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## Revision 3

# Water quantification in olivine and wadsleyite by Raman spectroscopy and study of errors and uncertainties

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### ABSTRACT

The study of nominally anhydrous minerals with vibrational spectroscopy, despite its sensitivity, tends to produce large uncertainties (in absorbance or intensity) if the observed dispersion of the values arising from the anisotropy of interaction with light in non-cubic minerals is not assessed. In this study, we focused on Raman spectroscopy, which allows the measurement of crystals down to few micrometers in size in back-scattered geometry, and with any water content, down to 200 ppm by weight of water. Using synthetic hydrous single-crystals of olivine and wadsleyite, we demonstrate that under ideal conditions of measurement and sampling, the data dispersion reaches  $\pm 30\%$  of the average (at  $1\sigma$ ) for olivine, and  $\pm 32\%$  for wadsleyite, mostly because of their natural anisotropy. As this anisotropy is linked to physical properties of the mineral, it should not be completely considered as error without treatment. By simulating a large number of measurements with a 3D model of the OH/Si spectral intensity ratio for olivine and wadsleyite as a function of orientation, we observe that although dispersion increases when increasing the number of measured points in the sample, analytical error decreases, and the contribution of anisotropy to this error decreases. With a sufficient number of

21 points (five to ten, depending on the measurement method), the greatest contribution to the error  
22 on the measured intensities is related to the instrument's biases, and reaches 12 to 15% in ideal  
23 cases, indicating that laser and power drift corrections have to be carefully performed. We finally  
24 applied this knowledge on error sources (to translate data dispersion into analytical error) on  
25 olivine and wadsleyite standards with known water contents to build calibration lines for each  
26 mineral in order to convert the intensity ratio of the water bands over the structural bands (OH/Si)  
27 to water content. The conversion factor from OH/Si to ppm by weight of water (H<sub>2</sub>O) is  
28  $93108 \pm 24005$  for olivine,  $250868 \pm 45591$  for iron-bearing wadsleyite, and  $57546 \pm 13916$  for iron-  
29 free wadsleyite, showing the strong effect of iron on the spectral intensities.

30 **Keywords:** wadsleyite, olivine, nominally anhydrous minerals, Raman spectroscopy,  
31 water quantification

## 32 INTRODUCTION

33 Even though the major mineral phases of the Earth's mantle are nominally anhydrous,  
34 many of them are known to contain water as OH point defects in their structure (Bell and  
35 Rossman, 1992; Smyth and Keppler, 2006; Peslier 2010; Demouchy & Bolfan-Casanova, 2016).  
36 The water storage capacity of the most abundant upper mantle mineral, namely olivine, has been  
37 the subject of many studies, however most reports concern simple systems or single crystal  
38 olivine (e.g. Kohlstedt et al. 1996; Withers & Hirschmann 2007 and 2008; Bali et al. 2008;  
39 Kovács et al. 2010; Férot & Bolfan-Casanova 2012; Litasov et al. 2014, Yang et al. 2016).  
40 Single-phase experiments allow the growth of single crystals large enough to be suitable for any  
41 analytical method, especially absorption infrared spectroscopy using Fourier transform infrared  
42 (FTIR), secondary ion mass spectrometry (SIMS), or elastic recoil detection analysis (ERDA).

43 In experiments with natural mantle compositions on the other hand, olivine,  
44 orthopyroxene, clinopyroxene and garnet can coexist, strongly limiting crystal growth. These  
45 samples often display crystal sizes from 20 to 50  $\mu\text{m}$ , limiting the use of the conventional  
46 methods cited above on the fine-grained samples. Investigation of the storage capacity in more  
47 complex systems such as peridotite has been carried out and the small grain size of the grains  
48 required the use of SIMS (few tens of cubic micrometers analyzed) or even nano-SIMS (one or  
49 two order of magnitude less) ( see Ardia et al., 2012; Tenner et al., 2012; Novella et al., 2014).  
50 This technique is complicated to use because of high background levels of H, complex  
51 preparation to avoid H contamination and the need for well-characterized standards (Koga et al.  
52 2003, Mosenfelder et al. 2011).

53 FTIR is frequently used sensitive technique to quantify hydroxyl content in nominally  
54 anhydrous minerals, which also gives structural information about H point defects. Reliable  
55 methods exist to quantify water in anisotropic minerals using FTIR, and a consequent literature  
56 exists on the subject (e.g., Libowitzsky and Rossman 1996; Asimow et al. 2006; Kovács et al.  
57 2008; Withers et al. 2012, Withers 2013; Qiu et al. 2018). However, in the case of very water-  
58 rich samples as, for example, wadsleyite, a high-pressure polymorph of olivine, that can contain  
59 up to 3.2 weight percent of water (Inoue et al., 1995), infrared spectroscopy requires an important  
60 thinning of the samples (which may cause their loss) in order to avoid the entire absorption of the  
61 infrared signal.

62 In this study, we used confocal polarized Raman spectroscopy (the laser source being  
63 polarized, the incident beam is therefore also polarized). This technique offers several advantages  
64 for water quantification in synthetic minerals with a small grain size and low to very high water  
65 contents. Regarding sample preparation, OH quantification using back-scattered Raman

66 spectroscopy requires only one side of the sample to be polished, while double polishing is  
67 required in the measurement of absorbance using FTIR. Unfortunately, very thin polishing of the  
68 sample can irremediably damage them, especially those sintered under conditions where fluids  
69 are highly wetting, which is the case of the conditions of the deep upper mantle (Yoshino et al.  
70 2007). The detection limit of water quantification using Raman spectroscopy (around  
71 50-100 ppm wt) may be a problem with samples synthesized under conditions of the uppermost  
72 mantle, where the water solubility is the lowest for many mineral species (Férot & Bolfan-  
73 Casanova 2012, Yang 2016), but any higher concentration can be measured (Bolfan-Casanova et  
74 al. 2014). The spot size of confocal Raman spectroscopy (3-5  $\mu\text{m}$ ) allows measurements on very  
75 fine-grained samples (down to crystal sizes around 5  $\mu\text{m}$ ) without difficulties. The time required  
76 for reasonably precise measurements (some minutes) is low enough to multiply the number of  
77 measured points on different crystals throughout the sample and have a statistically correct  
78 coverage of the whole sample. One major drawback of Raman spectroscopy is that the intensity  
79 absorption depends on many factors in addition to the concentration, such as the intensity of the  
80 incident laser, confocality and lens magnification, which control the volume of sample that is  
81 excited by the laser beam. Moreover, the chosen gratings and the optics of the spectrometer  
82 (instrument-dependent parameters), as well as the optical properties of the sample or its surface  
83 state will affect the efficiency of the measurement (see e.g. Mercier et al. 2009, Schiavi et al.  
84 2018; Zarei et al. 2018). In contrast, the absorbance measured using FTIR depends solely on the  
85 thickness, concentration and absorptivity of the sample itself, following a relationship known as  
86 the Beer-Lambert law. In addition, in absorbance spectroscopy the intensity transmitted by the  
87 sample is always normalized to that of the incident beam, which tends to eliminate instrumental  
88 biases on the intensity of the signal from the sample.

89 Raman spectroscopy is widely used to quantify H<sub>2</sub>O concentrations in glasses or melt  
90 inclusions (e.g., Thomas et al. 2008; Mercier et al. 2009; Schiavi et al., 2018). In these studies,  
91 quantification of the water concentration relies on the comparison of the OH/Si of the unknown  
92 to that of well-characterized standards measured under identical conditions, as the OH intensity  
93 has been shown to increase linearly with water content. Here, OH/Si is defined by the integrated  
94 intensity of the water band normalized to that of the silicate vibrations (see the following section  
95 for details). As numerous factors may affect the measurement efficiency (such as variation of  
96 focusing depth or surface quality), using the ratio of the OH band area over that of silica bands  
97 area reduces the data dispersion or scatter, as both regions are equally affected by focusing or  
98 surface variations. Calibrations of the method have been proposed by Thomas et al. (2008 and  
99 2015) for garnet, Bolfan-Casanova et al. (2014) for olivine, Thomas et al. (2015) for ringwoodite,  
100 and Weis et al. (2018) for orthopyroxene (this last study having used also forward-scattering).

101 Previous water content quantification in olivine conducted with Raman spectroscopy  
102 often display large error bars on their results (Bolfan-Casanova et al. 2014). In this study, we  
103 demonstrate that those error bars are significantly related to the dispersion (used in the statistical  
104 meaning of the term throughout this work) of the relative intensities of the different vibrational  
105 modes caused by the anisotropy of the minerals. As this anisotropy is a natural consequence of  
106 the structure and symmetry of the crystal, it is not directly related to error, and can even be used  
107 to get information on orientation (see for example Ishibashi et al. 2008). Firstly, we studied the  
108 relative effect of the different error sources and of anisotropy on the statistical dispersion of  
109 measurements in hydrated olivine and wadsleyite single crystals and used it to propose a method  
110 to estimate the analytical error from the data dispersion of the measurements using polarized

111 unanalyzed Raman spectroscopy. We then propose a calibration for water quantification in  
112 olivine and wadsleyite based on standards characterized by FTIR or ERDA methods.

## 113 **METHODS**

### 114 **Synthesis of olivine and wadsleyite**

115 Olivine and wadsleyite single crystals were synthesized in the multi-anvil press at 12 and  
116 15 GPa and at 1200 and 1350 °C from San Carlos olivine as starting material. Olivine single  
117 crystals and powder were placed in a folded rhenium foil capsule, placed itself in a welded gold-  
118 palladium capsule containing brucite powder. The experimental assembly consisted of an MgO  
119 octahedron containing Cr<sub>2</sub>O<sub>3</sub>, a zirconia thermal insulator, a LaCrO<sub>3</sub> heater with molybdenum  
120 electrodes in contact with the anvils and an MgO central part containing the capsule. Temperature  
121 was controlled using a W-Re thermocouple (5% and 26% Re). Experiments were conducted at  
122 the Laboratoire Magmas et Volcans (LMV, Clermont-Ferrand, France) on a Voggenreiter Mavo-  
123 press LP 1500 tons multi-anvil press equipped with a Kawai-Endo apparatus. Heating was  
124 performed and controlled by a Pacific 140-AMX AC power source. Secondary anvils were 32  
125 mm tungsten carbide cubes with 8 and 6 mm truncations. Olivine synthesis duration was 4.5  
126 hours at 1200 °C, and wadsleyite synthesis lasted 2 hours at 1350 °C. For both syntheses,  
127 temperature was gradually decreased after the experiment (around 50 °C per minute) instead of  
128 quenching to prevent crystal fracturation. Recovered crystals were oriented using polarized light  
129 microscopy for olivine and X-ray diffraction for wadsleyite, and then cut and mirror polished  
130 perpendicular to crystallographic axes (see **Figure 1**). Olivine and wadsleyite are both  
131 orthorhombic so display an anisotropic behavior with respect to light absorption. Wadsleyite has  
132 been reported to become monoclinic above 0.5 wt % H<sub>2</sub>O using X-ray diffraction (Jacobsen et al.

133 2005), however we did not detect any noticeable spectral difference that could be due to this  
134 small change in the  $\beta$ -angle.

### 135 **FTIR spectroscopy**

136 Most of the samples used in order to calibrate the Raman quantification method were  
137 olivines characterized using FTIR by Férot & Bolfan-Casanova (2012). These water content  
138 values were updated using the most recent calibration of the infrared extinction coefficient ( $\epsilon$ )  
139 determined using ERDA by Withers et al. (2012) of  $45200 \text{ l mol}_{\text{H}_2\text{O}}^{-1} \text{ cm}^{-2}$  instead of the  $28450 \text{ l}$   
140  $\text{mol}_{\text{H}_2\text{O}}^{-1} \text{ cm}^{-2}$  value given by Bell et al. (2003). This decreases all the water contents of olivine  
141 reported in Férot and Bolfan-Casanova (2012) by a factor of 1.589.

