuth, Germany
\textsuperscript{d} Université Lille 1 & CNRS, UMR 8207, Unité Matériaux et Transformation, Villeneuve d’Ascq, France

1. Introduction

Seismic anisotropy is a characteristic feature of the upper mantle, where it is dominantly associated with a strain-induced preferred orientation of anisotropic olivine crystals. Although less developed, analysis of surface wave data also suggests the existence of a weak seismic anisotropy in the transition zone (e.g., Montagner and Kennett, 1996; Trampert and van Heijst, 2002; Begheim and Trampert, 2004; Visser et al., 2008). At approximately 410 km of depth, orthorhombic olivine \((\text{Mg,Fe})_2\text{SiO}_4\) undergoes a polymorphic phase transformation to orthorhombic wadsleyite \(\beta-(\text{Mg,Fe})_2\text{SiO}_4\) that has a strong intrinsic elastic anisotropy (10% for P- and 13% for S-waves, e.g., Mainprice et al., 1990). Anisotropy at these depths may thus record a crystal-preferred orientation (CPO) of wadsleyite either formed by dislocation creep-assisted deformation (Tommasi et al., 2004) or inherited from the parent phase CPO (olivine in a downwelling flow). Deeper, at about 520 km depth, wadsleyite transforms to ringwoodite \(\gamma-(\text{Mg,Fe})_2\text{SiO}_4\), which has a
cubic symmetry and a weaker intrinsic elastic anisotropy (3% for P- and 8% for S-waves, e.g., Mainprice et al., 1990) and is therefore an inappropriate candidate to produce significant seismic anisotropy (Carrez et al., 2006; Tommasi and Mainprice, 2008).

The phase transformation of forsterite to wadsleyite has a fast kinetics and can occur within 5 min at pressures and temperatures relevant to the transition zone (Katsura and Ito, 1989). In high-pressure experiments, it is not rare however to observe metastable forsterite if the initial grain size of parent forsterite was large (Dupas-Bruzek et al., 1998). The presence of water has been suggested to enhance the kinetics of the forsterite to wadsleyite phase transformation (Wood, 1995; Kubo et al., 1998). Moreover, the mantle is undergoing convection, thus phase transformations do not occur in a static environment, but are syn-deformational. They may be affected by deviatoric stresses and by the internal deformation of the crystals.

Few attempts have aimed to study the rheological properties of olivine and wadsleyite at transition zone pressure and temperature conditions. Using a direct shear deformation assembly, Dupas-Bruzek et al. (1998) have shown that dislocation climb is an essential mechanism accommodating the deformation of wadsleyite at 15 GPa and 900 ◦C. Subsequently, Thurel et al. (2003a,b) performed direct shear deformation experiments on iron-bearing wadsleyite at higher temperature (1300 ◦C). They found that dislocation glide is the main active deformation mechanism at transition zone conditions and that the easiest slip systems were 1/2 [1 1 1]/(0 1 0), [1 0 0]/(0 1 0), and [1 0 0]/(0 1 1). Unfortunately, those two studies did not measure the CPO of the deformed aggregates.

Using a direct shear setup experiment in a multi-anvil press to deform polycrystalline wadsleyite aggregates under transition zone conditions, Couvy (2005) obtained wadsleyite CPO characterized by a [1 0 0] maximum at low angle to the shear direction, [0 1 0] axes concentrated roughly perpendicular to the shear direction in the shear plane, and [0 0 1] axes aligned toward the normal of the shear plane. This wadsleyite CPO was however found to be partially inherited from a forsterite CPO formed in the early stages of these stress-relaxation experiments as described by Couvy et al. (2004). Effectively, when forsterite (fo) transforms to wadsleyite (wads), the crystallographic lattices of the two minerals can be related by the relationships (1 0 0)fo/(0 1 1)wads and [0 0 1]fo/[1 0 0]wads derived from the parallelism of the oxygen sub-lattices. Using this relationship, one can predict the texture of wadsleyite from the forsterite texture or vice-versa.

More recently, Xu et al. (2005) have studied the development of CPO in wadsleyite during plastic deformation in a rotational Drickamer apparatus at a pressure of 15 GPa and temperatures of 1227, 1327 and 1427 ◦C. Their samples show alignment of the [0 1 0] axes in the shear direction and a concentration of the [0 0 1] axes normal to the shear plane. These CPO are consistent with neither the dislocation structures nor the CPO observed in previous deformation experiments on wadsleyite.

Here, we present coupled phase-transition and deformation experiments performed at transition zone pressure and temperature conditions to study the effect of deformation on the forsterite to wadsleyite phase transformation, the resulting CPO, and the implications of the results for the seismic properties of the upper part of Earth’s mantle transition zone.

