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1 **Incorporation of tetrahedral ferric iron in hydrous ringwoodite**

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13 ABSTRACT

14 Hydrous Fo₉₁ ringwoodite crystals were synthesised at 20 GPa and high-temperature conditions using
15 a multi-anvil press. Recovered crystals were analysed using electron microprobe analysis, Raman
16 spectroscopy, infrared spectroscopy, synchrotron Mössbauer spectroscopy, single-crystal X-ray
17 diffraction and single-crystal Laue neutron diffraction, to carefully characterise the chemistry and
18 crystallography of the samples. Analysis of the combined datasets provides evidence for the presence
19 of tetrahedrally coordinated ferric iron and multiple hydrogen incorporation mechanisms within these
20 blue-coloured iron-bearing ringwoodite crystals. Tetrahedral ferric iron is coupled with cation disorder
21 of silicon onto the octahedrally coordinated site. Cation disorder in mantle ringwoodite minerals may
22 be promoted in the presence of water, which could have implications for current models of seismic
23 velocities within the transition zone. Additionally, the presence of tetrahedrally coordinated ferric iron
24 may cause the blue colour of many ringwoodite, and other high-pressure, crystals.

25 Keywords:

- 26 • Ringwoodite
- 27 • Single-crystal diffraction
- 28 • Mössbauer spectroscopy

29

30 INTRODUCTION

31 The Earth's transition zone (TZ), delineated by global seismic velocity discontinuities at ~ 410 and
32 660 km depth (Dziewonski and Anderson 1981), has the potential to be Earth's largest volatile
33 reservoir with a maximum water storage capacity greater than the entirety of surface reservoirs
34 (Jacobsen 2005). This is possible because wadsleyite and ringwoodite, high-pressure polymorphs
35 forming after olivine, constitute over 60 wt.% of TZ phase assemblages, and are capable of
36 incorporating up to 3.3 wt.% and ~ 2 wt.% H₂O respectively (33,000 and 20,000 wt. ppm)ⁱ associated
37 with point defects (e.g. Smyth 1987; Inoue et al. 1995; Ye et al. 2012; Fei and Katsura 2020). Whilst
38 experiments clearly demonstrate the potential for TZ water storage, whether or not Earth's mantle is
39 actually hydrated, and exactly how this water is incorporated in TZ minerals, continue to be the
40 subjects of ongoing research.

41 There is significant variation between the range of estimates for the TZ's water content. A natural
42 single crystal of ringwoodite, trapped as a mineral inclusion in a Brazilian diamond, was estimated, via
43 FTIR, to contain ~ 1.4 wt.% H₂O (Pearson et al. 2014; Thomas et al. 2015). This observation suggests
44 that the TZ is at least locally hydrated. However, it is unclear how this isolated observation from a
45 microscopic diamond-hosted inclusion might relate to the bulk water content of the TZ more globally.
46 Seismological studies aiming to constrain the water content of the TZ to-date have remained
47 inconclusive, variously suggesting that both a dry (< 0.1 wt. % H₂O) or wet (~ 1 wt.% H₂O) TZ might
48 be consistent with observations based on seismic velocities as well as the depths and magnitudes of
49 discontinuities (van der Meijde 2003; Meier et al. 2009; Suetsugu et al. 2010; Houser 2016).
50 Interpretations of water contents using magnetotelluric (MT) observations are inconsistent, and
51 suggest the TZ contains between 0.001 and 1 wt.% H₂O (Karato and Wu 1993; Huang et al. 2005;

ⁱ Whilst it is convention to discuss the "water content" of hydrous and nominally anhydrous Earth-forming minerals, there is not actually additional water molecules (H₂O) stored in these phases. Instead hydrogen is incorporated in association with various cation defects in the "anhydrous" crystal structure, thus it would be more technically accurate to discuss the "proton" or "hydrogen" content of these samples.

52 Yoshino et al. 2008; Munch et al. 2020). Alternatively, explanation of mantle viscosity profiles seem
53 to require the TZ to be close to water saturation, based on constraints from rheological experiments
54 (Fei et al. 2017). Irrespective of the true TZ water content, understanding the incorporation
55 mechanisms of hydrogen in crystals of wadsleyite and/or ringwoodite is important since, even at low
56 concentrations, defects are known to affect fundamental physical properties vital for understanding the
57 mechanics of mantle convection, e.g. viscosity, conductivity and elasticity (Thomas et al. 2012;
58 Hustoft et al. 2013; Schulze et al. 2018).

59 Compared to the defect chemistry of wadsleyite, which is relatively well understood and in which
60 protons almost exclusively substitute for Mg^{2+} vacancies (Smyth 1994), the behaviour of ringwoodite
61 is less well constrained (Kudoh et al. 2000; Smyth et al. 2003). Previous studies variously using ab
62 initio calculations, X-ray diffraction, spectroscopy (including at low temperatures) and 1H NMR have
63 concluded that a combination of multiple hydrogen incorporation mechanisms occur in ringwoodite
64 (Smyth et al. 2003; Blanchard et al. 2009; Panero et al. 2013; Grüninger et al. 2017). Suggested
65 substitutions include those where hydrogen is charge balanced by Mg^{2+} or Si^{4+} vacancies alone, but
66 also have included more complex mechanisms involving Si-Mg cation disorder. The extremely
67 disordered O-H stretching region observed in FTIR spectra of ringwoodite attests to the complexity of
68 water incorporation mechanisms in ringwoodite (Kudoh 2001; Smyth et al. 2003; Blanchard et al.
69 2009; Panero 2010), which is discussed far more extensively later in this paper. To date only two
70 experimental studies have attempted to directly investigate the hydrogen incorporation mechanisms in
71 iron-free ringwoodite, one using 1H solid state NMR (Grüninger et al. 2017) and the other time-of-
72 flight single-crystal neutron diffraction (Purevjav et al. 2018). No published studies have directly
73 investigated the incorporation mechanism of water in iron-bearing ringwoodite samples; this study was
74 an attempt to do this.

75 We present analyses of Fo_{91} ringwoodite crystals using a variety of techniques, which were all
76 performed on crystals synthesised in a single high-pressure experiment. Employing Electron Probe

77 Micro Analysis (EPMA), Raman, Infrared and Synchrotron Mössbauer Spectroscopy (SMS), the
78 chemistry, water content and ferric/ferrous iron ratio of the samples were determined prior to
79 diffraction data. Subsequently single-crystal X-ray diffraction and Neutron Laue diffraction data were
80 collected from the synthetic samples. This combination of analytical techniques provides new insights
81 into the crystallography of hydrous iron-bearing ringwoodite, which may be a major component of
82 mantle assemblages throughout the transition zone.

83

84 METHODS

85 Sample synthesis

86 The ringwoodite crystals investigated in the present study were synthesised in a single multi-anvil
87 experiment using a 5000 tonne multi-anvil press at the Bayerisches Geoinstitut. The starting material
88 consisted of synthetic brucite ($\text{Mg}(\text{OH})_2$), FeO and SiO_2 , to form a Fo_{90} olivine composition, and
89 contained 5 wt.% H_2O . This material was packed in a 2.0 mm diameter Pt capsule, welded shut, and
90 loaded into an 18 mm Cr-doped MgO octahedron with a LaCrO_3 heater. 54 mm WC carbide cubes
91 with 8 mm truncations were used to generate the sample pressure. Conditions of approximately 20
92 GPa and 1470 °C were maintained for 30 minutes before slowly cooling to 1150 °C over 6.5 hours at
93 which point the temperature was rapidly quenched and pressure slowly released. The recovered
94 capsule was opened and blue crystals (figure 1), ranging in size up to ~ 0.5 x 0.5 x 0.5 mm, were
95 recovered. It is noted that different individual crystals, but all from this single high-pressure
96 experiment, were analysed throughout this study. Small fractions of what was, presumably, quenched
97 melt were observed on the capsule walls.