142 Polarized spectra acquired for this study were collected on a Vertex70 Bruker  
143 spectrometer coupled to a Hyperion microscope with a  $15\times$  lens, condenser and knife-edge  
144 apertures creating a rectangular target area of  $40\text{-}50 \mu\text{m}$ . Samples were analyzed on a  $\text{CaF}_2$  plate  
145 at a resolution of  $2 \text{ cm}^{-1}$ , with 200 to 300 accumulations. After background subtraction and  
146 atmospheric correction, a cubic baseline correction has been applied on the  $1500$  to  $4000 \text{ cm}^{-1}$   
147 area, and integration calculated in the  $2700$  to  $3720 \text{ cm}^{-1}$  area. The absorbance is then used to  
148 calculate the  $\text{H}_2\text{O}$  content based on Beer Lambert's law (see equation 1) with the integrated molar  
149 absorption coefficient (also called extinction coefficient) cited above, and a density factor  $X$  of  
150  $5521 \text{ l}\cdot\text{mol}_{\text{H}_2\text{O}}^{-1}$  (used to convert  $\text{mol}_{\text{H}_2\text{O}}\cdot\text{l}^{-1}$  to ppm by weight of  $\text{H}_2\text{O}$ , equal to  $18.02\times 10^6/\rho$ ). The  
151 density  $\rho$  has been calculated from Fischer & Medaris (1969) accounting for the olivine  
152 composition. The equation used is the following, with  $\epsilon$  being the infrared extinction coefficient,  
153  $A_{tot}$  the total absorbance, and  $d$  the thickness of the sample in centimeters:

154 **Equation 1**

$$C_{H_2O} = X \times \frac{A_{tot}}{\varepsilon \times d}$$

155 **Raman spectroscopy**

156 Raman spectra were collected at LMV using an InVia confocal Raman micro-  
157 spectrometer manufactured by Renishaw and equipped with a 532 nm diode laser (200 mW  
158 output power), a Peltier-cooled CCD detector of 1024×256 pixels, a motorized XYZ stage and a  
159 Leica DM 2500M optical microscope. Scattered light was collected in a back-scattered geometry.  
160 An edge filter effectively reduced both Rayleigh scattered photons and photons from the exciting  
161 laser source at 0 cm<sup>-1</sup> that had been reflected by the sample surface. A 2400 grooves/mm grating  
162 was used for the analyses, which resulted in a spectral resolution between 1.3 cm<sup>-1</sup> (around 100  
163 cm<sup>-1</sup>) and 0.72 cm<sup>-1</sup> (around 3700 cm<sup>-1</sup>). All spectra were acquired with polarized light without  
164 analyzer, and sample was rotated under the beam to change the polarization angle. A ×100  
165 microscope lens (numerical aperture 0.9) was used and the slit aperture was set to 20 μm (high  
166 confocality setting). Daily calibration of the spectrometer was performed based on a Si 520.5  
167 cm<sup>-1</sup> peak. The effective laser power (changed by filters) used was 65 to 71 mW for olivine, and  
168 8 to 9 mW for wadsleyite and glass (low enough power to prevent destabilization and  
169 dehydration) and was measured to normalize spectra to 1 mW. A power of 125 to 140 mW can  
170 cause some damages on water-rich olivine, and a power of 15 mW caused a slight OH intensity  
171 reduction in wadsleyite with very high water content (sample 2054, 3.4% in weight), but no  
172 dehydration or destabilization effect has been observed with the lower laser power values finally  
173 chosen. A hydrous basaltic glass (see Schiavi et al. 2018) is used to check and be able to correct  
174 for power drifts and efficiency drifts along the different area of measurement.

175 As already stated above, the quantification of water concentration is based on the  
176 measurement of the OH band integrated intensity normalized to the silicate band integrated  
177 intensity. Under static conditions of measurement, the window analyzed using a grating of 2400  
178 groves/mm decreases from approximately  $1200\text{ cm}^{-1}$  at low wavenumbers to  $800\text{ cm}^{-1}$  at high  
179 wavenumbers. For all samples and standards, Si area refers to wavenumbers from 61 to  $1318$   
180  $\text{cm}^{-1}$  centered on  $720\text{ cm}^{-1}$ , and OH area refers to wavenumbers from 2978 to  $3784\text{ cm}^{-1}$  centered  
181 on  $3400\text{ cm}^{-1}$ . Both areas were chosen to contain all the needed peaks and bands. Acquisition  
182 times are short for the Si area because of its high intensity, to prevent saturation of the CCD  
183 detector, and longer for the OH area to increase the signal to noise ratio, the OH bands being  
184 much weaker. Thus, acquisition times were  $2\times 5\text{ s}$  for the Si area, and  $5\times 60\text{ s}$  for the OH area of  
185 olivine and wadsleyite. For the glass, the acquisition times were  $4\times 10\text{ s}$  for the Si area, and  
186  $5\times 120\text{ s}$  for the OH area. The daily variations of the spectrometer were corrected by normalizing  
187 to the average OH/Si intensity ratio of the hydrated glass measured in each measurement session,  
188 each of those consisting on two random points on the glass sample, providing a more  
189 reproducible OH/Si intensity ratio here called  $(\text{OH/Si})_{\text{Smp\_Norm}}$ . The normalization operation is  
190 shown in equation 2, where  $(\text{OH/Si})_{\text{Smp\_Meas}}$  is the average OH/Si of the measured sample,  
191  $(\text{OH/Si})_{\text{Glass\_Meas}}$  is the standard glass OH/Si measured in the same session as the sample, and  
192  $(\text{OH/Si})_{\text{Glass\_Std}}$  is the measurement of the OH/Si of the glass measured in the same session as the  
193 standards. The result is the normalized OH/Si of the sample  $(\text{OH/Si})_{\text{Smp\_Norm}}$ .

194 **Equation 2**

$$\frac{\text{OH}}{\text{Si}}_{\text{Smp Norm}} = \frac{\text{OH}}{\text{Si}}_{\text{Smp Meas}} \times \frac{\frac{\text{OH}}{\text{Si}}_{\text{Glass Std}}}{\frac{\text{OH}}{\text{Si}}_{\text{Glass Meas}}}$$

195 The procedure of baseline correction is essential in obtaining reproducible values of  
196 OH/Si for each phase (see [Figure 2](#) and [supplementary materials 1](#)). The baseline shape is linear  
197 for the olivine Si area (rarely cubic), cubic for its OH area, cubic or polygonal for the wadsleyite  
198 Si area and cubic for its OH area. The anchor points used to define the baseline are shown in  
199 [Figure 2](#). The spectra used afterwards for integrations are the raw spectra subtracted of the  
200 baseline, and divided by the total acquisition time and the laser power, to normalize each  
201 spectrum to a power of 1 mW and an acquisition time of 1 s. It has to be noted that this is not the  
202 unit of the spectra, as the intensity measured on each spectrum depends on various parameters of  
203 the instrument such as the grating and the wave number, but can be labelled as  $\text{counts} \cdot \text{s}^{-1} \cdot \text{mW}^{-1}$ .  
204 Integration consists in the area under the curve of the baseline-corrected and normalized  
205 spectrum: [200, 1100] for the Si area and [3050, 3700] for the OH area of olivine, and [300,  
206 1100] for the Si area and [3150, 3700] for the OH area of wadsleyite (see [Figure 2](#)). The result of  
207 this integration defines thereafter the intensity of the spectra. In the case of wadsleyite, iron-  
208 bearing samples display a very intense band at  $171 \text{ cm}^{-1}$  that merges with the white line (at low  
209 wavenumbers) rendering its baseline correction unreliable due to the difficult anchoring of the  
210 baseline at low wavenumbers (see [supplementary materials 1](#)). This is why the integration of the  
211 Si area of wadsleyite starts at a higher wavenumber of  $300 \text{ cm}^{-1}$ .

212 For all the spectra of glass, the single-crystal spectra and some of the wadsleyite and  
213 olivine samples, one measurement point consists in the OH intensity divided by the Si intensity  
214 (OH/Si ratio) with the same polarization angle, and is referred as "single points". On most of the  
215 olivine and wadsleyite samples, one measurement point will be the average of two OH/Si ratio  
216 obtained from two measurements on the same crystal with orthogonal polarization angles, and is  
217 referred as "orthogonal couples".

218 The averaged OH/Si values of several measurement points on a sample is the value used  
219 to compare the different samples. Eight olivine and seven wadsleyite standard samples of various  
220 known water contents have been used to build the calibration lines allowing the conversion from  
221 OH/Si ratio to water content. Water contents of olivine standards have been determined by FTIR,  
222 using Withers et al. (2012) extinction coefficient, and those of wadsleyite standards were  
223 measured by ERDA (Bolfan-Casanova et al. 2018).

## 224 **RESULTS**

### 225 **Quantification of the OH/Si variation related to mineral orientation**

226 In order to assess the effect of orientation alone on the dispersion of the average OH/Si  
227 value of each phase, polarized Raman spectra have been acquired on each face of the prepared  
228 single crystals of olivine and wadsleyite. We acquired 19 spectra, from 0 to 180°, on each face  
229 for both OH and Si area, and values for 190 to 350° were calculated by symmetry. Normalized  
230 OH/Si values were then fitted using equation 3 for olivine and equation 4 for wadsleyite (see  
231 **Figure 3**).

#### 232 **Equation 3**

$$\frac{\text{OH}}{\text{Si}}(\theta) = H + a_1 \times \cos^2(\theta + d_1)$$

#### 233 **Equation 4**

$$\frac{\text{OH}}{\text{Si}}(\theta) = H + a_1 \times \cos^2(\theta + d_1) + a_2 \times \cos^2(2 * (\theta + d_2))$$

234 Here,  $H$  is a constant depicting the minimum value for a given face adjusting the vertical  
235 position of the curve;  $a_1$  is the amplitude (the difference between the maximum and minimum

236 intensities of the given face for equation 3) of the cosine describing the features with a period of  
237  $180^\circ$  (2-fold symmetry) shifted of an angle  $d_1$ ;  $a_2$  is the amplitude of the cosine describing the  
238 features with a period of  $90^\circ$  (4-fold symmetry) shifted of an angle  $d_2$ . Each parameter has been  
239 optimized to minimize the differences between the measurement data and the fitted curve. It has  
240 to be noted that the necessity for introducing parameters  $d$  arise from the fact that crystals are not  
241 exactly polished following the crystallographic axes. These fits are thus empirical and only serve  
242 the purpose of creating a model of the analyzed crystals. For olivine, this misalignment is around  
243  $10^\circ$  (as visible in Figure 3), and has later been neglected (the maxima of the faces (100) and (010)  
244 have been aligned along crystallographic axes in the 3D model). On the other hand, the  
245 misalignment of wadsleyite is high, and orientation has been lost, rendering necessary the use of  
246 the shift parameters  $d$ . The observed component with a  $90^\circ$  period is necessary in the case of  
247 wadsleyite to fit correctly the measured intensity, and can mostly be noticed in the fits of the  
248 intensity variations on the faces arbitrarily called F1, F2 and F3 (see M F1 and M F2 fit curves  
249 around  $150$  and  $330^\circ$ ).