2. Experimental procedure and analytical techniques

2.1. High-pressure shear experiments

A series of high-pressure experiments have been performed at the Bayerisches Geoinstitut in the 6–8 multi-anvil apparatus using the direct shear assembly developed by Karato and Rubie (1997). In this assembly, a 200-μm-thick slice of hot-pressed polycrystalline forsterite (Mg2SiO4) is sandwiched between two dense alumina (99.97%) pistons cut at 45 ◦C/min. The increase in temperature allows both plastic shear and phase transformation to take place in the sample column during compression to be converted, at high temperature, to plastic shear strain in the sample.

Deformation experiments were performed at 16 GPa and 1400 ◦C, well within the stability field of wadsleyite (Katsura and Ito, 1989). The hot-press assembly and deformation assembly are heated using a LaCrO3 furnace. A cylindrical zirconia sleeve is employed as a thermal insulator. The temperature is monitored using a W5Re–W26Re thermocouple inserted axially into the furnace inside an alumina tube. In the deformation assembly, a disc of Re was placed between the thermocouple and the top of the capsule to prevent the thermocouple from puncturing the capsule. Pressure was first raised at room temperature. Then the temperature was increased with a rate of 200 ◦C/min. The increase in temperature allows both plastic shear and phase transformation to take place in the specimen. Heating was maintained constant for durations of 1, 15, 35, 40, and 60 min before quenching by shutting down

Table 1

<table>
<thead>
<tr>
<th>Run #</th>
<th>Starting material</th>
<th>Nominal pressure (GPa ± 0.5 GPa)</th>
<th>Temperature (°C)</th>
<th>Duration (min)</th>
<th>Recovered phase</th>
<th>Sample thickness (μm)b</th>
<th>Grain size range (μm)c</th>
<th>Mean grain size (μm)c</th>
<th>Water contentc (wt ppm H2O)</th>
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<td>180</td>
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<td>6</td>
<td>1100</td>
<td>180</td>
<td>α</td>
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<td>12.8</td>
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<td>16.2</td>
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<td>40</td>
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<td>2–51</td>
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α forsterite; β, wadsleyite.

a Temperature was uncertain, thermo-couple was broken and temperature was estimated from power input.

b Thickness after the deformation experiment, thickness before the experiment was 200 ± 5 μm.

c Water content was obtained using the calibration of Paterson (1982) from unpolarized infrared radiation, uncertainties are ±30% on the water content.

d Average of the apparent grain size. True average diameter of grains d = Kf × L, where Kf is a constant depending on the grain shape equals to 1.5 for equidimensional grains and L is the mean interval between two grain boundaries (i.e., ≈mean apparent grain size obtains suing EBSD maps), see Etheridge and Wilkie (1981) and Vauchez (1987) for details.
the electrical power to the furnace. Thermal gradients across the forsterite capsule are estimated to be approximately 50 °C across the entire multi-anvil assembly (Canil, 1991, 1994). They are significantly less along the thin slab of wadsleyite in a simple shear assembly. Experimental conditions for all runs are presented in Table 1.

In previous deformation experiments (Couvy et al., 2004; Couvy, 2005), a platinum strain marker was added, but it was poorly preserved due to deformation and grain growth in the experiments. Thus, in the present study, no strain marker was added to the experimental set-up. After deformation, the samples are recovered and prepared for microstructural characterizations by scanning electron microscopy (SEM), electron back-scattered X-ray diffraction (EBSD), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR).

2.2. SEM observations, EBSD mapping and data treatment

Oriented polished sections have been prepared from the recovered specimens (with sections being cut perpendicular to the shear plane, which contained the shear direction). SEM imaging and EBSD analyses were obtained with a CamScan X500FE CrystalProbe equipped with an EBSD system at Geosciences Montpellier (France). The operating conditions were 15 kV, 3.5 nA, and a working distance of 20 mm under low vacuum conditions (5 Pa of gaseous Nitrogen) to avoid charging of the experimental samples. Texture analysis was performed using the EBSD technique. EBSD requires high integrity of the analyzed surface layers. A final polishing with colloidal silica suspension was performed to remove the damage in near surface layers introduced by mechanical grinding and polishing. The samples were not carbon-coated. The incoming electron beam is at an angle of 20° to the horizontal sample stage. Interaction of the electrons with a small volume of the sample (a few nm³) produces a diffraction pattern that reflects the crystal symmetry and orientation. This pattern is projected onto a phosphor screen and recorded by a digital CCD camera. The image is then processed and indexed in terms of crystal orientation using the CHANNEL5 software from Oxford Instruments HKL.