98 Infrared, Raman and Mössbauer spectroscopy

99 Fourier transform infrared (FTIR) spectra were collected from doubly-polished single-crystal wafers of
100 40-60 μm thickness using a Thermo Scientific iN10 MX instrument operated in transmission mode at

101 University College London. Incident beam size was controlled using motorised apertures, and varied
102 from 30 x 30 μm to 100 x 100 μm . Unpolarised spectra were collected between 675 and 7000 cm^{-1}
103 from three randomly oriented crystals through a CaF_2 substrate (figure 2b). Sample thicknesses were
104 measured using a reflected light microscope with calibrated z-motion, and are estimated to be accurate
105 to within $\pm 2 \mu\text{m}$ (uncertainty of $\sim \pm 3.5 - 4.8 \%$). Raman spectra, with 4 cm^{-1} resolution using a 532
106 nm excitation laser (figure 2a), were collected using a WiTek Raman system in the Department of
107 Earth Sciences, University College London, UK.

108 Energy-domain Mössbauer transmission spectroscopy was performed on a single ringwoodite crystal
109 ($\sim 100 \times 100 \times 100 \mu\text{m}$ in size) at the nuclear resonance beamline ID18 at European Synchrotron
110 Radiation Facility (ESRF) using the synchrotron Mössbauer source (SMS) (Potapkin et al. 2012). The
111 velocity scales of all Mössbauer spectra were calibrated relative to 25 μm -thick $\alpha\text{-Fe}$ foil, and all
112 spectra were fitted using the software package MossA (Prescher et al. 2012).

113 Electron probe micro analysis

114 The major element chemistry of several crystals from within the recovered products was determined
115 with wavelength-dispersive spectroscopy using the Field Emission Gun Jeol JXA8530F Hyperprobe
116 situated in the School of Earth Sciences at the University of Bristol. In preparation for these analyses,
117 approximately ten ringwoodite crystals from the synthesis products were randomly picked, mounted in
118 epoxy, and polished using a range of grits down to 0.25 μm diamond paste. Samples were carbon
119 coated alongside a range of natural silicate and metal standards, beam conditions used were 15 keV
120 and 10 nA, and the calibrations were verified by analysing a range of in-house secondary standards
121 prior to analysing samples. Suitable crystals (a total of eight) were analysed in multiple locations using
122 a 30 nm incident electron beam, resulting in a spatial resolution of ~ 2 microns at the sample surface.
123 Data were reduced using a Phi-Rho-Z scheme accounting for the ferric iron (rounded to the nearest
124 absolute 10 %) and water contents measured by SMS and difference from 100 % total respectively.

125 Analyses with totals outside 98-100 wt.% (~ 99 – 101 wt.% after accounting for water incorporation as
126 quantified by FTIR) were rejected.

127 X-ray and Neutron diffraction

128 Single-crystal X-ray diffraction data were collected from a randomly selected crystal (~ 100 x 100 x
129 100 μm in size) using the standard setup on beamline ID15B of the ESRF. A monochromatic x-ray
130 beam ($\lambda=0.410884 \text{ \AA}$) of 10 x 10 μm size was used in conjunction with a MAR555 detector to collect
131 diffraction data in a $\pm 40^\circ \phi$ scan, integrating over 0.5° increments, Merlini & Hanfland (2013).
132 Integration of the reflection intensities and absorption corrections were performed using CrysAlisPro
133 (RED 171.32.29) software, prior to averaging and structure refinement using Jana2006, Petříček et al.
134 (2014).

135 Single-crystal Laue neutron diffraction of a large (~ 500 x 500 x 500 μm) crystal was performed on the
136 KOALA instrument on the reactor neutron source at the Australian Nuclear Science and Technology
137 Organisation (ANSTO), Australia. KOALA is a vertical-axis Laue diffractometer situated at the end of
138 a thermal-neutron guide. The incoming polychromatic neutron beam, which has a Maxwellian
139 distribution with wavelengths from ~ 0.5 to 4.5 \AA , was reduced to 0.8 – 1.7 \AA using beam choppers
140 (Piltz 2018a), and diffracted by the sample onto neutron sensitive image plate detectors that surround
141 the sample position in a cylindrical geometry extending $\pm 144^\circ$ in the horizontal and $\pm 52^\circ$ in the
142 vertical directions. Sample data were collected at 300 and 100 K (using the standard CF-2 cryostat on
143 KOALA), at a total of 33 sample positions. The total collection time for each dataset lasted ~ 3 days.
144 Reflection intensities were corrected for extinction and absorption using the LAUEG program
145 following the methodology of (Piltz 2018b). Subsequent structure refinement was performed using
146 Jana2006.

147 RESULTS

148 Spectroscopy and water content

149 Raman spectra collected from the sample consist of a doublet at ~ 796 and 841 cm^{-1} and broad peak(s)
 150 between 192 and 238 cm^{-1} (figure 2a), features which are very similar to previous ringwoodite spectra
 151 (Kleppe et al., 2002). The collected spectra were otherwise unremarkable, with no significant water
 152 related peaks observed between 3000 - 4000 cm^{-1} (figure 2b).

153 As observed for other OH-bearing ringwoodite samples, the FTIR spectra of samples in this study are
 154 dominated by an extremely broad absorption band caused by O-H stretching modes extending from \sim
 155 $2000 - 4000 \text{ cm}^{-1}$. This O-H band can be de-convolved into five, or more, symmetric peak
 156 contributions centred at 2512 , 2854 , 3124 , 3399 and 3653 cm^{-1} (figure 2c). This suggests the presence
 157 of multiple defect-related hydrogen positions in the ringwoodite structure, as discussed later. Water
 158 concentration in the sample was quantified by integrating the area beneath the background corrected
 159 absorption spectrum from $2000 - 4000 \text{ cm}^{-1}$ and applying the Beer-Lambert law,

160 $\epsilon = (A_i \times 1.8) / (d \times \rho \times c_{H_2O})$, where ϵ is the absorption coefficient (in $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-2}$), A_i = three
 161 times the integrated absorption between 2000 and 4000 cm^{-1} , d is sample thickness in cm, ρ is density
 162 (in $\text{g} \cdot \text{cm}^{-3}$) and c_{H_2O} is the concentration of H_2O in the sample (in wt.%). As absorption coefficients
 163 vary significantly between, and within, individual literature studies (Libowitzky and Rossman 1997;
 164 Thomas et al. 2015) we have assumed that a weighted average using a range of coefficients will
 165 provide a more accurate estimate of water concentration in the samples. Assuming uncertainties in
 166 sample thickness of $\pm 2 \text{ }\mu\text{m}$ and reported uncertainties in ϵ (or $\pm 20\%$ if not explicitly provided in the
 167 relevant publication) we calculate the ringwoodite samples studied contain between $0.84(16)$ and
 168 $1.32(25)$ wt.% H_2O (table 1, figure 3). The weighted average water concentration in the studied
 169 samples, including the water content estimated using EPMA (see below), is 1.05 ± 0.08 wt % H_2O .

170 Mössbauer spectroscopy

171 The SMS spectra (figure 4, table 2) from the ringwoodite sample is dominated by an asymmetric
 172 quadrupole doublet (centre shift [CS] $\sim 1.03 \text{ mm} \cdot \text{s}^{-1}$, quadrupole splitting [QS] $\sim 2.75 \text{ mm} \cdot \text{s}^{-1}$), with a
 173 smaller second component (CS $\sim 0.09 \text{ mm} \cdot \text{s}^{-1}$, QS $\sim 0.55 \text{ mm} \cdot \text{s}^{-1}$). As expected for the ringwoodite

174 structure, and following previous interpretations, the dominant doublet (coloured green in figure 4) is
 175 assigned to octahedral ferrous iron, i.e. Fe^{2+} substituting for magnesium in octahedral coordination.
 176 The smaller second component (blue in figure 4), which is visually similar to previous observations
 177 interpreted as a non-specific “charge-transfer” mechanism, is well resolved and consistent with the
 178 presence of tetrahedral ferric iron, i.e. Fe^{3+} substituting for Si^{4+} cations (Burns and Solberg 1990). The
 179 relative intensity of the two fitted doublet signals, assuming a constant recoil-free fraction, implies a
 180 ferric iron concentration on the tetrahedral site of 17.7 ± 2.6 % of the ringwoodite crystal’s total iron
 181 content (table 2).