250         Considering that the single-crystal analyzed is homogeneous in water content, the only  
251 source of deviation between the modeled curve and the measured data is the combination of data  
252 treatment error and measurement error. Data treatment error has been estimated from the  
253 differences between repeated baseline correction and treatments of Raman spectra, and will be  
254 referred as  $E_{Tr}$  in following equations, tables and figures. The estimated values for  $E_{Tr}$  on OH/Si  
255 are 3.6% for olivine and 4.0% for wadsleyite. This error tends to remain small when the signal to  
256 noise ratio is high enough. The second error source taken into account is the one caused by all  
257 measurement uncertainties, such as surface irregularities or focus offset, and will be referred as  
258  $E_{Meas}$ . Supposing that  $E_{Meas}$  and  $E_{Tr}$  are independent sources of error, the deviation of

259 measurement points from the model is the square root of the sum of the two error sources  
260 squared, and is provided by the fit shown in **Figure 3**. From this calculation, we obtain a  
261 measurement related uncertainty  $E_{Meas}$  reaching 4.4% for olivine, and 4.1% for wadsleyite. The  
262 last source of error arises from the daily variation of the spectrometer efficiency and the method  
263 used to correct it. Hence, the treatment and measurement errors related to this correction are the  
264 cause of an additional error of 11.9%, and will be referred as  $E_{Cor}$ . This value has been estimated  
265 accounting for the measurement and data treatment errors related to the standard glass  
266 measurement. The first two error,  $E_{Meas}$  and  $E_{Tr}$ , sources apply on each point separately, while the  
267 correction error  $E_{Cor}$  applies to all the points of a measurement session. The values of the  
268 estimated errors are reported in **table 1**.

269         The intensity versus angle model curves (as shown in **Figure 3**) were then used to build a  
270 3D model of OH/Si variation as a function of crystallographic orientation. In **Figure 3** it is visible  
271 that the fitted curves do not coincide with the corresponding minima and maxima from the other  
272 faces (for example, the maxima of the “a” and “b” curves for olivine are different, but both  
273 describe the OH/Si intensity parallel to the “c” axis and should be equal). These differences are  
274 very likely to be caused by misalignment of the polished faces with respect to the  
275 crystallographic axes. To obtain a continuous set of three curves in 3D (as depicted by the bold  
276 lines in **Figure 4**), the amplitudes of the curves have been increased or decreased so that they  
277 cross each other along the crystallographic axes, keeping at the same time the average value of  
278 each curve constant. Intermediate orientation values were completed by combining those  
279 acquired along crystallographic axes, each point of any orientation being obtained with equation  
280 5:

281 **Equation 5**

$$\left(\frac{OH}{Si}\right)_{\alpha} = \sum \left(\frac{OH}{Si}\right)_i \times \cos^2(\alpha_i)$$

282 In this equation, any orientation  $\alpha$  is defined by a vector with a norm equal to the  
283 corresponding  $(OH/Si)_{\alpha}$  value. This vector has one projection on each of the “a”, “b” and “c”  
284 planes corresponding to values  $(OH/Si)_i$  fitted with equation 3 or 4 for a given angle (see **Figure**  
285 **3**).  $(OH/Si)_{\alpha}$  is then calculated as being the sum of these three  $(OH/Si)_i$ , each multiplied by the  
286 squared cosine of the angle between the defined vector and its projection on the corresponding  
287 plane. This operation results in a peanut-shaped three-dimensional OH/Si model for each phase  
288 when displayed in a 3D polar graph (see **Figure 4**, depicting OH/Si variation in olivine and  
289 **supplementary materials 2** for wadsleyite). The OH/Si is depicted here as the distance between  
290 the peanut-shaped surface and the intersection of the a, b, and c axes. In both olivine and  
291 wadsleyite cases, it can be observed that high OH/Si values are located along one axis, identified  
292 as the c-axis for olivine, and that variations seem approximately axisymmetric for both of them.  
293 This modelling process can be applied to other orthorhombic minerals (or quadratic), each model  
294 being based on its own measured OH/Si values (as shown in **Figure 3**). Minerals with other  
295 crystal system could still be modelled, but they might require a different procedure of polishing,  
296 measurement and 3D model extrapolation.

297 **Distinguishing OH/Si natural dispersion and errors**

298 The 3D OH/Si distribution models for olivine and wadsleyite have then been used as basis  
299 to simulate measurements, in order to untangle the effects of natural dispersion (i.e. due to  
300 crystallographic orientation) and analytical uncertainties on the final error for any type of  
301 measurement (single points or orthogonal couples) and as a function of the number of

302 measurement points. To achieve this, the first step is to generate a set of random uniformly  
303 distributed crystal orientations that simulates a polycrystalline sample. A random “longitude”  
304 angle between 0 and 360° is first generated (uniform distribution), and a second “latitude” angle  
305 is generated with a semicircle distribution with a maximal probability for 0° and a probability of  
306 reaching zero when approaching 90 or -90°. To each orientation corresponds an OH/Si value  
307 determined as described for the construction of the 3D model. On each point chosen among those  
308 of this surface, the estimated measurement and treatment errors are applied, using equation 6.  
309 Here,  $X_{Meas}$  and  $X_{Tr}$  represent normally distributed random values with an average of zero, and a  
310 standard deviation equal to the desired error component  $E_{Meas}$  or  $E_{Tr}$ . Each “modeled”, or  
311 simulated point (OH/Si)<sub>M</sub> has its own  $X_{Meas}$  and  $X_{Tr}$  values, because those errors do apply on  
312 every point separately and independently, finally yielding the "real" value (OH/Si)<sub>R</sub>.

313 **Equation 6**

$$\frac{OH}{Si}_R = \frac{OH}{Si}_M \times (1 + X_{Meas}) \times (1 + X_{Tr})$$

314 For single point measurements, the simulated sample value will be the average of all the  
315 (OH/Si)<sub>R</sub>, multiplied in the same way by  $1 + X_{Cor}$  to simulate the errors arising from the laser  
316 power drift correction. In the case of orthogonal couples measurements, the two resulting  
317 (OH/Si)<sub>R</sub> values of each measurement point are averaged, then all points are again averaged  
318 before applying the  $1 + X_{Cor}$  factor.

319 All the error and dispersion values used in the following section are expressed as relative  
320 errors, in percent of deviation from the average. Hereafter, the goal is to get the standard  
321 deviation and the average of each simulated measurement session for any number of  
322 measurement points and repeat the operation a large number of times to get a result as

323 statistically significant as possible. In this study, final values have been obtained for sets of 2 to  
324 30 points in both single point and orthogonal couples, with one million draws for each case. For  
325 each number of points, the average of all the standard deviations of all sets of values has been  
326 interpreted as the expected measured dispersion  $D_{Th}$ , and the standard deviation of all the  
327 averages of all the set of points has been interpreted as the error expected for the measurement  
328 ( $E_{Th}$ ). Both  $D_{Th}$  and  $E_{Th}$  depend on the number of measurement points and on the technique used  
329 for the measurement (single point or orthogonal couples). Dispersion increases when adding  
330 points, reaching an approximate plateau past 10 points, and error decreases when adding points,  
331 but stabilizes much slower past 30 points, limited by the contribution of  $E_{Cor}$  to the final error  
332 (see Figure 5).

333 The dispersion and error values obtained by the above simulation were then fitted to  
334 obtain error propagation equations as a function of the number of points, the measurement  
335 method, and the different errors sources. The natural dispersion caused by anisotropy can be  
336 estimated from equation 7 below. Here  $D_{Nat}$  is the natural dispersion, which is the expected  
337 relative standard deviation obtained on a random set of measurements without any kind of error  
338 added as a function of the number of points ( $N$ ).  $D_{An}$  represents the total anisotropy, and is the  
339 same standard deviation as  $D_{Nat}$ , but for an infinite set of points, and finally "a" is a fitting  
340 parameter (all the values of the different parameters are shown in Table 1).

341 **Equation 7**

$$D_{Nat} = D_{An} - \frac{a}{N - 1}$$

342 Equations 8 and 9 also express the dispersion of values and in addition takes into account  
343 the errors arising from measurement and data treatment. As the normalization related errors ( $E_{Cor}$ )

344 apply on all the points in the same way, it does not have any effect on the relative dispersion.  
345 Equation 8 gives the expected dispersion for single points measurements, and equation 9 for  
346 orthogonal couples. Here,  $D_{An}$ , "a" and  $N$  are the same as in equation 7,  $E_{Meas}$  is the measurement  
347 error, and  $E_{Tr}$  is the data treatment error.

348 **Equation 8**

$$D_{Th} = \sqrt{D_{An}^2 + E_{Meas}^2 + E_{Tr}^2} - \frac{a}{N - 1}$$

349 **Equation 9**

$$D_{Th} = \sqrt{D_{An}^2 + \frac{E_{Meas}^2 + E_{Tr}^2}{2}} - \frac{a}{N - 1}$$

350 The theoretical uncertainties follow a simple error propagation equation, which is  
351 expressed as shown in equation 10 for single points measurements, and equation 11 for  
352 orthogonal couples. Here,  $E_{Cor}$  plays a role on the final relative error and tends to account for  
353 most of the uncertainty when the number of points increases (see Figure 5).

354 **Equation 10**

$$E_{Th} = \sqrt{\frac{D_{An}^2 + E_{Meas}^2 + E_{Tr}^2}{N} + E_{Cor}^2}$$

355 **Equation 11**

$$E_{Th} = \sqrt{\frac{D_{An}^2 + \frac{E_{Meas}^2 + E_{Tr}^2}{2}}{N} + E_{Cor}^2}$$

356 Each of the above equations can be applied for both olivine and wadsleyite. All the  
357 parameters are displayed in **Table 1**.

358 It can be noted that all the dispersions and errors in this simulation neglect the initial  
359 asymmetry of the distribution of the OH/Si values (see distribution histograms in **supplementary**  
360 **materials 3 and 4**) which, although abnormal and strongly asymmetric (towards high values for  
361 single points measurements and low values for the orthogonal couples), rapidly tends toward a  
362 Gaussian-shaped distribution above 10 to 15 points. Moreover, the asymmetry of the distribution  
363 might be very difficult to observe on a real set of measurement because of the limited set of  
364 points in which the distribution of values may not have any statistical significance. Hence, the  
365 deviation caused by this hypothesis tends to be negligible above 10 to 15 measurement points,  
366 but very low number of points should still follow a very asymmetric distribution, increasing  
367 error.

368 It can be noted that the measurement and treatment errors have a very small effect on both  
369 the dispersion and the error (see **Figure 5**). On the other hand, power drift correction related  
370 errors ( $E_{Cor}$ ) have a very strong effect on the final error, demonstrating that this step must be  
371 carefully performed in order to get correct values. An important result is that the use of averaged  
372 orthogonally polarized measurements roughly halves the theoretical dispersion of the values, thus  
373 decreasing the associated error. The total expected dispersion directly related to anisotropy  
374 (neglecting all the other error sources) for olivine is around  $\pm 29.4\%$  for single points and  $\pm 14.8\%$   
375 for orthogonal couples. Wadsleyite displays slightly higher values, with 32.5% and 16.8% (all  
376 these values are shown in **Table 1**). The same effect could be reached on single points  
377 measurements with approximately four times more points. Another advantage of using the

378 orthogonal couples is that it forces to measure more diverse grain orientations in the sample,  
379 hence limiting the effect of a potential preferential crystallographic orientation within the sample.

380 To sum up, assuming a chemically homogeneous sample (in terms of water content), if  
381 the standard deviation is close to the expected dispersion (calculated with equations 8 or 9), the  
382 real analytical error is given by equations 10 or 11. It follows that, in the ideal case of randomly  
383 oriented crystals, the error on OH/Si for 5 to 10 measurement points is between 15 and 18% for  
384 single points, and 12 and 15% for orthogonal couples. A deviation inferior to the expected  
385 deviation (still assuming that the sample is homogeneous) would point out an insufficient  
386 sampling of the natural dispersion. A rough estimation of the real error in this case can be  
387 obtained with equation 12. Here, the difference between the expected deviation  $D_{Th}$  and the  
388 measured value  $D_{Smp}$  causes the final error ( $E_{Smp}$ ) to increase from the ideal value  $E_{Th}$  to the total  
389 dispersion  $D_{Th}$ , equal to the error expected on a measurement based on one single measurement  
390 point.

391 In contrast, if the standard deviation is higher than  $D_{Th}$ , whether because the sample is  
392 heterogeneous or the measurements are too defective, the error "reduction" from  $D_{Smp}$  to  $E_{Smp}$   
393 (from equations 8 or 9 to equations 10 or 11) may not be reasonable to apply directly.  
394 Considering that the sampling is sufficient in this case, an error approximation can be obtained  
395 from equation 10 (variables are the same as in equation 13).