For each sample and through automation of this procedure, we obtained crystallographic orientation maps covering almost the entire surface of the thin slab of deformed wadsleyite (usually 1.5 mm long and ~150 μm wide) or, in the undeformed samples, 2/3 of the forsterite starting material. Sampling steps were 10 μm for the forsterite starting material and 1 μm for wadsleyite, because of the smaller grain sizes in the latter. Detailed maps with a sampling step of 0.2 μm were also acquired in selected areas of the deformed wadsleyite aggregates.

Data treatment allowed increasing the indexation rate by (i) filling the non-indexed pixels that have up to 8 identical neighbours with this orientation and (ii) repeating this operation using, respectively, 7 and 6 identical neighbours. It also allowed to identify the grains (i.e., continuous domains characterized by an internal misorientation <10°). At each step, the resulting orientation maps were verified to avoid over-extrapolation of the data. Finally, data were
reduced to one point of measurement per grain in order to limit the potential oversampling of abnormally coarse grains. Between 800 and 2531 grains were measured per sample, insuring a good statistical analysis of the crystal preferred orientations and grain sizes.

Crystal preferred orientation measurements are plotted as pole figures showing the orientation of each crystal axis relative to the sample coordinates. The discrete point distributions of Euler angle triplets (i.e., orientation distribution function ODF) are converted into densities by grouping them within 1° ODF cells and then smoothing with a Gaussian function with a 8.5° full-width-at-half-maximum (FWHM). Finally, the resulting density distributions are normalized and contoured.

2.3. TEM observation

TEM has been used to characterize the microstructures after transformation and deformation. Doubly polished thin sections (25 μm thick) have been prepared from the recovered specimens for TEM observation (with the same orientation as for SEM imaging and EBSD mapping). The samples have been glued on a Mo grid and ion milled at 5 kV under a low beam angle of 15° until electron transparency is reached. TEM observations were carried out in the University of Lille (France) using a Philips CM30 microscope operating at 300 kV. Phase identification was achieved using selected-area electron-diffraction and precession electron diffraction with a “Spinning Star” precession module from the Nanomegas Company. The sample being potentially quite sensitive to electron irradiation, the diffraction patterns were obtained with a low-dose parallel electron beam, using a 5 μm selected-area aperture. Simulated kinematical diffraction patterns were calculated using the “electron diffraction” software (Morniroli and Steeds, 1982).

2.4. FTIR spectroscopy and water content

Water contents in our samples were obtained using unpolarized mid-infrared radiation collected with a FTIR Bruker IFS66V/S spectrometer coupled with an Bruker IR microscope at the Laboratoire des Colloïdes, Verres et Nanomatériaux (LCVN) at Université Montpellier 2 (France). The technical setup of the IR microscope and the MCT detector is identical to those described by Demouchy and Mackwell (2003). A small circular aperture of 0.75 mm was used, yielding a spot of 30 μm in diameter; between 200 scans were accumulated for each spectrum at a resolution of 4 cm$^{-1}$. Thin section thickness of the aggregate samples for FTIR analyses was 133 μm and 208 μm for forsterite and wadsleyite, respectively. Despite their infrequent occurrence, cracks were strictly avoided. However, due to small grain size of the samples, several grain boundaries were unfortunately included in the analyses.

After background-baseline correction and thickness normalization to 1 cm, the hydroxyl content was determined for each spectrum using the calibration from Paterson (1982), which is based on an empirical correlation between OH$^-$ stretching frequency and extinction coefficient; it leads to the following expression:

$$C_{OH} = \frac{\psi_i}{150\xi} \int \frac{k(v)}{3780 - \nu} \, d\nu,$$

(1)

where $C_{OH}$ is the concentration of hydroxyl, $\xi$ is an orientation factor that equals $1/3$ for unpolarized measurements, $k(v)$ is the absorption coefficient for a given wavenumber $\nu$, $\psi_i$ is the density factor, which is chemistry and density dependent; $\psi_i = 2793$ wt ppm $H_2O$ for iron-free forsterite and $\psi_i = 2590$ wt ppm $H_2O$ for iron-free wadsleyite (for calculation method see Bolfan-Casanova et al., 2000). Spectrum integration was performed between 3650 cm$^{-1}$ and 3000 cm$^{-1}$. The calibration from Paterson (1982) may underestimate the water content in some nominally anhydrous minerals (Libowitzky and Rossman, 1997; Bell et al., 2003; Demouchy and Mackwell, 2006), but the aim of the measurements is not to quantify the absolute water contents in forsterite and wadsleyite, but to give an estimate of the water content in the system and of the relative variation between samples.