182 Crystal chemistry

183 The chemical compositions of eight crystals from the experimental run products are reported in Table
 184 3. This confirms the chemical homogeneity between crystals randomly chosen from the run products,
 185 and provides a well-characterised composition for constraining diffraction refinements. The average
 186 H_2O concentration calculated by difference of EPMA totals from 100% is 1.06 ± 0.45 wt.%, which is
 187 in good agreement with FTIR analyses (figure 2, table 3). Compositions for all analyses were reduced
 188 to cation formulae by assuming the presence of four oxygens per formula unit (pfu, table 3). The
 189 uncertainty in the mean sample composition is reported (to 1σ), and is less than ± 0.01 pfu for all
 190 cations.

191 Following the results from SMS, initial cation site assignments were made assuming that the entire
 192 Fe^{3+} content in the ringwoodite was present on the B site (within the general formula $\text{A}_2\text{BO}_{4-x}(\text{H}_2\text{O})_x$).
 193 This suggests a general mineral formula, based on stoichiometric assignments and the assumption that
 194 no tetrahedral vacancies are present, of $(\text{Mg}_{1.728}\text{Fe}^{2+}_{0.146}\text{Si}_{0.041}[\text{V}]^{\text{A}}_{0.085})(\text{Si}_{0.967}\text{Fe}^{3+}_{0.033})\text{O}_{3.915}(\text{H}_2\text{O})_{0.085}$.

195 Single-crystal diffraction

196 X-ray diffraction data from ID15B were refined using Jana2006 software in the $Fd\bar{3}m$ space group,
 197 with the octahedrally coordinated cations in the 16d sites at 0.5, 0.5, 0.5, the tetrahedrally coordinated

198 cations in the 8a sites at 0.125, 0.125, 0.125 and the oxygen anions in the 32e sites at $(x, x, x; x \sim 0.25)$.
 199 The overall sample composition was constrained during refinement, using stoichiometric assignments
 200 from EPMA as the starting point for refinements and keeping overall chemistry constrained
 201 throughout. From this initial state, complete octahedral/tetrahedral order/disorder of Si, Mg and Fe
 202 cations was permitted by refinement of site occupancies. It was observed that no Mg disorder was
 203 predicted, so this refinement option was removed after initial investigation. Isotropic thermal
 204 parameters were constrained to be equal for all atoms occupying each specific crystallographic site;
 205 this appears to be common practice for such refinements (e.g. Smyth et al. 2003). The resulting x-ray
 206 refinement has the formula $(\text{Mg}_{1.728}\text{Fe}^{2+}_{0.133(1)}\text{Si}_{0.123(2)}[\text{V}]^{\text{A}}_{0.016})(\text{Si}_{0.885(2)}\text{Fe}^{3+}_{0.045(1)}[\text{V}]^{\text{B}}_{0.07})\text{O}_4$
 207 (Supplementary Information), implying an $\text{Fe}^{3+}/\text{Fe}^{\text{tot}}$ of 25% if all tetrahedral iron is assumed to be
 208 ferric. It is noted that, if the starting point for refinement is changed such that all Mg/Fe cations are in
 209 octahedral and all Si in tetrahedral coordination (i.e. 100% ordered cations), the final refined site
 210 occupancies do not change significantly from those reported in the supplementary information, and the
 211 same minimum is found. The identification of Si-Fe cation disorder, with ~ 12 % Si in octahedral
 212 coordination, appears to be reliably constrained in spite of the similarity in scattering factors for Mg
 213 and Si (Smyth et al. 2003).

214 Refinement of the single-crystal Laue neutron diffraction datasets, collected at 100 and 300 K, were
 215 undertaken in a similar manner. This resulted in similar results from both neutron datasets; both
 216 robustly identifying 8-12 % Si cation disordering onto the octahedral site prior to inclusion of H atoms
 217 in refinements (Supplementary Information). We emphasise that the neutron refinements were
 218 conducted completely separately from treatment of X-ray diffraction data, and the consistency of
 219 cation disorder provides further support for the robustness of this observation. It is also notable that
 220 both datasets refine to have between 13 ± 3.3 and 28 ± 2.8 % tetrahedrally coordinated iron, which is
 221 comparable with the measured ferric iron content from SMS (17.7 ± 2.6 %). The ringwoodite formulae
 222 from the two neutron diffraction refinements, on an anhydrous basis, are
 223 $(\text{Mg}_{1.728}\text{Fe}^{2+}_{0.156(6)}\text{Si}_{0.085(14)}[\text{V}]^{\text{A}}_{0.031})(\text{Si}_{0.923(14)}\text{Fe}^{3+}_{0.023(6)}[\text{V}]^{\text{B}}_{0.054})\text{O}_4$ and

224 $(\text{Mg}_{1.728}\text{Fe}^{2+}_{0.129(5)}\text{Si}_{0.085(12)}[\text{V}]^{\text{A}}_{0.058})(\text{Si}_{0.922(12)}\text{Fe}^{3+}_{0.050(5)}[\text{V}]^{\text{B}}_{0.028})\text{O}_4$ at 300 K and 100 K respectively.

225 In both cases it is implied that hydrogen is present on both tetrahedrally and octahedrally coordinated
226 sites, to charge balance the cation vacancies.

227 Following anhydrous refinement of the neutron datasets, identification of potential hydrogen positions
228 was attempted using Fourier difference maps. This process was conducted by examining difference
229 maps, looking for regions of negative neutron scattering intensity (red colours in Figure 5) that could
230 be caused by the presence of ^1H atoms in the ringwoodite structure. Visual inspection of the data
231 revealed many such negative anomalies (Figure 5), and automated peak finding procedures in
232 Jana2006 were used to identify candidate positions. Subsequently, candidate sites were inspected to
233 ensure only physically reasonable positions were chosen. Since at lower temperatures there is reduced
234 thermal energy in the system, and therefore atoms should produce stronger Fourier anomalies, the 100
235 K dataset was examined first.

236 In this case two potential hydrogen positions were identified, one associated with each of the
237 tetrahedral and octahedral sites. Fourier difference maps demonstrate these red peaks of negative
238 scattering intensity associated with the octahedra near the face of the octahedral site, and, for the
239 tetrahedral sites, as negative intensity halfway along each tetrahedral edge (indicated with black arrows
240 in Figure 5a and b respectively). These observations are reminiscent of those described by Purevjav et
241 al. (2018), collected with ToF single crystal neutron diffraction from an iron-free ringwoodite crystal.
242 We further discuss the reliability of this type of observation in both this study and in Purevjav et al.
243 (2018) in a subsequent section, but if both the anomalies observed here are adopted as hydrogen
244 positions in the structure then a successful refinement of their occupancy and U_{iso} alongside other
245 refinement parameters can be achieved. This refinement implies both sites identified are partially
246 occupied, with approximately twice as many hydrogen atoms associated with tetrahedral vacancies
247 than are associated with vacant octahedral sites. We note that the uncertainties in site occupancies are
248 particularly large for the octahedral site ($\pm 107\%$ of the refined total occupancy), but the hydrogen

249 content of the tetrahedral site has a relative uncertainty of $\pm 19\%$. The two hydrogen sites have thermal
250 parameters approximately 2.5-6 times larger than those for the magnesium, iron, silicon and/or oxygen
251 cations, suggesting the hydrogen positions are a diffuse cloud, even at 100K. The total water content,
252 which was unconstrained in the refinement, is predicted to be 1.16 ± 0.61 wt.% H₂O, which is within
253 2σ uncertainty of the weighted average water content estimate from FTIR. This water-bearing
254 refinement charge balances the overall ringwoodite structure, but does not completely protonate all
255 individual vacancies (i.e. not every [V]^A or [V]^B can be filled with 2 or 4 protons respectively). At face
256 value this refinement result seems reasonable and will be discussed further below.