396 **Equation 12**

$$E_{Smp} = D_{Th} - (D_{Th} - E_{Th}) \times \frac{D_{Smp}}{D_{Th}}$$

397 **Equation 13**

$$E_{Smp} = \sqrt{\left(D_{Smp} \times \frac{E_{Th}}{D_{Th}}\right)^2 + (D_{Smp} - D_{Th})^2}$$

398 **Olivine and wadsleyite calibration lines**

399 The water content of the samples used to build the calibration lines are shown in **Table 2**,  
400 along with the values of OH/Si measured with Raman spectroscopy. The calibration lines (see  
401 equation 14 and **Figure 6**) are built with least-square minimization, always pass by the origin, and  
402 take into account the effect of the water content uncertainties arising from FTIR and ERDA  
403 measurements as well as the Raman measurement. All the error bars on the OH/Si have been  
404 estimated with the method described above. Some samples thus display a relatively large error  
405 bar (such as 949 or M380b, see **Figure 6** and **Table 2**) because the measured dispersion was  
406 significantly greater than the expected dispersion (obtained from equations 8 to 11). On the other  
407 hand, some samples, such as M382, displayed a very low dispersion that may be related to  
408 insufficient sampling, once again resulting in a larger error bar. The factor to convert from OH/Si  
409 to ppm in weight of water ( $F$  in equation 11) is  $93108 \pm 24005$  for olivine,  $250868 \pm 45591$  for  
410 wadsleyite (with iron), and  $57546 \pm 13916$  for wadsleyite (without iron). This result shows the  
411 tremendous effect of iron on the spectrum's shape and intensity, implying that chemical  
412 composition has to be verified in order to quantify the water content of wadsleyite. There are two  
413 identified causes to this difference, the first being that for two samples with comparable water  
414 contents, the Si area of an iron-free wadsleyite displays sharper peaks, even if their heights are  
415 comparable, implying a lower Si intensity. However, at the same time, its OH area is more  
416 intense. This causes the OH/Si of an iron-free wadsleyite to be much higher than the one of an

417 iron-bearing wadsleyite with a comparable water content (see [supplementary materials 5](#)). [Figure](#)  
418 [6](#) displays the calibration lines for olivine and wadsleyite.

419 **Equation 14**

$$C_{H_2O}(ppm\ wt) = F \times \frac{OH}{Si_{Smp\ Norm}}$$

420 The uncertainty on the slope obtained for each calibration has to be added to the final  
421 error  $E_{Smp}$  described above, the total uncertainty on the water content being given by equation 15,  
422 where  $E_{H_2O}$  is the total error,  $E_{Smp}$  is the total relative error on the OH/Si of the sample, and  $E_{Cal}$  is  
423 the calibration-related relative error. The same can be applied to dispersions.

424

425 **Equation 15**

$$E_{H_2O} = \sqrt{E_{Smp}^2 + E_{Cal}^2}$$

426 The uncertainty on the slope of the calibration line (as shown in [Figure 6](#)) arising from the  
427 errors in water quantification of the standards and from the error on their OH/Si *often* becomes  
428 the major component of the total uncertainty on the water content compared to the error on the  
429 measurement of OH/Si with Raman spectroscopy.

430 Regarding olivine, the 26% uncertainty on the calibration line is much larger than the  
431 12% error on the OH/Si measurement attained for a large number of points (in the case of  
432 orthogonal couples, see [Figure 5](#)). Following equation 15, this 12% error ( $E_{Smp}$ ) increases to 29%  
433 only because of the uncertainty on the calibration ( $E_{Cal}$ ). The same problem applies to wadsleyite  
434 with the 18% error on the calibration line for iron-bearing wadsleyite and the 24% error for iron-

435 free wadsleyite. The greater is the error on the OH/Si of the sample (because of insufficient  
436 sampling or sample heterogeneities), the smaller the contribution of calibration uncertainties to  
437 the total error will be (see Figure 7).

## 438 **DISCUSSION**

439         The quantification of as much error and uncertainty sources as possible provides a better  
440 understanding of the data dispersion inherent to the use of Raman spectroscopy on anisotropic  
441 crystals. The relative impact of each source of error highlights what affects the more the final  
442 error, showing where further progress and developments could be made. The first issue is the  
443 laser-drift during and between different sessions. The method used to overcome this problem  
444 brings an additional source of error (referred as  $E_{Cor}$  throughout this study), as it implies two  
445 OH/Si ratio measurements on a standard glass, thus adding twice data treatment and  
446 measurement error to the result (divided by  $\sqrt{2}$ , as the value measured is supposed to be the same  
447 for the two measurements). Moreover, as this correction has to be applied on all the points of a  
448 sample, its contribution to the total error does not decrease with an increasing number of points.  
449 Consequently, its relative contribution increases, and becomes the major part of the error on the  
450 OH/Si ratio above around 20 to 25 single points, or 5 orthogonal couples (see Figure 5). This  
451 power-drift correction error is also responsible for a significant part of the calibration error, thus  
452 acting in two different ways in the final error. On the other hand, insufficient sampling of the  
453 natural dispersion rapidly causes the final error to be larger than the measured dispersion (see  
454 equation 11). Orthogonally polarized averaged measurements, improving by force the sampling  
455 of various orientations (and thus, anisotropy) help to prevent from orientation biases.

456         Secondly, the effect of the calibration uncertainty (caused by the errors on each standard  
457 point) on the final error acts similarly as the power-drift correction uncertainty (both are

458 insensitive to the number of points), rapidly becoming the major part of the error, particularly for  
459 olivine. Focusing on the ideal case where the dispersion observed on the sample ( $D_{Smp}$ ) equals the  
460 theoretical dispersion ( $D_{Th}$ ), implying that  $E_{Smp}$  and  $E_{Th}$  are equal, the conversion factors  $D_{H2O}/$   
461  $E_{H2O}$  (following equation 15, and applying this to the dispersion by replacing  $E_{Smp}$  with  $D_{Smp}$  to  
462 obtain  $D_{H2O}$ ) and  $D_{Smp}/E_{Smp}$  of wadsleyite are superior to those of olivine in all cases (except for  
463 two points in the orthogonal couples case, see **Figure 7**). This is caused by the higher effect of the  
464 error sources on  $D_{Th}$  than on  $E_{Th}$  in the case of wadsleyite, where  $E_{Cor}$  mitigates their effect, hence  
465 increasing  $D_{Smp}/E_{Smp}$ . Adding  $E_{Cal}$  does not change this observation, except that it mitigates these  
466 effects, lowering the expected "gain" on errors, with higher attenuation for higher  $E_{Cal}$  (see **Figure**  
467 **7**). In the case of a poor sampling, accounting for  $E_{Cal}$  tends to mitigate the effect of the error  
468 augmentation (see equation 9) by increasing  $E_{Smp}$  to a much higher  $E_{H2O}$ , lowering the effect of  
469 equation 15.

470 Water content heterogeneities may cause the measured dispersion to be larger than the  
471 expected one. In such cases, when the ratio of observed over expected dispersion is close to one,  
472 even if the gain may seem high, it is important to consider that chemical heterogeneities should  
473 remain as low as possible (see the discussion around equation 13). The present water  
474 quantification method by Raman spectroscopy relies on the hypothesis that only the orientation  
475 varies from one crystal to another, and that these orientations are distributed randomly and  
476 uniformly. This means that chemically heterogeneous samples (should it be a major element  
477 content variation, or in water content variation) are unsuitable for precise water quantification  
478 with this method. In the case of wadsleyite, we observed that the iron content has a tremendous  
479 effect on the calibration line slope, implying that composition has to be measured to verify if all  
480 the analyzed crystals have a similar iron content. The problem of the random distribution of

481 orientations in samples also has to be considered, as preferential orientation may occur in some  
482 samples. However, if a sample is chemically homogeneous, a sample with a strong disparity of  
483 orientations could be identified if it displays values dispersion much smaller than the expected  
484 dispersion (see discussion around equation 12).

## 485 **CONCLUSION**

486 Raman spectroscopy allows the water content measurement of samples of any size above  
487 few micrometers, and with water contents down to 150-200 ppm in weight (see Bolfan-Casanova  
488 et al. 2014), with no observed upper limit, where many other methods may require large samples,  
489 or are unsuitable for very high water contents (FTIR). Even if vibrational spectroscopy is very  
490 useful to discriminate OH point defects over contamination, the sensitivity to crystallographic  
491 orientation in anisotropic samples often leads to high standard deviations in the measurements of  
492 water content (Férot and Bolfan-Casanova 2012). Here we show that a large part of this  
493 dispersion may be related to the natural anisotropy of the measured mineral, and is thus normal.  
494 The main objective of this work was to be able to calculate the error associated to the  
495 measurement of water content in olivine and wadsleyite, using Raman spectroscopy, knowing the  
496 anisotropy of the OH/Si ratio for each phase. We identified throughout this study various sources  
497 of error. The major parameters (beside anisotropy) affecting errors on the final values are the  
498 uncertainties on the calibration line, insufficient sampling of anisotropy, and the laser-drift  
499 correction errors. Nevertheless, most of the errors obtained with this procedure fall in a range of  
500 20-25% of relative error for wadsleyite, and 25-30% for olivine, making Raman spectroscopy  
501 still suitable for quantification water content in olivine and wadsleyite. The detailed study of the  
502 error sources has provided a greater understanding of the method, and has allowed an

503 improvement of the treatment methods, reducing significantly the uncertainties arising from this  
504 part of the procedure.

## 505 **IMPLICATIONS**

506 The high spatial resolution of Raman spectroscopy allows the study of water distribution  
507 among different phases of fine polymineralic samples of complex (natural) composition, with a  
508 wide range of measurable water contents. Although relatively high, the uncertainties on water  
509 concentration are sufficiently low to infer the effect of thermodynamic intensive parameters on  
510 water incorporation. The method proposed here can also be applied to all orthorhombic minerals.

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- 629 Zarei, A., Klumbach, S., and Keppler, H. (2016) The relative Raman scattering cross sections of  
630 H<sub>2</sub>O and D<sub>2</sub>O, with implications for in situ studies of isotope fractionation. *ACS Earth*  
631 *and Space Chemistry*, 2, 925-934.
- 632

633 Table 1: Fitting parameters ( $D_{An}$  and  $a$ ) and estimated error sources values ( $E$ ) for  
 634 dispersion and error equations (equations 6 to 13).  $D_{An}$  is the calculated anisotropy contribution to  
 635 the observed values deviation;  $E_{Meas}$  is the measurement related error,  $E_{Tr}$  the treatment related  
 636 error, and  $E_{Cor}$  the laser-drift correction related error.

	Olivine		Wadsleyite	
	Single points	Orthogonal couples	Single points	Orthogonal couples
$D_{An}$	28.1	14.1	32.5	16.8
$a$	6	3	6.74	3.37
$E_{Meas}$	4.44	4.44	4.25	4.25
$E_{Tr}$	3.58	3.58	3.82	3.82
$E_{Cor}$	11.9	11.9	11.9	11.9

637

638 Table 2: Standards used for the olivine and wadsleyite calibrations of OH/Si versus H<sub>2</sub>O  
 639 concentration in ppm by weight of water. Wadsleyite\* standards are iron-free. Raman  
 640 measurement type "1" refers to the case of single point measurement and "2" to the case of  
 641 orthogonal couples.