3. Results

3.1. Samples description

Phase identification was performed using EBSD. All diffraction patterns in the starting material (hot press runs) were indexed using the forsterite structure, whereas the deformed polycrystalline aggregates, independently of the experiment duration, could only be correctly indexed using the wadsleyite structure.

3.1.1. Starting material: hot-pressed forsterite polycrystals

SEM characterization of the forsterite starting material reveals a relatively homogeneous small grain size in all runs (Table 1 and Fig. 1), but the apparent average grain size differs from run to run, ranging between 12.3 μm and 16.2 μm (corresponding to a true mean grain size between 18.45 and 24.3 μm; Vauchez, 1987). Well-developed triple junctions are observed and grain boundaries are...
generally straight (Fig. 1). No shape preferred orientation (SPO) is observed.

3.1.2. Deformed wadsleyite polycrystals

SEM images of wadsleyite reveal well-developed triple junctions and dominantly straight polygonal grain boundaries (Fig. 3). However a few curved shortening and lengthening grain boundaries (as defined by Dillon and Rohrer (2009) in yttrium aluminium garnet) as well as rare atypical four-grain junctions are also visible in the shortest run material. Analysis of the EBSD maps highlights a mean grain size finer than the forsterite starting material (Table 1 and Figs. 2, 3 and 6), with an apparent average grain size increasing from 7.6 to 9.7 μm (corresponding to a true mean grain size from 11.4 to 14.5 μm; Vauchez, 1987). The maxi-
mum grain size increases from 22 to 51 μm with increasing run duration from 1 to 60 min (Fig. 6) indicating that grain growth occurred. As in the forsterite aggregates, no SPO was observed despite the clear simple shear deformation of the wadsleyite aggregates indicated by the shape of the deformed assemblages (Fig. 2).

In contrast to the results of Dupas-Bruzek et al. (1998) and Couvy (2005) experiments, metastable forsterite was not detected in the deformed aggregates independently of the run duration. Therefore the potential inheritance relationship between the two crystallographic lattices (i.e., (1 0 0)$_{fo}$//[0 1 $\bar{1}$]$_{wads}$ and [0 0 1]$^o_{fo}$//[1 0 0]$_{wads}$) and consequence for the wadsleyite CPO could not be investigated.

Fig. 5. Crystallographic preferred orientation (CPO) of wadsleyite after the deformation experiments in a lower hemisphere equal-area projection. The shear direction is dextral. $N$ is the number of analyzed grains, maximum and minimum density contours are given at the top and bottom of the grey scale, respectively.
Each starting forsterite slab was 200 μm thick. After deformation, wadsleyite slabs have thicknesses ranging from 113 μm to 160 μm (Table 1 and Fig. 6), implying either a volume decrease associated with the phase transformation or a transpressional deformation (simple shear and shortening) of the samples. Extrusion of the wadsleyite aggregate between the alumina pistons is visible at the lateral extremities of the deformation assembly (Fig. 2), confirming that shearing of the sample actually occurred.

### 3.2. CPO patterns

Indexation rates of the raw EBSD maps for forsterite range from 35 to 64%. Indexation rates for wadsleyite range from 58 to 73%. The lower indexation rates are essentially due to (i) shadows from the thick silver paint applied around the sample to reduce charging, (ii) inclusion of sample edges and pistons in the mapped area, (iii) no indexing of grain boundaries, which are noticeably visible in 1 and 0.2 μm step size maps, and (iv) holes created by the plucking out of crystals during polishing. Post-acquisition data treatments allowed increasing indexation rates that attain 42–81% for forsterite and 58–77% for wadsleyite.

Analysis of pole figures for the hot-pressed forsterite aggregates reveals an almost random orientation of the crystals (minimum and maximum concentrations are >0.5 and <2.1 multiples of an uniform distribution, respectively, Fig. 4). Despite the approximately isotropic stress field in the multi-anvil assembly, all samples show only a very weak preferred orientation of [1 0 0] axes at 45° to the capsule length direction, i.e., normal to the surface of the sliced slab. [0 1 0] and [0 0 1] axes are more dispersed and show a poor axially symmetric distribution around the [1 0 0] axes concentration.