257 In the dataset collected at 300 K it is no longer possible to discern a signal that might be associated
258 with ¹H at the tetrahedral site. However, there continues to be a peak, although weaker than at 100K,
259 in negative scattering density associated with the same locations at the octahedral site which can be
260 assigned as hydrogen for refinement (black arrows in Figure 5c). In this case, free refinement of both
261 occupancy and U_{iso} results in a structure containing 2.19 ± 0.55 wt.% H₂O in the octahedral site, with a
262 U_{iso} that is 75% smaller than for any other atom in the structure. Additionally, this refinement results in
263 the octahedral site being 10% overfilled. Given that the temperature has increased, so thermal
264 parameters should have increased (not decreased) from 100 K, and the broad O-H stretch observed in
265 FTIR this seems highly unlikely and is considered to be an unreliable result. Thus, we believe that the
266 neutron diffraction data collected at 300 K are unable to reliably constrain the hydrogen positions in
267 the structure.

268 DISCUSSION

269 In contrast with previous studies of iron-bearing ringwoodite samples, our combined results from SMS
270 and diffraction refinements appear to conclusively demonstrate the presence of tetrahedrally co-
271 ordinated ferric iron in the ringwoodite structure. Whilst previous studies have identified elevated
272 ferric iron concentrations in hydrous Fo₉₀ ringwoodite when compared with anhydrous samples, these
273 have not been definitively associated with tetrahedral coordination (e.g. McCammon et al. 2004).

274 Instead, Mössbauer spectroscopy in these studies had assigned the secondary “ferric iron” component
275 as explained by a rapid Fe^{2+} - Fe^{3+} charge transfer mechanism believed to be possible only if the iron
276 was completely in octahedral coordination (e.g. McCammon et al. 2004). Mössbauer spectra presented
277 by Mrosko et al. (2013) did suggest that, after annealing a sample of Fo_{90} ringwoodite in air and
278 observing a colour change in the sample, there was some evidence for a minor component (< 3%) of
279 tetrahedral ferric iron that was consistent with their FTIR spectroscopy. The presence of tetrahedral
280 ferric iron in samples from this study also necessarily demonstrates the presence of cation disorder in
281 the ringwoodite structure as, given the chemistry of the samples analysed by EPMA, it is an inevitable
282 consequence that the tetrahedral ferric iron must displace an equivalent portion of Si atoms onto the
283 octahedral sites. Disorder of silicon onto the octahedral site has been suggested in previous studies via
284 refinement of X-ray data alone, with studies reporting up to 4% Si-Mg exchange between the
285 tetrahedral and octahedral sites (Kudoh et al. 2000). This type of exchange has also often been cited as
286 a potential hydrogen incorporation mechanism (see below). However, neither the confirmation of
287 cation disorder with multiple techniques analysing the same samples nor the involvement of ferric iron
288 in this exchange reaction have previously been documented. Independent X-ray and 2 separate neutron
289 diffraction refinements, as well as SMS results in this study all independently suggest that 13 – 28 %
290 of the iron in these samples is ferric and in tetrahedral coordination. It is unclear whether or not this is
291 a unique result of the synthesis method, but since the crystals were grown with excess water in a
292 welded platinum capsule, as in previous studies, this seems unlikely. More likely, perhaps, is the
293 superiority of synchrotron Mössbauer spectroscopy over a lab approach when analysing small samples
294 synthesised at high-pressure, and the increased capability of neutron diffraction for discrimination of
295 iron, magnesium and silicon compared to X-ray scattering techniques.

296 The neutron diffraction refinements, presented above, do not unambiguously identify the hydrogen
297 incorporation mechanism in these samples. Thus, in addition to the presented refinements in $Fd\bar{3}m$
298 symmetry, neutron data were also refined assuming $F\bar{4}3m$, $F4_132$ or $Fd\bar{3}$ space groups in case the
299 presence of hydrogen atoms in ringwoodite, which are more “visible” to neutrons, alters the crystal

300 symmetry. Ultimately, however, none of these additional refinements positively identified hydrogen
301 sites.

302 The difficulty in identifying hydrogen positions using neutron diffraction might be explained by
303 considering whether or not a sufficient concentration of ^1H is present that features observable in a
304 Fourier map are to be expected. Assuming that oxygen and hydrogen atoms occupy the same volume,
305 equivalent to equal U_{iso} 's, we use the relative coherent neutron scattering lengths of ^{16}O and ^1H and the
306 observed Fourier intensity of ^{16}O atoms to estimate the peak Fourier scattering density expected from
307 ^1H atoms. Based on the observed peak scattering density from oxygen ($\sim 26 \text{ fm}/\text{\AA}^3$), hydrogen atoms
308 completely filling the oxygen sites would be expected to have peak scattering densities of ~ -16.7
309 $\text{fm}/\text{\AA}^3$ (ratio of $^1\text{H}/^{16}\text{O}$ coherent scattering lengths * observed ^{16}O peak; $(-3.74/5.80)*26$). If we assume
310 only one hydrogen incorporation mechanism is present, e.g. all 0.17 H atoms pfu (as determined by
311 EPMA) occupy a single site, then, depending on whether the occupied site is 48-fold, 96-fold or 192-
312 fold (which are the most likely in this study and Purevjav et al. 2014; 2018), the expected peak
313 scattering density from ^1H is then -0.47, -0.23 or -0.12 $\text{fm}/\text{\AA}^3$. In reality it is likely that hydrogen will
314 be more diffusely distributed than oxygen, having a larger U_{iso} , and will additionally be partitioned
315 between multiple sites in the crystal structure. Thus, it is expected that the peak scattering from ^1H
316 atoms in difference Fourier maps will be at least 2-4 (and possibly as much as 10) times smaller than
317 these values. Quick inspection of difference Fourier maps from our samples (fig. 5) reveals that there
318 are many features of much larger positive and negative scattering densities than these predicted
319 theoretical values, and that true signals from hydrogen atoms could easily be hidden within the green
320 colours on figure 5. This makes it virtually impossible to argue that visual identification of all ^1H
321 atoms using Fourier maps is robust. Successful hydrogen identification is only convincing if proton
322 positions are assigned and successfully refined for occupancy and thermal parameters with reasonable
323 results. An example of this is seen in the case of the tetrahedrally coordinated hydrogen position in the
324 100 K neutron dataset in this study. However, even in this case, the observed scattering density in the
325 Fourier map is approximately 10 times larger than the expected anomaly, casting doubt on the fidelity

326 of the refinement. Looking at the proposed octahedral hydrogen sites in this, and previous, studies
327 (Purevjav et al. 2018), we note observed negative scattering densities in Fourier maps are at least 20
328 times larger than expected, whilst nearby positive scattering peaks of equal, but opposite, magnitude
329 were unexplained. We conclude that the successful identification of H atoms, especially in general
330 crystallographic sites within the ringwoodite structure, is extremely challenging, and we are cautious
331 to avoid similar interpretations here based on neutron data alone.

332 FTIR and NMR spectroscopy as well as first-principles calculations have all been used to provide
333 additional constraints on hydrogen locations in the ringwoodite structure. We look to previously
334 published studies to provide a framework in which to interpret our FTIR observations, which have
335 frequently identified that hydrogen is likely incorporated in a mixture of protonated cationic defects
336 associated with tetrahedral and octahedral vacancies, as well as via cation disorder mechanisms. On
337 the basis of calculations Blanchard et al. (2009) concluded that simple vacancy defects $[V_{\text{Mg}}(\text{OH})_2]^x$
338 and $[V_{\text{Si}}(\text{OH})_4]^x$ most likely explain the lowest ($\sim 2500\text{-}2600\text{ cm}^{-1}$) and highest ($3500\text{-}3750\text{ cm}^{-1}$)
339 frequency O-H stretches observed by FTIR respectively. However, a plethora of cation-disorder
340 related substitutions were suggested, including $[\text{Mg}_{\text{Si}}(\text{OH})_2]^x$ and $[\text{V}_{\text{Mg}}(\text{OH})_2\text{Mg}_{\text{Si}}\text{Si}_{\text{Mg}}]^x$, and several
341 mechanisms may contribute to the main broad peak observed in $\gamma\text{-Mg}_2\text{SiO}_4$ centred around ~ 3150
342 cm^{-1} .