Sample	Phase	Source measurement			Raman measurement			
		Method	ppm wt H <sub>2</sub> O	error	Type	Points	OH/Si	error
<b>949</b>	Olivine	FTIR	1304	290	1	8	0.01534	0.00371
<b>M497</b>	Olivine	ERDA	750	38	1	10	0.00405	0.00081
<b>M589</b>	Olivine	FTIR	1244	596	1	57	0.01127	0.00141
<b>1033</b>	Olivine	FTIR	522	176	2	11	0.00806	0.00118
<b>895b</b>	Olivine	FTIR	180	21	2	12	0.00382	0.00156
<b>1044b</b>	Olivine	FTIR	1766	674	2	10	0.01924	0.00250
<b>M817</b>	Olivine	FTIR	640	215	2	10	0.00350	0.00103
<b>M818</b>	Olivine	FTIR	291	72	2	10	0.00269	0.00104
<b>M230</b>	Wadsleyite	ERDA	1045	52	1	10	0.01591	0.00270
<b>M226A</b>	Wadsleyite	ERDA	4209	210	2	12	0.03863	0.00642
<b>M380b</b>	Wadsleyite	ERDA	12206	610	1	10	0.04219	0.01833
<b>M382</b>	Wadsleyite	ERDA	27271	1364	2	13	0.10122	0.01864
<b>M226B</b>	Wadsleyite*	ERDA	4000	200	2	10	0.10574	0.01457
<b>2053</b>	Wadsleyite*	ERDA	21600	1080	1	10	0.46945	0.10382
<b>2054</b>	Wadsleyite*	ERDA	34000	1700	1	10	0.49357	0.07957

642

643 **FIGURE CAPTIONS**

644 Figure 1 : Optical image of the olivine and wadsleyite samples used for the anisotropy  
645 quantification.

646  
647 Figure 2 : Raman spectra of olivine (grey) and wadsleyite (black) in the silicate region  
648 and the OH region. The wide bars underneath each graph (light bar for olivine, dark bar for  
649 wadsleyite) depict the integration window used for water quantification. The darker short lines  
650 depict the anchor point area used for baseline correction. The baseline shape is linear for olivine  
651 Si area, and cubic for OH area, and is polylinear for wadsleyite Si area, and cubic for OH area.

652  
653 Figure 3 : OH/Si values of olivine (top) and wadsleyite (bottom) as a function of the  
654 orientation of the crystal relative to the beam, for three perpendicular faces. Error bars are the  
655 estimated uncertainties linked to measurement errors and data treatment (see text). Horizontal  
656 error bars are an estimation of the angle's error. Solid and dashed lines (M) represent the fitted  
657 curves obtained through equation 3 (or 4 for wadsleyite). Olivine crystallographic faces were  
658 identified, whereas for wadsleyite, faces are named arbitrarily (F1, F2 and F3).

659  
660 Figure 4 : Three-dimensional plot of OH/Si values of olivine (as fitted in **Figure 3**) as a  
661 function of crystallographic orientation. Values obtained with incident beam parallel to the *a* axis  
662 are displayed in the (100) (bc) plane, and so on for the other faces. Grey points (which due to

663 their density may be displayed as light grey lines here) are the extrapolations of the solid lines  
664 (derived from Figure 3) for any given orientation (see equation 5).

665  
666 Figure 5 : Simulated relative dispersions (empty circles) and errors (solid circles) for  
667 olivine (top) and wadsleyite (bottom), for the case of single point measurements (left) and  
668 orthogonal couples (right), expressed in percent deviation from the average. Light grey symbols  
669 stand for the contribution of anisotropy ( $An$ ) alone. Adding the measurement ( $Meas$ ) uncertainties  
670 yields the intermediate grey symbols (mostly hidden by the dark grey ones). Adding treatment  
671 ( $Tr$ ) uncertainties gives the dark grey symbols, and finally adding the uncertainty arising from the  
672 power correction ( $Cor$ ) yields the black circles.

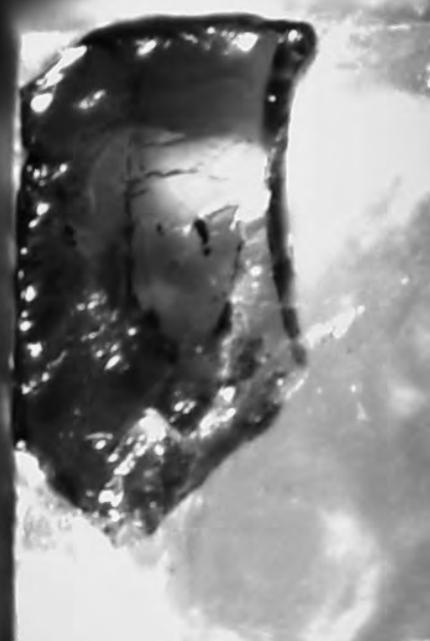
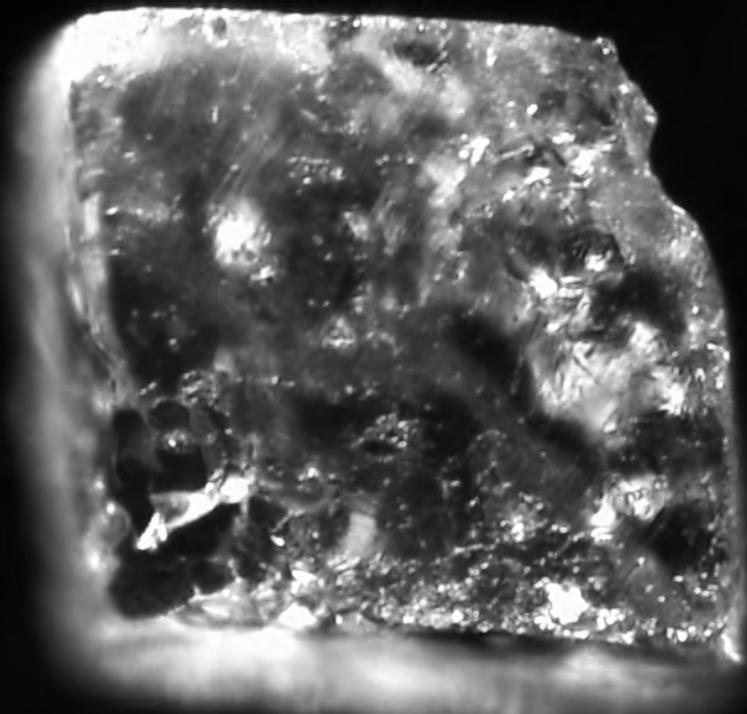
673  
674 Figure 6 : Calibration lines for olivine (top), iron-bearing wadsleyite (center) and iron-free  
675 wadsleyite (bottom). The straight line corresponds to the fitted value. The dashed and dotted lines  
676 show the  $1\sigma$  and  $2\sigma$  uncertainties respectively.

677  
678 Figure 7 : Dispersion over error ratio ( $D/E$ ) as a function of the number of points, for  
679 analytical uncertainties only (grey circles and discs, representing  $D_{Smp}$  and  $E_{Smp}$ ), and for total  
680 uncertainty, including calibration related uncertainty (black circles and discs, for  $D_{H2O}$  and  $E_{H2O}$ ).  
681 Full circles represent the ideal case where  $D_{Smp} = D_{Th}$  (ideal sampling), thin circles represent the  
682 insufficient sampling case (here,  $D_{Smp}$  is 75% of  $D_{Th}$ ), and thick circles represent the case of a  
683 dispersion  $D_{Smp}$  50% superior to  $D_{Th}$ .