Pole figures of three wadsleyite samples, H2926, H2923, and H2924 show a weak, but consistent CPO (Fig. 5), where [1 0 0] axes are aligned with the shear direction of the shear plane, [0 1 0] axes are concentrated at a low angle from the normal to the shear plane, and [0 0 1] axes are more dispersed. H2925 and H2927 samples have contrasting CPO patterns, characterized by [0 0 1] axes concentrated at a low angle to the shear direction, [1 0 0] dispersed in a wide girdle normal to it, and a stronger dispersion of [0 1 0]. The weakest wadsleyite CPO is displayed by sample H2927, which is the sample submitted to the longest run duration (60 min) (Fig. 5).

### 3.3. FTIR and water contents

#### 3.3.1. Forsterite

Unpolarized FTIR spectra for both post-mortem forsterite and wadsleyite record the presence of moderate amounts of water in the starting material and deformed aggregates. Infrared spectra for iron-free forsterite are shown in Fig. 7a. It displays well-defined peaks at 3612, 3578, 3567, 3476 and 3391 cm⁻¹. These peaks are characteristic for high-pressure forsterite and are similar to infrared spectra reported in previous studies (e.g., Kohlstedt et al., 1996; Demouchy and Mackwell, 2003; Mosenfelder et al., 2006; Smyth et al., 2006; Bali et al., 2008). Water contents in iron-free forsterite are homogeneous within one sample but different from run to run and range from 65 to 124 wt ppm H₂O (Table 1). These water contents are only slightly below concentrations reported for deformed forsterite by Couvy et al. (2004) at 11 GPa. They are however well below water solubility concentrations reported by Kohlstedt et al. (1996) at 1100 °C (above 290 wt ppm H₂O at 6.5 GPa and 1070 wt ppm H₂O at 10 GPa). They are also lower than the water contents in wadsleyite reported by Mosenfelder et al. (2006), Smyth et al. (2006), and Bali et al. (2008).

#### 3.3.2. Wadsleyite

Unpolarized FTIR spectra for iron-free wadsleyite are shown in Fig. 7b. The spectra show typical IR peaks for iron-free wadsleye with a small doublet at 3615–3578 cm⁻¹ and a major peak at 3328 cm⁻¹, similar to those presented in Bolfan-Casanova et al. (2000) and Jacobsen et al. (2005). The water content varies from 114 wt ppm H₂O to 736 wt ppm H₂O (±30%). These values are well below water solubility values given by Kohlstedt et al. (1996), Bolfan-Casanova et al. (2000) and Demouchy et al. (2005).

### 3.4. TEM observations of shear deformed samples

The microstructures are very similar for all samples. They are therefore described together. The samples appeared not to be very sensitive to electron irradiation, which could be easily avoided using standard low-dose procedures. All characterized grains have shown to be wadsleyite (Fig. 8a). Most grains are free of defects. The characteristic (0 1 0) stacking faults of wadsleyite were however observed in several grains (Fig. 8c). Some dislocations could be found, but their occurrence is quite rare. The few observed dislocations have [1 0 0] or 1/2 [1 1 1] Burgers vectors and are in glide configuration (Fig. 8d). However, the extremely low dislocation density, even in the 1 min run sample, suggests that dislocation glide did not play a major role in the deformation of these samples. No sub-grain boundaries have been found.

The absence of forsterite in sample H2926 that was only deformed for 1 min indicates that the forsterite to wadsleye phase transformation was almost instantaneous (<1 min).

### 4. Discussion

Before discussing the results of these experiments, one has to bear in mind that most finite shear strain takes place at the very early part of the run when the deviatoric stress is relatively high, just after the high temperature conditions are reached. The subsequent part of the experiment is essentially a stress relaxation involving very little finite strain under decreasing stress, plastic strain increments, and strain rates. Moreover, the high temperature conditions during the entire run duration can assist recovery of the microstructure by processes such as diffusion and grain growth both during and after deformation (Cordier and Rubie, 2001; Thurel et al., 2003a,b).

CPO intensities of our wadsleyite aggregates are weaker than previous results (Couvy, 2005; Xu et al., 2005). One may question:
why? The weaker CPO could result from lower finite strains in current experiments, but the geometry of the deformed samples (cf. Llana-Fúñez and Rutter (2008) and our Fig. 2) characterized by a clear relative displacement of the pistons suggests that the applied shear strain was similar to the one obtained in other direct shear experiments. Weak CPO may also result from a deformation accommodated largely by diffusion processes. TEM analysis revealed very low dislocation densities or even the absence of dislocations in
Fig. 8. Characteristic microstructures observed in the deformed wadsleyite samples at the TEM: (a) sample H2923, deformed during 35 min, grain free of defect, TEM bright field; (b) sample H2923, precession electron diffraction, [0 0 1] zone axis pattern corresponding to (a); (c) sample H2926, deformed during 15 min, and showing stacking faults. Weak-beam dark-field micrograph; g: 002; and (d) sample H2925, deformed during 1 min, [1 0 0] and 1/2 ⟨1 1 1⟩ dislocations. Weak-beam dark-field micrograph; g: 244.