343 Whilst other studies using calculations (Panero 2010) and FTIR spectroscopy (Bolfan-Casanova et al.
344 2000) alone have also concluded that a mixture of vacancy associated hydrogen incorporation
345 mechanisms likely occur in ringwoodite, neither of these studies assigned FTIR bands to specific
346 defects. Instead, studies using coupled observations from multiple techniques, e.g. FTIR and XRD,
347 FTIR and calculations, or the pressure/temperature evolution of FTIR spectra, have more frequently
348 attempted to assign specific spectroscopic observations. Smyth et al. (2003) and Chamorro Perez et al.
349 (2006) interpreted the main O-H stretch around 3150 cm^{-1} as the expression of hydrogen along the
350 edge of vacant tetrahedral sites. In contrast, Panero et al. (2013), Kudoh et al. (2000), Ross et al.

351 (2003) and Mrosko et al. (2013) have all favoured a model where the broad 3150 cm^{-1} stretch is
352 associated with octahedral vacancies $[V_{\text{Mg}}(\text{OH})_2]^x$. The weaker FTIR stretches at higher frequencies
353 between $3500\text{-}3700\text{ cm}^{-1}$, where assigned, are most commonly associated with the tetrahedral vacancy
354 substitution (Mrosko et al. 2013). Studies investigating the temperature and/or pressure dependence of
355 FTIR spectra clearly identify that multiple H-incorporation mechanisms are required to explain peaks
356 following different pressure/temperature evolution (Chamorro Pérez et al. 2006; Mrosko et al. 2013;
357 Panero et al. 2013; Yang et al. 2014). Interpretation of NMR spectra collected from a hydrous iron-free
358 ringwoodite sample (Grüninger et al. 2017) also requires multiple H-sites in ringwoodite. Grüninger et
359 al. (2017) concluded that the substitution into octahedral vacancies was the most dominant hydrogen
360 incorporation mechanism, presumably explaining the large 3150 cm^{-1} stretch, but also identified that
361 up to $\sim 50\%$ of the hydrogen was incorporated in tetrahedral and cation disorder related defects. With
362 one exception, Mrosko et al. (2013), none of these studies have interpreted the FTIR spectra of iron-
363 bearing ringwoodite samples specifically in terms of iron-bearing defects.

364 Although FTIR spectra from iron-free and iron-bearing hydrous ringwoodite samples are broadly
365 similar, they possess subtle, yet important, differences (e.g. Smyth et al. 2003). FTIR spectra of iron-
366 free ringwoodite consist of a dominant peak centred around 3100 cm^{-1} with a full-width-at-half-
367 maximum height (fwhm) of $\sim 400\text{ cm}^{-1}$. Additional small peaks occur around $\sim 2500\text{-}2600\text{ cm}^{-1}$ and
368 3700 cm^{-1} in samples with high water content. FTIR spectra of Fo_{90} ringwoodite, like that in this study
369 (fig 2b), consist a much broader central peak ($\sim 3150\text{ cm}^{-1}$, $\text{fwhm} > 600\text{ cm}^{-1}$) with a distinctive high
370 frequency shoulder ($\sim 3400\text{ cm}^{-1}$); this can readily be deconvolved into multiple components.
371 Additionally, the contribution at the highest frequencies ($\sim 3650\text{ cm}^{-1}$) is much more significant, whilst
372 the peak at $\sim 2500\text{-}2600\text{ cm}^{-1}$ appears visibly similar to iron-free samples. Thus, it seems logical that
373 the additional FTIR contribution at $\sim 3400\text{ cm}^{-1}$ is associated with a new defect mechanism only
374 occurring in iron-bearing samples. The relative increase in intensity and downward frequency shift of
375 the peak at $\sim 3650\text{ cm}^{-1}$ presumably also has some contribution from the presence of iron in
376 ringwoodite's structure. Using optical and FTIR spectroscopy Mrosko et al. (2013) identified that

377 heating of a Fo_{90} ringwoodite crystal above 773 K, at ambient-pressure, caused irreversible water loss
378 and conversion of ferrous to ferric iron. This process caused the area of the broad 3150 cm^{-1} stretch to
379 decrease (in their study), presumably explained by a drop in $[\text{V}_{\text{Mg}}(\text{OH})_2]^x$ concentration, whilst the area
380 under peaks at higher frequencies ($\sim 3650\text{ cm}^{-1}$ and 3450 cm^{-1}) increased. These are the two peaks we
381 suggest are likely to be associated with ferric iron. Given that the peak, or shoulder, at $3400\text{-}3450\text{ cm}^{-1}$
382 is only observed in iron-bearing samples and is known to increase with increasing Fe^{3+} , we propose
383 that this component arises directly from hydrogen incorporation associated with tetrahedrally co-
384 ordinated ferric iron. The second peak at 3650 cm^{-1} , as it is present - although at slightly higher
385 frequencies ($\sim 3700\text{-}3750\text{ cm}^{-1}$) - in Fo_{100} ringwoodite is perhaps related to a change in O-H bond
386 length associated with the presence of iron, and following the interpretation of Mrosko et al. (2013) we
387 suggest this is due to the expanded iron-bearing octahedra shortening O-H bond lengths in adjacent
388 tetrahedra.

389 Based on the discussion above, we believe that there is evidence for at least four different hydrogen
390 substitution mechanisms in the samples investigated in this study. This interpretation is consistent with
391 the results from ^1H NMR (Grüninger et al. 2017). The four sites, with their assumed associated FTIR
392 shifts, are (i) hydrogen sites associated with octahedral vacancies (3125 cm^{-1}), (ii) hydrogen associated
393 with tetrahedral vacancies ($\sim 3650\text{ cm}^{-1}$), (iii) hydrogen associated with ferric iron disorder onto the
394 tetrahedral site ($\sim 3400\text{ cm}^{-1}$) and presumably (iv) hydrogen associated with disordered silicon on the
395 octahedral site ($2510/2850\text{ cm}^{-1}$). We assume that mechanisms (i) and/or (iv) and (ii) and/or (iii) are
396 associated with the octahedral and tetrahedral hydrogen sites observed in the 100 K neutron diffraction
397 refinement respectively. We also note that the presence of multiple sites may explain why the
398 identification of hydrogen from refinement of single-crystal neutron diffraction patterns is particularly
399 problematic.

400 IMPLICATIONS

401 Assuming the Earth's interior composition is approximately pyrolitic, we expect ringwoodite to be the
402 dominant chemical component throughout the lower portion of the transition zone (e.g. Ringwood
403 1968). There is direct evidence, in the form of an exhumed diamond-hosted ringwoodite inclusion
404 found in a Brazilian diamond, that at least one natural ringwoodite sample is hydrous. If the samples
405 examined throughout this study are in any way representative of the mantle ringwoodite component
406 then there are a few interesting consequences. In addition to the possibility that the incorporation of
407 water in ringwoodite significantly lowers its seismic velocities (Jacobsen 2006; Schulze et al. 2018),
408 and therefore allowing mantle water contents to potentially be "mapped" using geophysical
409 techniques, the observation in this study that water could promote primary cation disorder in the
410 ringwoodite structure may amplify these effects. Panero et al. (2008), using first principles
411 calculations, demonstrated that the presence of cation disorder in the ringwoodite structure may cause
412 anomalous, and otherwise unpredicted, softening of the elastic moduli. Panero et al.'s (2008)
413 calculations predict that ringwoodite's acoustic velocities (v_p and v_s) will be between 1 and 2% slower
414 at transition zone conditions as a consequence of ~ 4% Si disorder onto the octahedral site when
415 compared with a fully ordered structure. Given we observe ~ 8-12% disorder in ringwoodite, due to a
416 Si-Fe³⁺ substitution that is seemingly promoted in the presence of water, it may be expected that
417 ringwoodite's velocities would be reduced by 2-6% more than currently expected in regions of the
418 mantle that are hydrated. Alternatively, observed reductions in transition zone velocities might be
419 explained by smaller concentrations of H₂O than currently believed to be present, and mantle water
420 content may be overestimated if the contribution of Si disorder is ignored.