Figure 1

Olivine

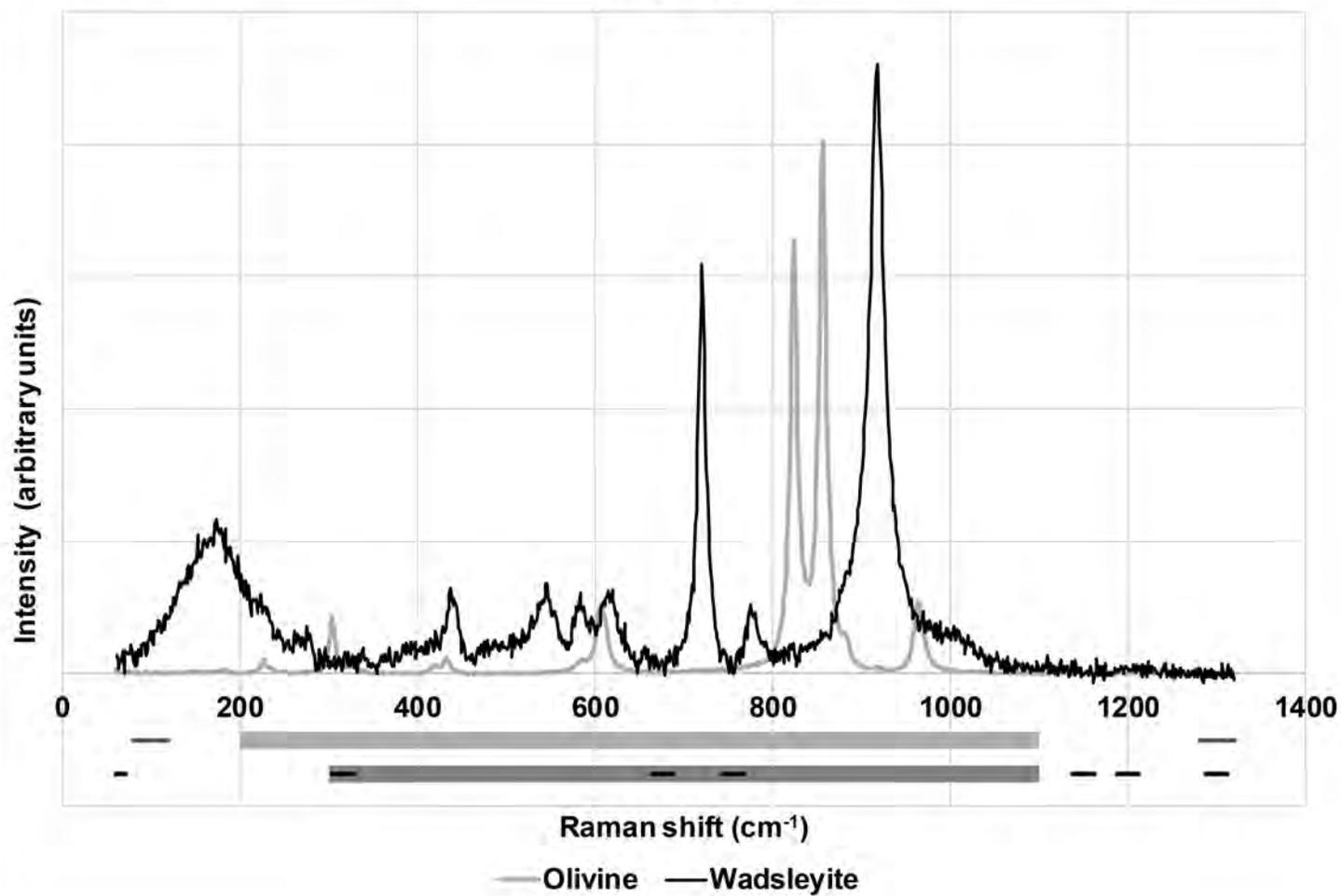
Wadsleyite



250  $\mu\text{m}$

Figure 2

### Si area



### OH area

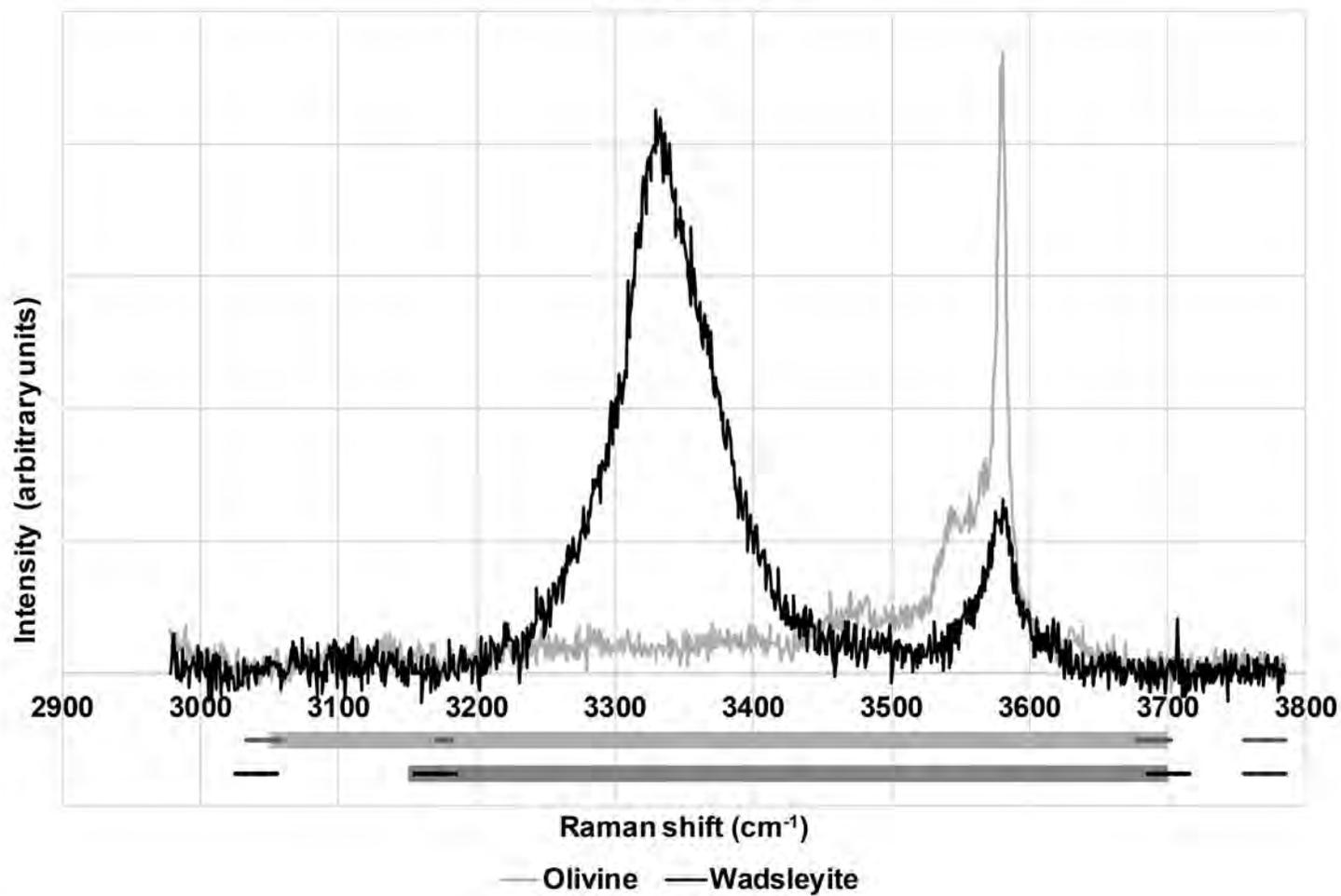
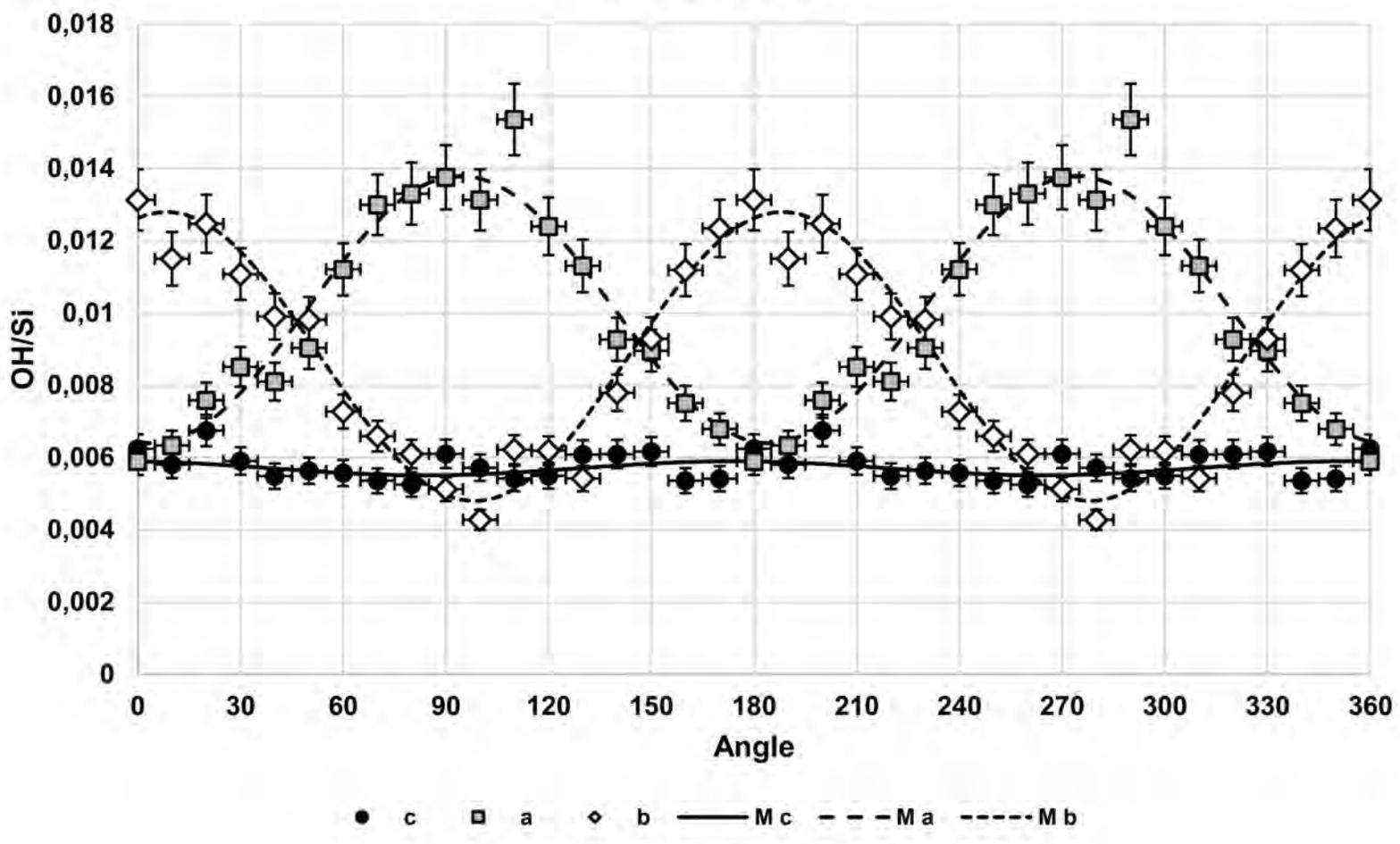