Some grains, including in the samples from very short run durations (e.g., H2926-1 min). This, together with the observed increase in grain size with increasing experiment duration (Table 1 and Fig. 6), implies that grain boundary migration and grain growth occurred in our experiments, leading to notable recovery of the wadsleyite aggregates, which is consistent with the decreasing stress history. The smaller grains sizes of our samples relatively to those from previous experiments (Table 1 and Fig. 6) may also have favored diffusion, promoting fast grain growth. We also observe that no SPO developed in our samples. According to Langdon (2000), diffusion creep results in SPO development, whereas grain boundary sliding under low stress conditions does not produce grain elongation. These observations are thus consistent with activation of grain boundary sliding. However we have to emphasize that finite strain in the present experiments may not have been high enough to produce significant SPO.

On the other hand, although wadsleyite CPO are weak and vary from sample to sample, two coherent patterns are observed (Fig. 5). Three wadsleyite aggregates display weak CPO patterns with [1 0 0] axes concentrated at low angle to the shear direction, [0 1 0] axes are perpendicular to the shear plane, and almost random [0 0 1] axes. Two other wadsleyite aggregates display weak CPO patterns with [0 0 1] axes concentrated at low angle to the shear direction, and dispersed [1 0 0] and [0 0 1] axes. Moreover, there is a correlation between the water contents of the wadsleyite samples and their CPO patterns (Fig. 9). In theory, wadsleyite may contain up to 3 wt% H₂O (Smyth, 1987), but these values are reduced to 1 wt% H₂O at pressure and temperature conditions of the transition zone (Demouchy et al., 2005). Thus water contents in the present experiments are well below the saturation limits. Nevertheless our wadsleyite aggregates with low water contents (between 1 0 0 and 350–400 wt ppm H₂O) show a concentration of [1 0 0] axes parallel to the shear direction (pole figure density, PFD > 1) and a high dispersion of [0 0 1] axes distribution (PFD < 1). For higher water contents (>350 wt ppm H₂O), i.e., in samples H2925 (15 min) and H2927 (60 min), the concentration of [1 0 0] axes parallel to the
shear direction decreases (PFD < 1), while the [0 0 1] concentration parallel to the shear direction slightly increases (PFD > 1). Consequently, the density ratio (DR) of [1 0 0] axes and [0 0 1] axes parallel to the shear direction rises above the value of 1 with increasing water content (Fig. 9). We may thus classify the samples into two groups: (1) samples with water contents <350–400 wt ppm H2O and concentration of [1 0 0] axes parallel to the shear direction (H2926, H2923 and H2924 with experimental durations of 1, 35 and 40 min, respectively), which we will call A-CPO and (2) samples with higher water contents and concentration of [0 0 1] axes parallel to shear direction (H2925, H2929 and H2925 with experimental durations of 15 and 60 min, respectively), which we will call C-CPO. One should notice that there is not a direct correlation between the water content and the experiment duration, suggesting that water content in wadsleyite does not result from a simple linear and continuous diffusive intake (i.e., from the water-bearing aluminous cement or Cr-doped MgO octahedron) or release (due to high temperature annealing) of hydrogen from, or into, the high pressure assembly during the experiment (see Hae et al. (2006) for hydrogen diffusion coefficients in wadsleyite). A comparable correlation between CPO variations and water content was already proposed for olivine (Jung and Karato, 2001), but to date no detailed TEM studies on their samples are available. Moreover, neither in the early article by Jung and Karato (2001) nor in subsequent publications from the same group, has a satisfactory physical mechanism been proposed for the change of slip system in olivine under hydrous conditions was proposed. The present study on wadsleyite faces the same difficulty.