421 The samples analysed in the present study have a deep royal blue colouration, typical of iron-bearing
422 hydrous ringwoodites. The origin of blue colouration in ringwoodite and other high-pressure
423 ferromagnesian silicates is currently uncertain, having been attributed to light scattering (e.g.,
424 Lingemann and Stöffler, 1998; Nagy et al. 2011), or intervalence charge transfer (e.g., Taran et al.
425 2009). Iron-bearing magnesian ringwoodite can vary in colour from colourless through pale green to
426 deep blue/purple. Ringwoodites studied using optical and near-infrared spectroscopy possess

427 absorption bands in the visible spectrum that have been attributed to electronic transitions in
428 octahedrally-coordinated Fe^{2+} (8000-12000 cm^{-1}) and/or Fe^{2+} - Fe^{3+} intervalence charge transfers that
429 are centred on green wavelengths around 16000-18000 cm^{-1} (Keppler and Smyth, 2005; Taran et al.
430 2009). It appears that previous samples tend towards a pale green, rather than blue, colour when
431 synthesised under more reducing conditions (Taran et al. 2009). In this study we also observed, at least
432 in one case, that a sample we synthesised under water-free conditions (confirmed by IR spectroscopy)
433 was also pale green. This anhydrous sample, which also contained excess ferroperricite, did not
434 appear to contain tetrahedrally-coordinated ferric iron (Supplementary figure 1). This implies that the
435 blue colouration in ringwoodite and, by extension, other high-pressure hydrous iron-magnesium
436 silicates which sometimes show similar royal blue colouration, including Phase E (Crichton et al.
437 1999, Crichton and Ross 2000) and Phase A (personal comm. D. Dobson), could be related to the
438 presence of a combined ferric iron-proton defect. As crystal-field electronic transitions are spin-
439 disallowed for Fe^{3+} , the blue colouration could instead be related to intervalence charge transfers,
440 supporting the assignment of absorption bands by Taran et al. (2009). While strong blue colouration is
441 not a common feature of Fe^{2+} - Fe^{3+} charge transfer in low-pressure silicates, it is clearly the cause of
442 blue in vivianite, $(\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O})$, as discussed in Burns (1981). A question remains regarding why
443 the charge transfer absorption band moves to higher frequencies in ringwoodite compared to low-
444 pressure silicates where it typically occurs around 12000-15000 cm^{-1} . The presence of Fe^{3+} in
445 tetrahedral coordination, combined with its absence from octahedral sites in the present study, would
446 make ringwoodite a class I mixed-valence compound where intervalence-charge transfer, between
447 structurally dissimilar Fe^{2+} and Fe^{3+} sites, would ordinarily occur beyond the visible band. It is
448 possible that proton delocalisation enhances additional charge transfer, by providing fluctuations in
449 local charge environments. Whilst we believe the observations in the present study suggest that the
450 presence of a tetrahedrally coordinated Fe^{3+} - H^+ defect in ringwoodite might be related to its blue
451 colouration, further work is required to verify this.

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596

597 FIGURE CAPTIONS

598 **Figure 1:** Photomicrograph of selected ringwoodite crystals recovered from synthesis.

599 **Figure 2:** (a) Raman spectra collected in this study, at 1 cm^{-1} and 4 cm^{-1} resolution, compared with a
600 reference spectrum from Kleppe et al. (2002). (b) Raman spectra extended out to 4500 cm^{-1} , covering
601 the spectral region where stretches associated with O-H might be expected. (c) FTIR absorption
602 spectra collected from a single crystal ringwoodite sample at ambient conditions, normalised to 1 cm
603 thickness. Inset: baseline-corrected absorption from $2000 - 4000\text{ cm}^{-1}$, for H_2O concentration
604 quantification and deconvolved into contributing peaks after Monique-Thomas et al (2016).

605 **Figure 3:** Water content of ringwoodite sample based on individual FTIR calibrations, EPMA by
606 difference and an overall weighted average.

607 **Figure 4:** Synchrotron Mössbauer spectra collected at ID18, fitted with two spectral components using
608 MossA. Raw data is shown by the black points and the complete model fit by the red curve. The model
609 fit is composed of two components; the green asymmetric doublet is interpreted as the signal from
610 octahedral ferrous iron whilst that highlighted in blue is assigned as tetrahedral ferric iron.

611 **Figure 5:** Fourier difference maps from single-crystal Laue neutron diffraction data (with elements of
612 the crystal structure superimposed) which allow visualisation of possible hydrogen positions (a) 110
613 plane and (b) 100 through 100 K data collection focussed on the (a) octahedral site of Mg, Fe and Si
614 whose relative proportions are indicated by the orange, brown and blue coloured segments
615 respectively, (b) tetrahedral site contain Si and Fe. (c) 110 plane through 300 K data focussed on the
616 octahedral site in $Fd\bar{3}m$ symmetry.

617 **Table 1:** Results of FTIR analysis to determine sample H₂O concentration using various absorption
 618 coefficients

Sample	d (μm)	Ai	cH ₂ O (MT _a)		cH ₂ O (MT _b)		cH ₂ O (LR)		cH ₂ O (MT _c)		cH ₂ O (BC)	
a	50 2	1055.9	0.94	<i>0.19</i>	1.06	<i>0.22</i>	0.83	<i>0.17</i>	1.27	<i>0.26</i>	0.78	<i>0.06</i>
b	57 2	1505.9	1.17	<i>0.24</i>	1.33	<i>0.27</i>	1.04	<i>0.21</i>	1.59	<i>0.32</i>	0.97	<i>0.07</i>
c	42 2	760.6	0.81	<i>0.17</i>	0.91	<i>0.19</i>	0.71	<i>0.15</i>	1.09	<i>0.22</i>	0.67	<i>0.05</i>
average			0.97	<i>0.20</i>	1.10	<i>0.22</i>	0.86	<i>0.18</i>	1.32	<i>0.27</i>	0.81	<i>0.06</i>

619 Numbers in italics are estimated uncertainties in thickness and water content measurements.

620 MT_a ($\epsilon = 111,815 \text{ L}\cdot\text{mol}^{-1}\text{cm}^{-2}$) (Thomas et al. 2015)

621 MT_b ($\epsilon = 98,830 \text{ L}\cdot\text{mol}^{-1}\text{cm}^{-2}$) (Thomas et al. 2015)

622 LR ($\epsilon = 126,393 \text{ L}\cdot\text{mol}^{-1}\text{cm}^{-2}$) (Libowitzky and Rossman 1997)

623 MT_c ($\epsilon = 82,640 \pm 16,530 \text{ L}\cdot\text{mol}^{-1}\text{cm}^{-2}$) (Thomas et al. 2015)

624 BC ($\epsilon = 135,133 \pm 8,794 \text{ L}\cdot\text{mol}^{-1}\text{cm}^{-2}$) (Bolfan-Casanova et al. 2018)

625

626

627 **Table 2:** Fitting parameters from SMS spectra of sample crystals.

	Intensity	CS (mm/s)	QS (mm/s)
Fe ²⁺	82.3 ± 2.6	1.030 ± 0.005	2.757 ± 0.009
Fe ³⁺	17.7 ± 2.6	0.091 ± 0.076	0.551 ± 0.086