Figure 3

### Olivine OH/Si



### Wadsleyite OH/Si

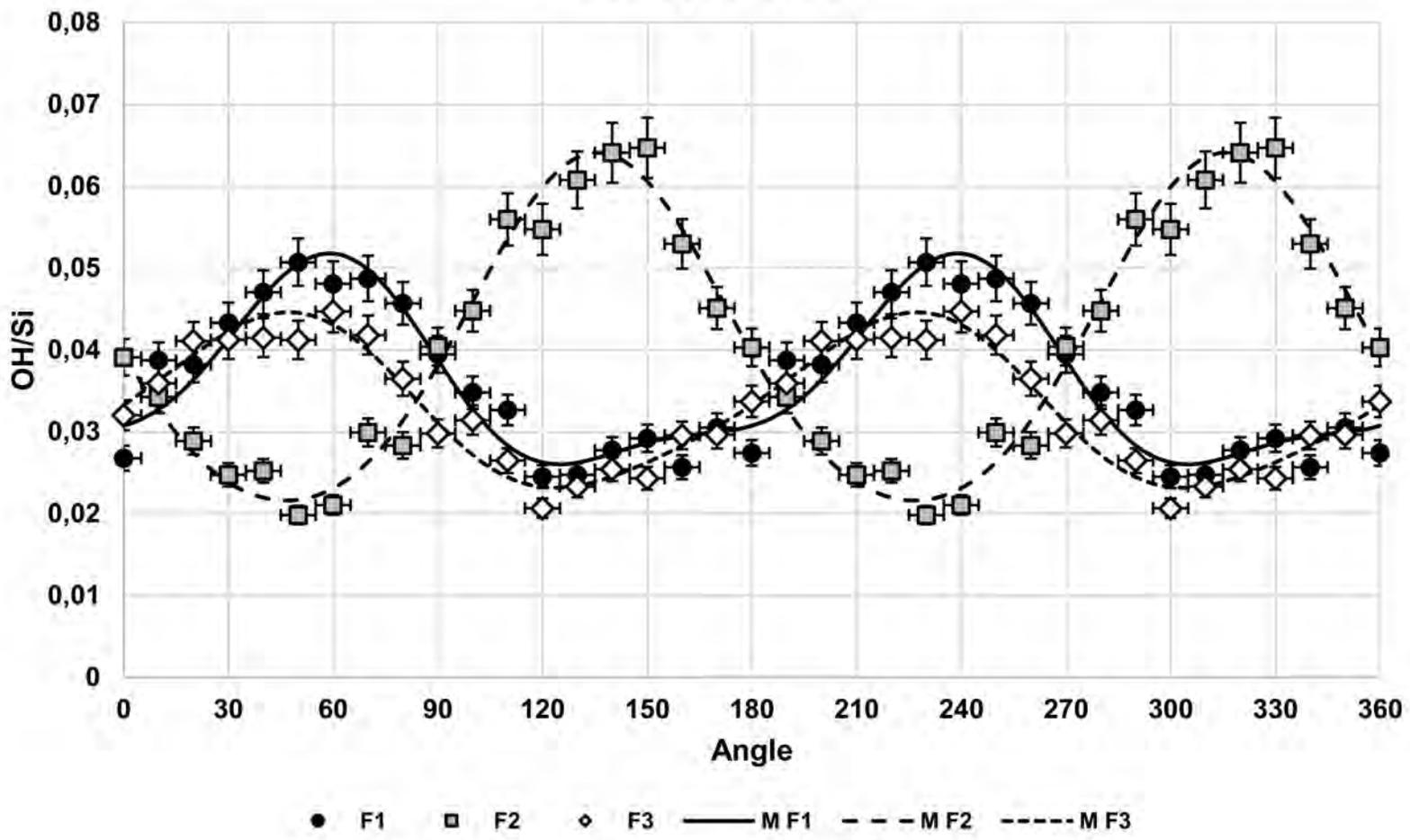


Figure 4

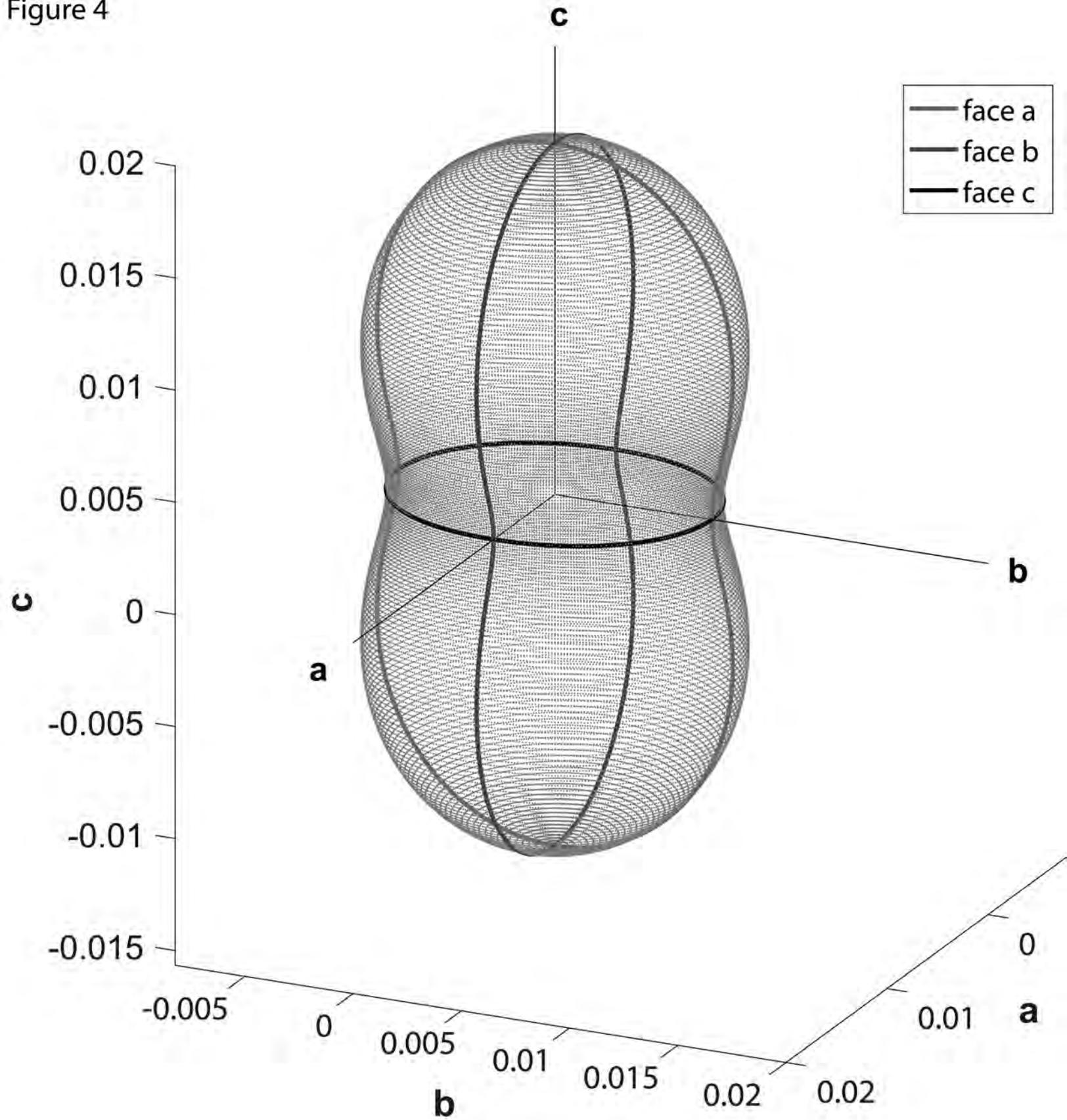
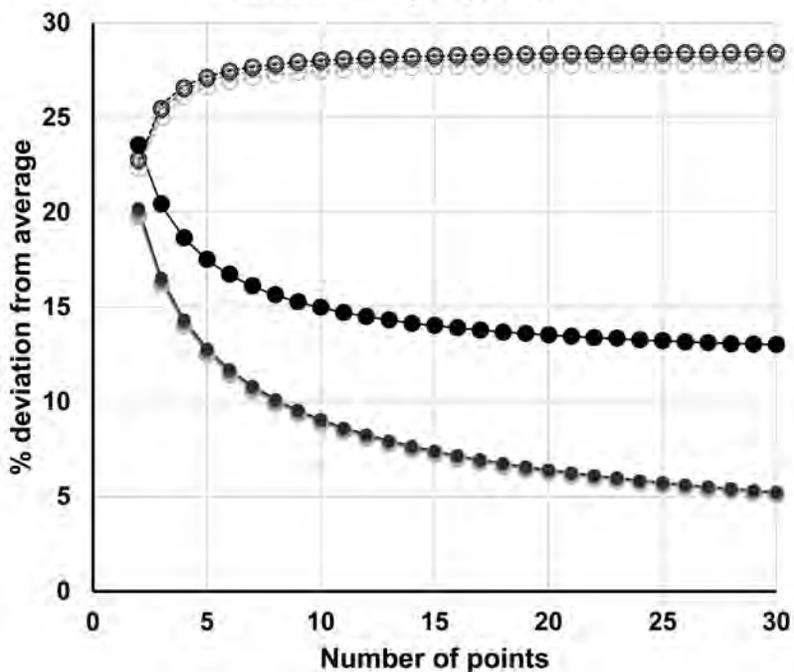
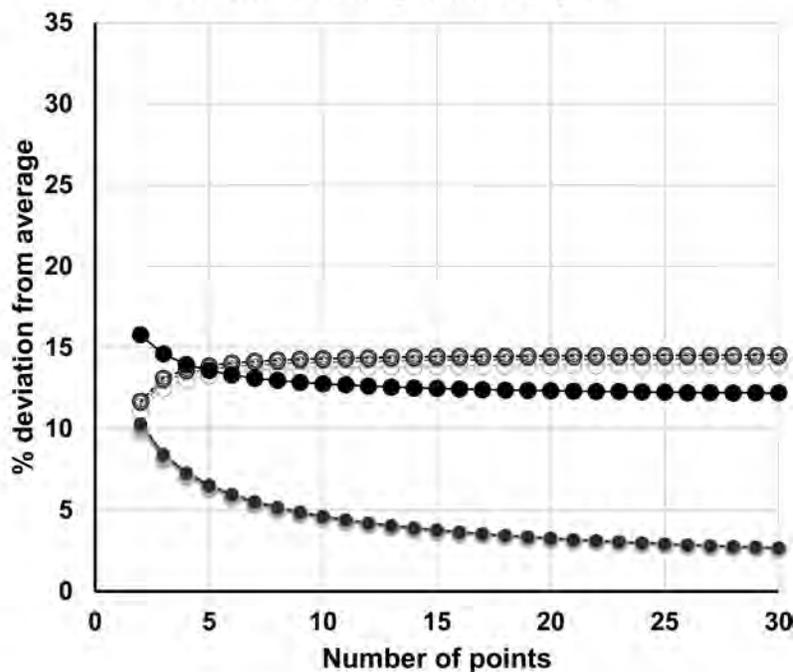


Figure 5

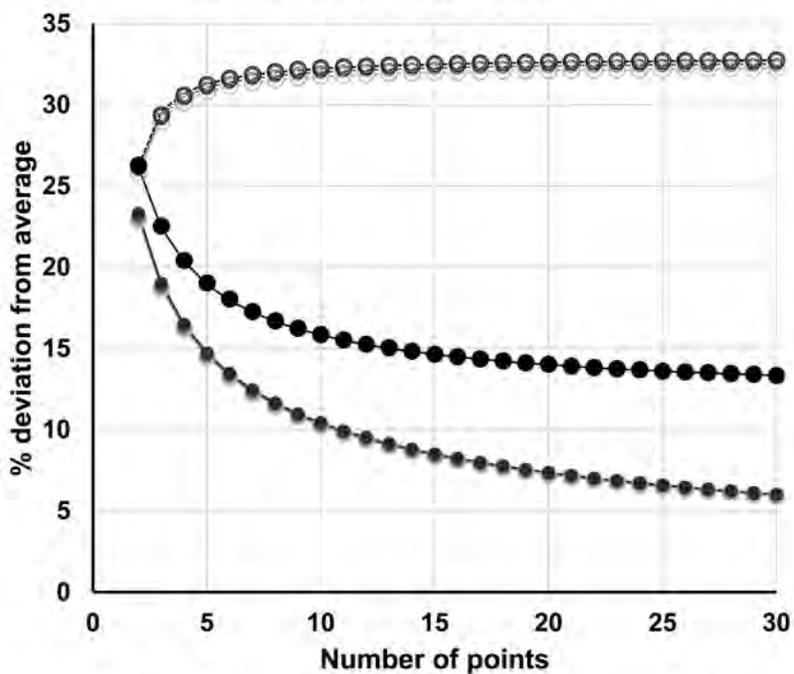
### Olivine single points



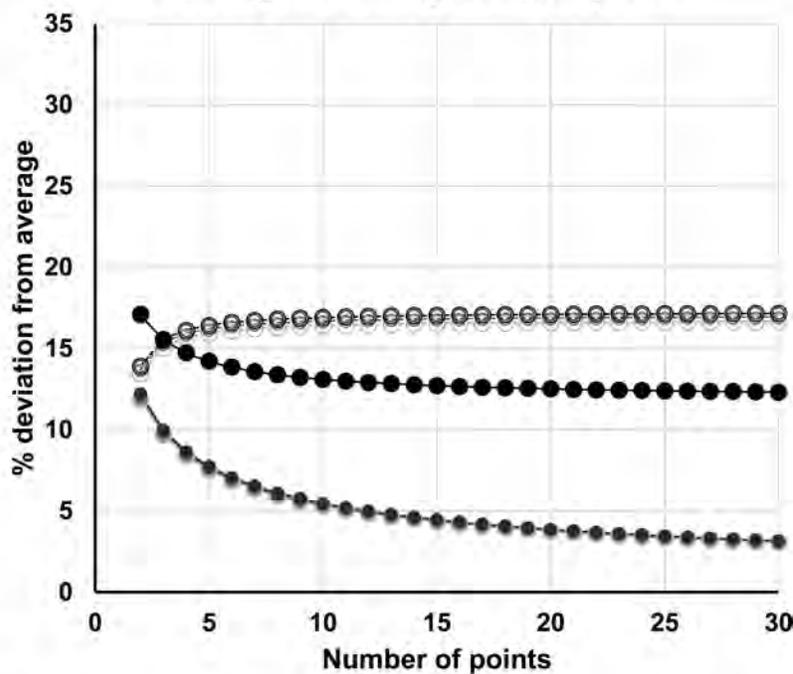
### Olivine orthogonal couples



### Wadsleyite single points



### Wadsleyite orthogonal couples



— Disp An    - - - - +Disp Meas    - - - - +Disp Tr    - - - - +Disp Cor  
 ○ Disp An    ○ +Disp Meas    ○ +Disp Tr    ○ +Disp Cor

— Err An    — +Err Meas    — +Err Tr    — +Err Cor  
 ● Err An    ● +Err Meas    ● +Err Tr    ● +Err Cor