There is very little available experimental data on strain-induced CPO in wadsleyite (all together results for only 20 experiments were published before the present study; see Couvy, 2005; Xu et al., 2005). Thus, to test if both CPO patterns may result from plastic deformation by dislocation glide, we compare the CPO from our experimental samples to those modeled using the viscoplastic self-consistent (VPSC) approach developed by Lebensohn and Tomé (1993). Modeled wadsleyite CPO using known glide systems for polycrystalline wadsleyite deformed in the multi-anvil apparatus (Dupas-Bruzek et al., 1998; Thurel et al., 2003a) and different critical resolved shear stresses sets (Tommasi et al., 2004) are shown in Fig. 10a. None of these simulations can reproduce the wadsleyite CPO observed in this study. Simulations in which slip on [1 0 0][0 0 1] systems is five times easier than slip on 1/2 ⟨1 1 1⟩[1 0 1] do develop a [1 0 0] maximum close to the shear direction, and girdles of [0 0 1] and [0 0 1] axes normal to it, but [0 0 1] is more concentrated than [0 1 0], in contrast to the CPO in the present study. Concentration of [1 0 0] close to the shear direction and of [0 0 1] towards the normal to the shear plane, similar to the CPO of samples H2926, H2923, and H2924, only develops in models where an additional [0 0 1][0 1 0] system is added (Fig. 10b). [0 0 1] dislocations were not observed by TEM neither in our experimentally deformed wadsleyite polycrystals nor in those from previous shear experiments (Thurel et al., 2003a), but a few [0 0 1] dislocations were observed in wadsleyite deformed in compression by Thurel and Cordier (2003). Recent Peierls–Nabarro–Galarkin models of dislocations (Metsue et al., 2010) also point to possible activation of [0 0 1] glide in wadsleyite. These models show that [0 0 1] glide is precluded in ⟨1 0 0⟩, but is possible in ⟨0 1 0⟩ where [0 0 1] dislocations may dissociate into two non-collinear partials, ⟨0 1 0⟩[0 0 1] glide is harder to activate than [1 0 0] or 1/2 ⟨1 1 1⟩ glide. It may however have been active at the very beginning of the present experiments when the stresses were high.

The CPO pattern of high water content samples H2923 and H2925, which is characterized by a weak concentration of [0 0 1] axis close to the shear direction, cannot be reproduced by a combination of known wadsleyite slip systems. However, VPSC models only predict the effect of dislocation glide on the CPO evolution.

The absence of agreement between the measured and modeled CPO patterns for wadsleyite may thus suggest that the latter do not result uniquely from dislocation glide and that recovery processes, such as atomic diffusion and grain growth, were activated. A stronger contribution of diffusion is consistent with the higher water contents in these samples, since these processes are enhanced by the presence of hydrogen in the system (Karato, 1990; Hier-Majumder et al., 2004; Nishihara et al., 2006; Demouchy et al., 2007; Costa and Chakraborty, 2008).

Despite special care during sample preparation, hydrogen contamination from the high-pressure assembly (i.e., from pyrophyllite gaskets, aluminous cement, and Cr-doped MgO) occurred in our experiments. There is no correlation between the hydrogen content of the initial forsterite starting material and of the subsequent transformed wadsleyite (Table 1), suggesting that the water content of wadsleyite must be fixed by an external factor, possibly during the phase transformation, due to the ability of wadsleyite to incorporate a significant amount of hydrogen for a nominally anhydrous mineral.

The three-dimensional distribution of seismic velocities in a polycrystalline aggregate may be estimated by averaging the individual grain elastic tensors as a function of the crystallographic orientations and mineralogical composition of the aggregate (e.g., Mainprice and Humbert, 1994). Seismic properties of an aggregate of pyrolitic composition under upper transition zone conditions

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Fig. 10. (a) Wadsleyite CPO predicted by VPSC models. CRSS for [1 0 0] and 1/2 ⟨1 1 1⟩ slip systems (models 1–4) are displayed to the left of each pole figure and (b) CPO for model 5, where an additional [0 0 1]/[0 1 0] slip system, which is not observed in TEM, was added. Lower hemisphere equal-area stereoplots with contours at intervals of 0.5 multiples of a uniform distribution of 500 grains. Shear direction (SD) is dextral. Solid line marks the shear plane and NSP is the normal to the shear plane. Dashed line marks the foliation.
Fig. 11. Modeled three-dimensional compression and shear waves velocity distribution ($V_p$ and $V_s$, respectively) as well as polarization anisotropy (AVs) of a sheared aggregate with a pyrolitic composition (60% wadsleyite and 40% majorite) for a pressure of 15.2 GPa (~450 km depth) and a temperature of 1456.5 °C. Voigt–Reuss–Hill averages plotted in a lower hemisphere equal-area projection. Solid line marks the shear plane. Arrow in the upper left corner indicates the shear direction (dextral). Elastic constants used for these models are given in Table 2.
(60% wadsleyite and 40% majorite) were estimated using elastic constants tensors of wadsleyite (Zha et al., 1997; Sinogeikin et al., 1998) and pyrope-rich garnet (Chai et al., 1997) as an analogue for majorite. For most rock-forming minerals temperature has a strong effect on seismic velocities, but a minor influence on anisotropy (Mainprice et al., 2000). The calculation of the elastic constants of a pyrolitic composition was nevertheless performed for a temperature of 1456.5 °C at a pressure 15.2 GPa (Table 2). Previous VPSC simulations show that majorite-like garnet CPO is always very weak (Mainprice et al., 2004; Tommasi et al., 2004) and its contribution is nearly elastically isotropic, leading to significant reduction of the rock (bulk) anisotropy.