628

629 **Table 3:** EPMA analyses, in wt.%, of synthetic ringwoodite crystals, assuming Fe³⁺/Fe^{tot} from SMS
 630 measurements and H₂O by difference

crystal	Wt.% oxides						Atoms per 4 oxygens (pfu)						
	SiO ₂	FeO	Fe ₃ O ₃	MgO	Total	H ₂ O	Si	Fe ²⁺	Fe ³⁺	Mg	H	O	Mg#
a	41.81	7.51	1.88	47.75	98.95	1.05	1.009	0.152	0.034	1.719	0.171	4	0.90
	41.54	7.43	1.86	47.63	98.46	1.54	1.008	0.151	0.034	1.722	0.172	4	0.90
b	41.99	7.49	1.87	47.76	99.11	0.89	1.012	0.151	0.034	1.715	0.171	4	0.90
	41.63	7.50	1.88	48.05	99.07	0.93	1.005	0.151	0.034	1.728	0.171	4	0.90
	41.65	7.43	1.86	47.63	98.56	1.44	1.009	0.150	0.034	1.720	0.172	4	0.90
	41.98	7.38	1.84	47.84	99.04	0.96	1.011	0.149	0.033	1.718	0.171	4	0.90
c	41.24	6.90	1.72	47.99	97.85	2.15	1.004	0.140	0.032	1.742	0.173	4	0.91
	41.94	6.70	1.67	48.76	99.07	0.93	1.007	0.134	0.030	1.745	0.170	4	0.91
	42.26	6.76	1.69	48.84	99.55	0.45	1.009	0.135	0.030	1.739	0.169	4	0.91
	41.89	6.89	1.72	47.77	98.26	1.74	1.014	0.139	0.031	1.724	0.172	4	0.91
d	41.89	7.13	1.78	48.19	99.00	1.00	1.009	0.144	0.032	1.730	0.171	4	0.91
	41.52	7.16	1.79	48.33	98.79	1.21	1.003	0.145	0.033	1.740	0.171	4	0.91
	41.41	7.02	1.76	47.97	98.16	1.84	1.005	0.143	0.032	1.736	0.172	4	0.91
e	41.70	7.16	1.79	47.86	98.51	1.49	1.009	0.145	0.033	1.727	0.172	4	0.91
f	41.92	6.84	1.71	48.95	99.42	0.58	1.004	0.137	0.031	1.747	0.170	4	0.91
g	42.15	7.03	1.76	48.21	99.14	0.86	1.012	0.141	0.032	1.726	0.170	4	0.91
	41.99	7.17	1.79	48.35	99.31	0.69	1.008	0.144	0.032	1.730	0.170	4	0.91
	42.07	7.12	1.78	48.08	99.06	0.94	1.012	0.143	0.032	1.724	0.171	4	0.91
h	42.01	7.56	1.89	47.96	99.42	0.58	1.010	0.152	0.034	1.718	0.170	4	0.90
	41.74	7.62	1.91	48.13	99.39	0.61	1.004	0.153	0.035	1.726	0.171	4	0.90
	41.61	7.71	1.93	47.74	98.98	1.02	1.006	0.156	0.035	1.721	0.171	4	0.90
	41.57	7.66	1.92	47.81	98.96	1.04	1.005	0.155	0.035	1.723	0.171	4	0.90
	42.02	7.41	1.85	48.20	99.49	0.51	1.008	0.149	0.033	1.724	0.170	4	0.90
Mean	41.80	7.24	1.81	48.08	98.94	1.06	1.008	0.146	0.033	1.728	0.171	4	0.91
± (1σ)	0.25	0.30	0.08	0.37	0.45	0.45	0.003	0.006	0.001	0.009	0.001		0.00