Figure 6

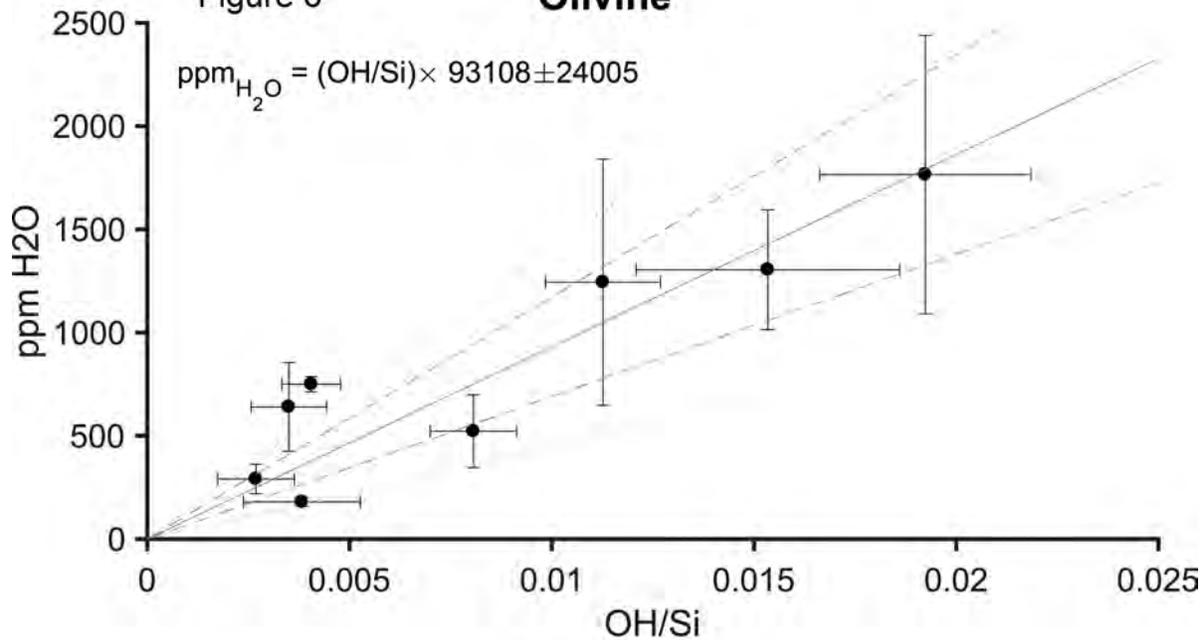
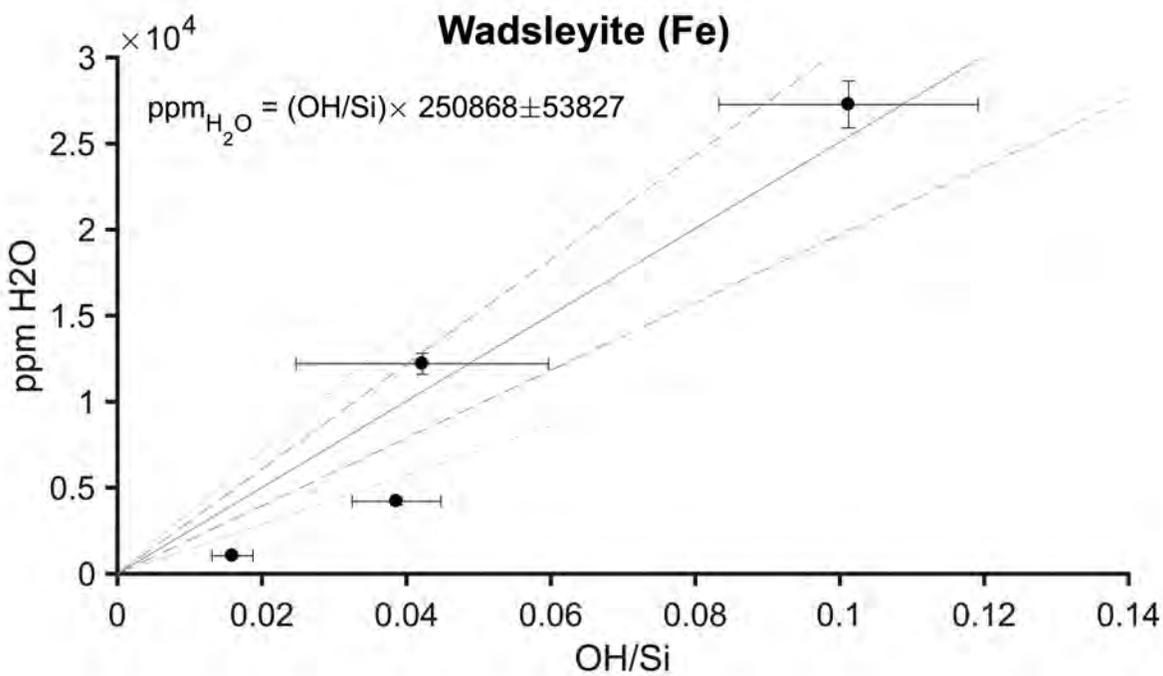
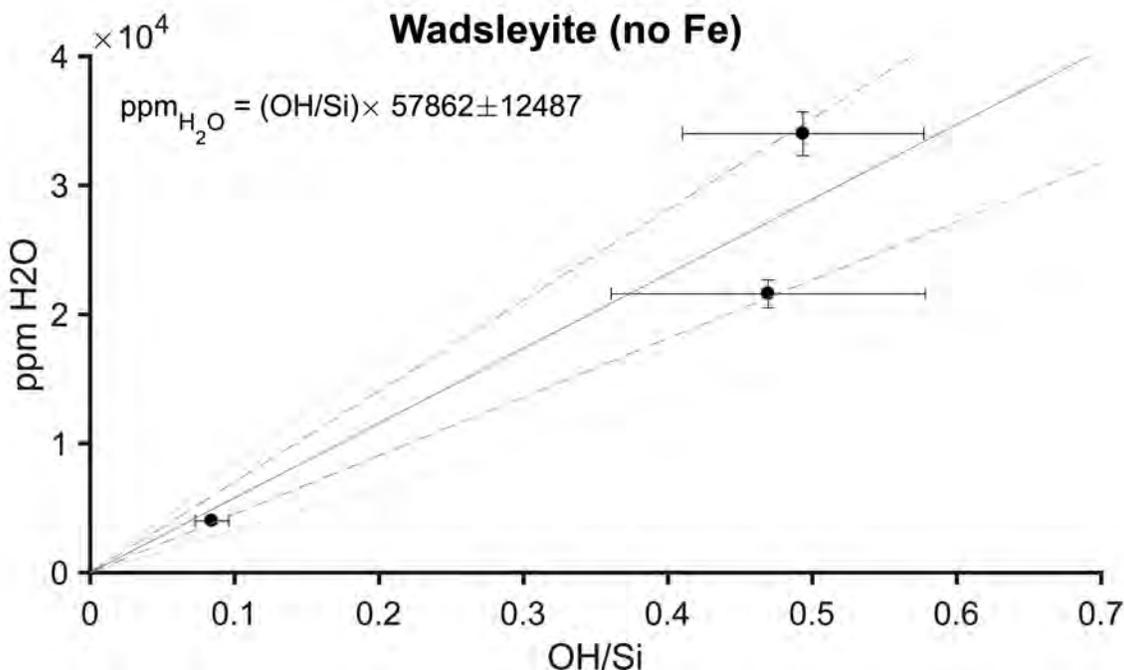
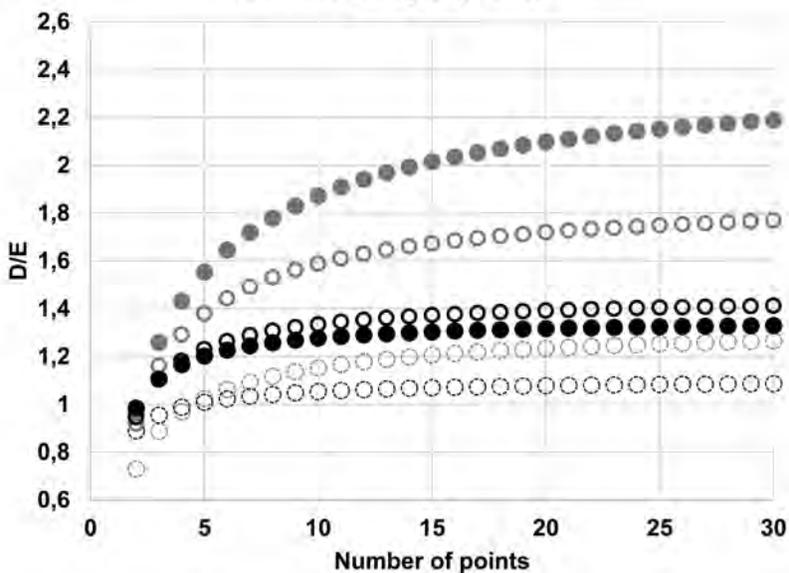
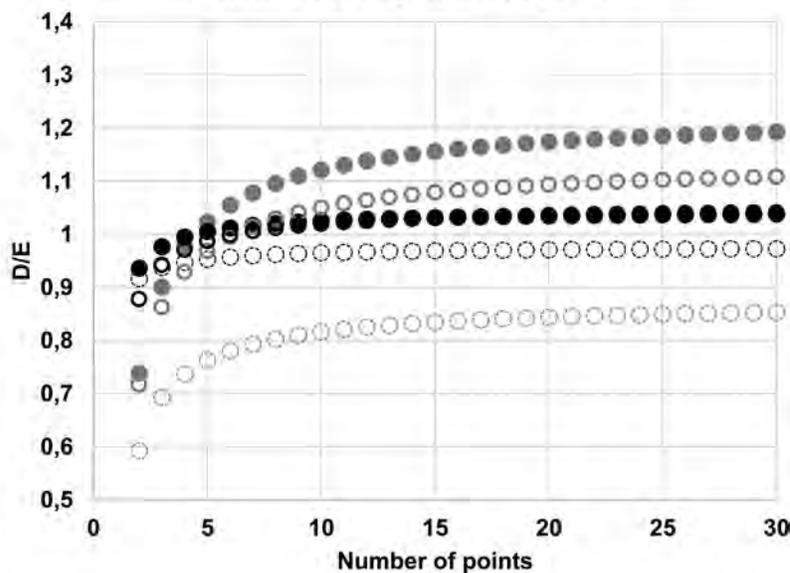
**Olivine****Wadsleyite (Fe)****Wadsleyite (no Fe)**

Figure 7

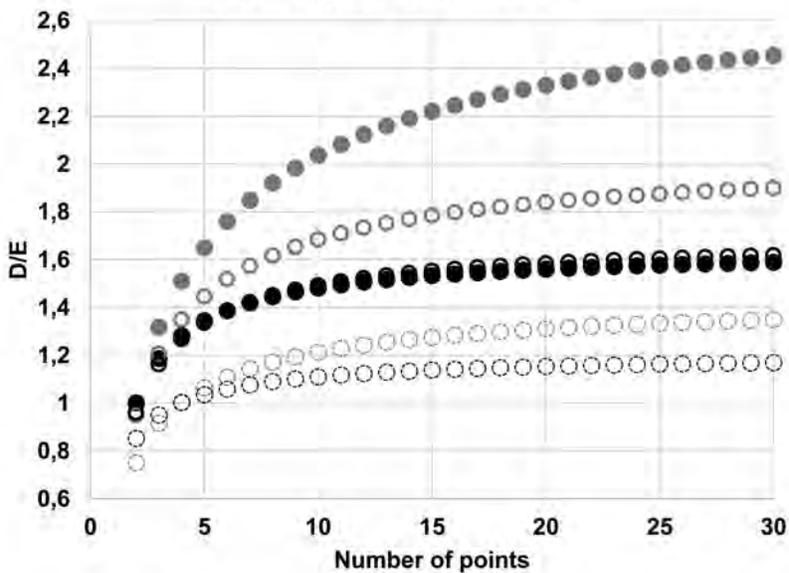
### Olivine single points



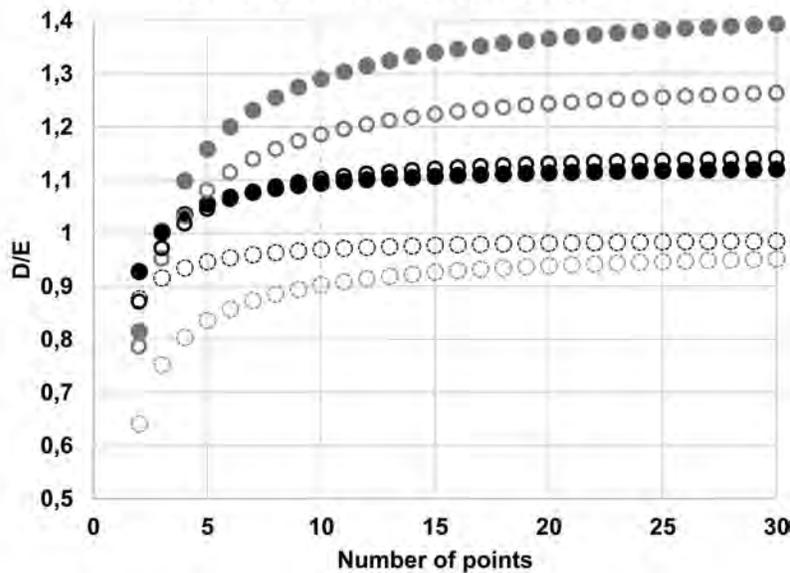
### Olivine orthogonal couples



### Wadsleyite single points



### Wadsleyite orthogonal couples



○ Smp 75%   ○ H<sub>2</sub>O 75%   ○ Smp 100%   ○ H<sub>2</sub>O 100%   ● Smp 150%   ● H<sub>2</sub>O 150%