The seismic properties for a rock of pyrolytic composition, in which wadsleyite has the CPO given in Fig. 5 are displayed in Fig. 11. Azimuthal anisotropies for both P- and S-waves and the S-waves polarization anisotropy are always below 1%, even for the most water-rich samples (H2925-15 min and H2927-60 min). These calculations predict therefore a very weak seismic anisotropy in the upper transition zone. One has to bear in mind however, that finite strains achieved in the present experiments are very low and stronger wadsleyite CPO might develop at higher finite strains. In a previous study, Tommasi et al. (2004) used VPSC simulations to quantify this effect. However, we cannot use the same approach here, because we were unable to reproduce the wadsleyite CPO observed in the present experiments using the known slip systems in wadsleyite. The change in wadsleyite CPO with increasing hydration results in subtle variations in the resulting seismic anisotropy pattern. For the orientations where a polarization anisotropy can be detected, the fastest shear wave is always polarized normal to the shear direction, implying that for horizontal flow in the mantle transition zone will result in \( V_S \neq V_H \). A-CPO patterns in wadsleyite lead however to apparent isotropy propagation directions for S-waves normal to the shear plane; if the flow is horizontal, SKS waves will therefore sample this direction and will not be affected by the transition zone anisotropy. In contrast, C-CPO pattern in wadsleyite results in non-null birefringence for S-waves propagating normal to the shear direction; for horizontal flow in the transition zone would thus contributes to the SKS anisotropy measured at the surface.

5. Conclusion

Shear deformation experiments have been performed on forsterite aggregates using the multi-anvil apparatus in the stability field of wadsleyite at 16 GPa, 1400 °C. In the absence of direct mechanical data, a detailed multi-scale microstructural characterisation has been conducted in samples deformed in experiments with durations ranging from 1 min to 60 min to investigate how deformation proceeds as a function of time and if it influences the forsterite to wadsleyite phase transformation. The experimental samples show two types of weak CPO patterns in wadsleyite. The first pattern is characterized by \( 1 \) axes aligned with the shear direction (A-CPO). With increasing water content (>350–400 wt ppm), wadsleyite CPO patterns evolve to a second type with \( 0 \) axes aligned with the shear direction (C-CPO). TEM observations, on the other hand, suggest that either very little deformation occurred by dislocation glide in the wadsleyite or that thermal recovery (implying ionic diffusion and grain growth) has affected the samples. Obvious shearing of the wadsleyite slab in the deformation assembly and CPO favors the second hypothesis. The fine grain size and the low stresses in the final stages of the experiment may have nevertheless allowed some deformation by grain boundary sliding. The TEM observations also suggest that most dislocations stored during the cold compression of forsterite were activated and rapidly consumed by the forsterite to wadsleyite phase transformation. After only 1 min, the forsterite slab is completely transformed into wadsleyite, implying that deformation probably enhances the kinetics of the phase forsterite–wadsleyite transformation. The present study also reveals that stress, grain size, and water content are critical factors in the forsterite to wadsleyite phase transformation and in the subsequent deformation in the transition zone. The seismic anisotropy of a pyrolytic rock with such wadsleyite CPO is very weak (<1%), although, this might be a consequence of the low finite strains attained in these experiments. The observed change in wadsleyite CPO as a function of the water content results nevertheless in subtle variations of the seismic anisotropy pattern. Fast S-wave polarizations are always normal to the shear direction, but apparent isotropy propagation directions differ between the two patterns. They are normal to the shear plane for the A-CPO and parallel to the shear direction for the C-CPO.

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References


Katsura, T., Ito, E., 1989. The system Mg2SiO4–Fe2SiO4 at high pressures and temper-
Karato, S.-I., Rubie, D.C., 1997. Toward an experimental study of deep mantle rhe-
Jacobsen, S.D., Demouchy, S., Frost, D.J., Boffa-Ballaran, T., 2005. A systematic study
Hae, R., Ohtani, E., Kudo, T., Koyama, T., Hisashi, U., 2006. Hydrogen diffusivity in
Hae, R., Ohtani, E., Kudo, T., Koyama, T., Hisashi, U., 2006. Hydrogen diffusivity in
Mori, I., Steeds, J.W., 1982. Microdiffraction as a tool for crystal-structure identi-