631

Figure 1

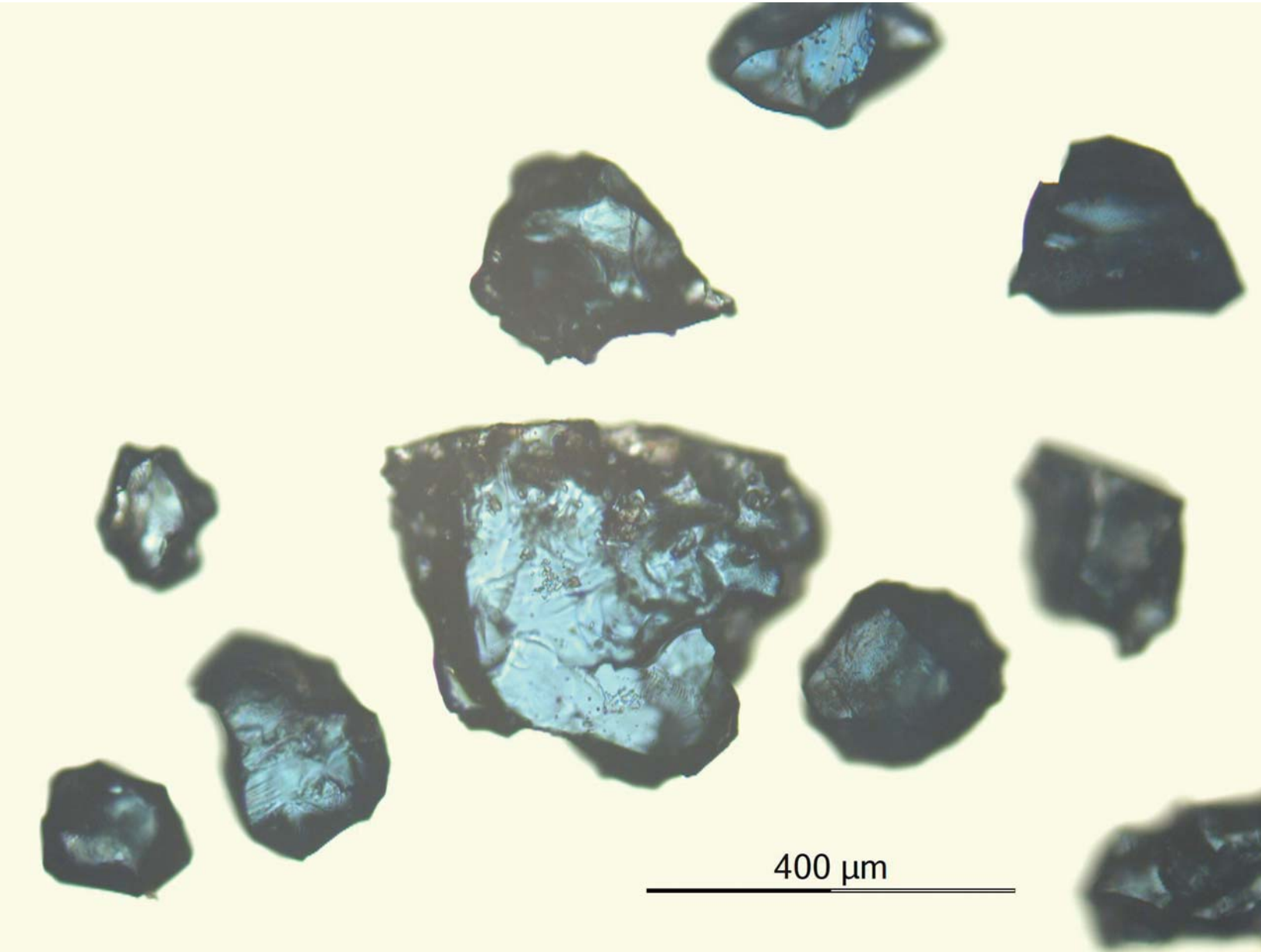


Figure 2

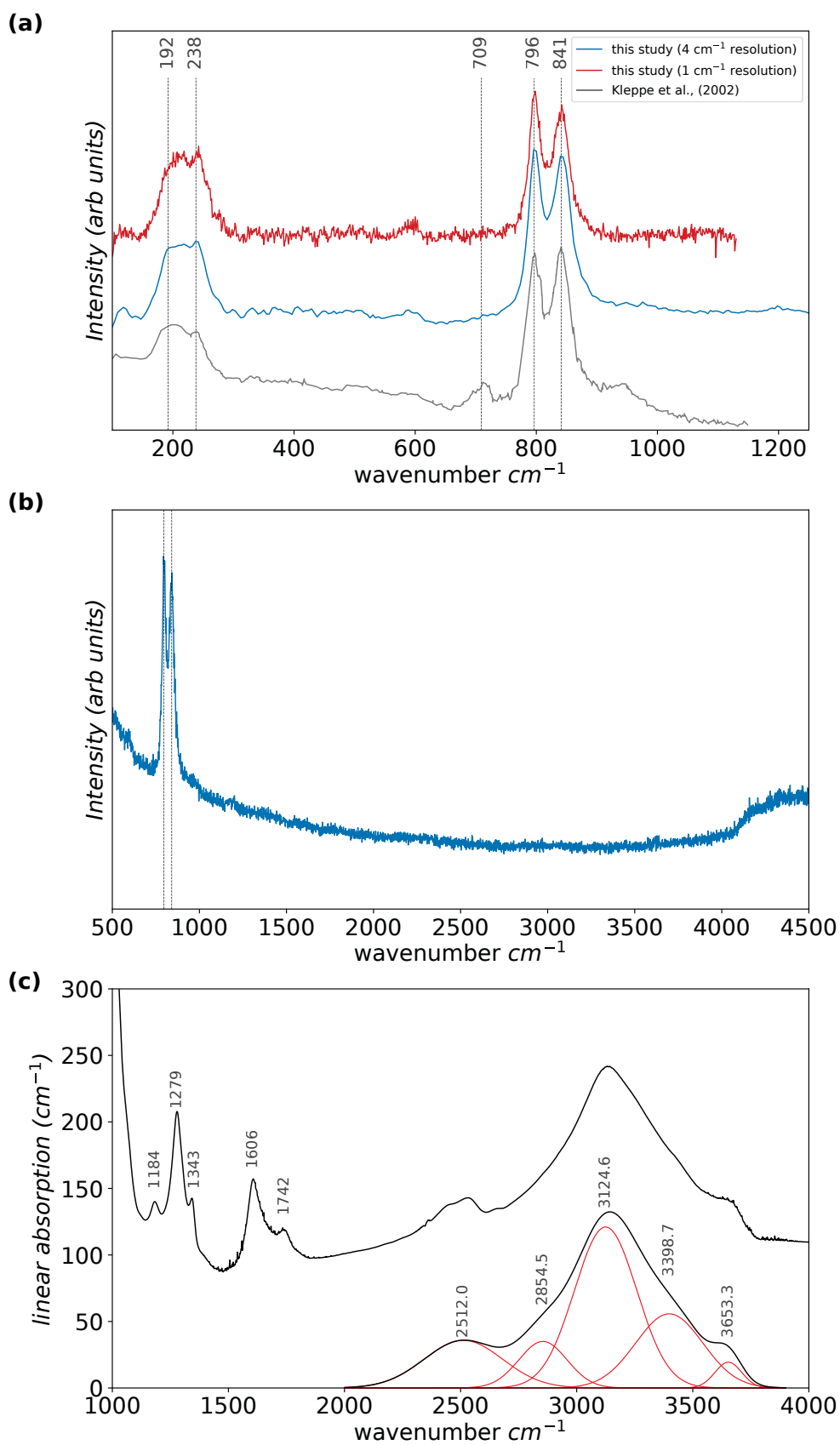


Figure3

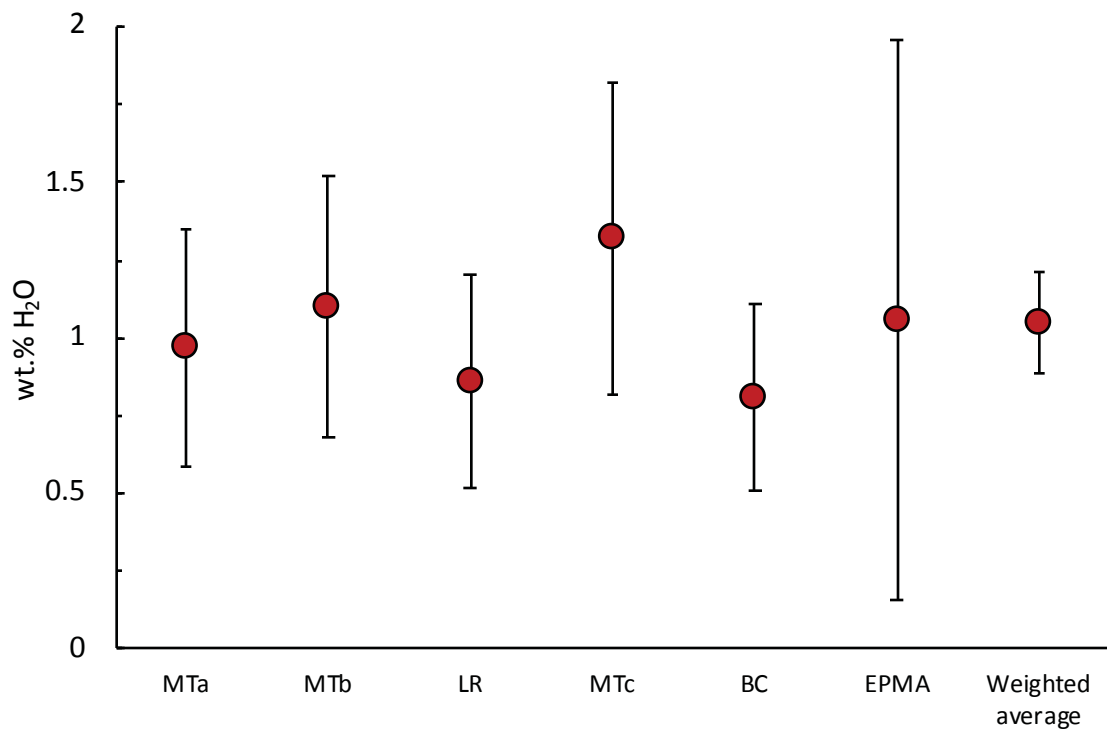


Figure 4

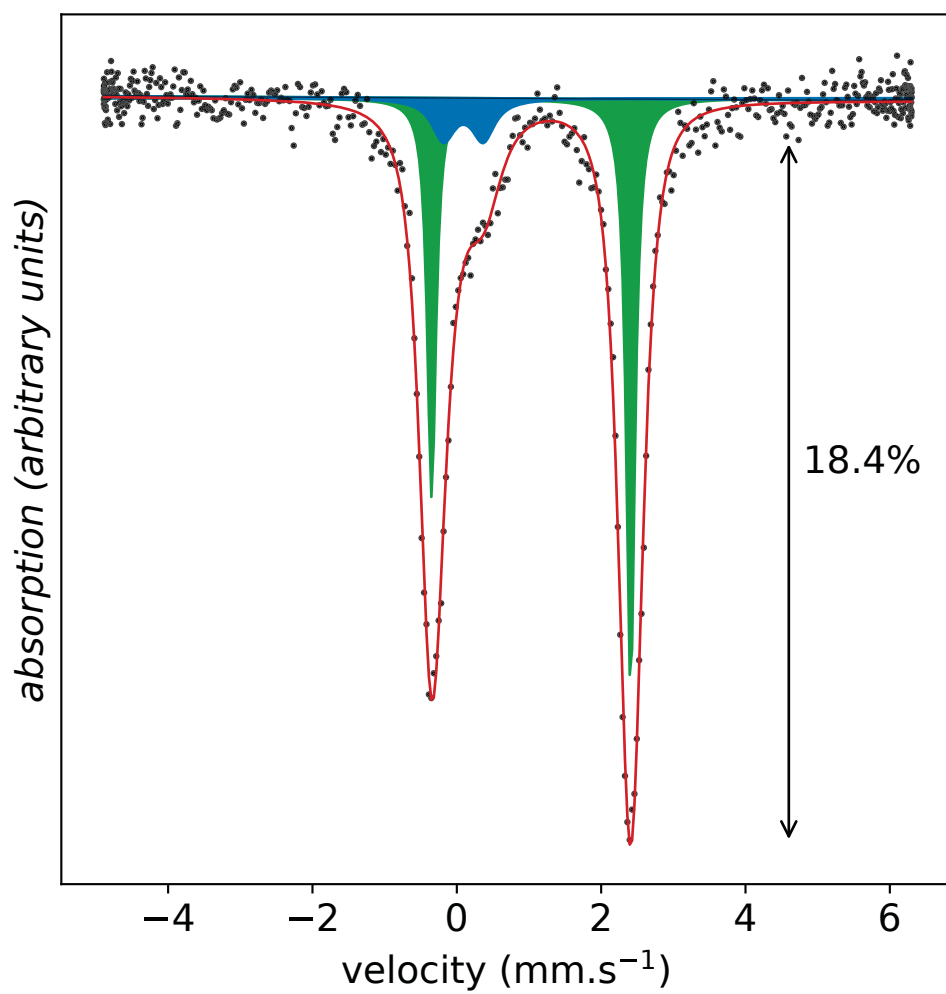


Figure 5

