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# 1 **Hydrogen in the Deep Earth**

2 Jed L. Mosenfelder<sup>1</sup>, H el ene Bureau<sup>2</sup>, and Anthony C. Withers<sup>3</sup>

3

## 4 **ABSTRACT**

5 Hydrogen remains one of the most difficult elements to characterize in geological materials. Even at  
6 trace levels, it has a major impact on the properties of minerals, silicate melts, and fluids, and thus  
7 on the physical state of the mantle and the crust. The investigation of H-bearing species in deep  
8 minerals, melts and fluids is challenging because these phases can be strongly modified during  
9 transport to Earth's surface. Furthermore, interpretation of experimental studies can be clouded by  
10 kinetic inhibitions and other artifacts. Nevertheless, recent improvements in analytical,  
11 experimental, and modeling methodologies have enabled advances in our understanding of how  
12 hydrogen is incorporated in the deep Earth, which is essential for constraining hydrogen cycling  
13 and storage through geologic time.

14

15

16 **KEYWORDS:** water; mantle; incorporation; speciation

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## 17 **INTRODUCTION**

18 Hydrogen is one of the most difficult elements to characterize in geological materials, partly  
19 because it is often only a trace component in minerals that are defined as nominally anhydrous,  
20 with no hydrogen in their chemical formula (hereafter referred to as NAMs). Yet hydrogen, even at  
21 trace levels, has a major impact on the properties of minerals, silicate melts and fluids, and  
22 consequently on the evolution and physical state of the interior of the Earth and other planetary  
23 bodies. The distribution of hydrogen in Earth's deep interior and its evolution over geologic time  
24 will be covered in later chapters of this Elements issue. We focus here on current challenges to  
25 measuring ppm levels (see sidebar for a discussion of units used in this issue) of hydrogen and  
26 recent advancements in understanding how it is incorporated in the deep Earth, concentrating on  
27 NAMs, fluids, and melts in the mantle while neglecting the important role of hydrous minerals in  
28 the crust and upper mantle.

29

30 The incorporation mechanisms of hydrogen in mantle minerals, fluids and melts depend on many  
31 factors, including pressure, temperature, chemistry and redox conditions. This dependence  
32 generates a variety of H-bearing species, from oxidized to reduced, which in theory can be used to  
33 map deep mantle redox conditions if they are not altered during transport to the Earth's surface.  
34 The analysis of hydrogen in minerals, quenched melts, and inclusions in diamond that preserve  
35 evidence of deep-seated hydration has seen major improvements in the past two decades.  
36 Concurrently, efforts are continuously being devoted to developing and combining analytical,  
37 experimental and modeling methodologies to describe the incorporation and transport processes  
38 for hydrogen in mineral structures, silicate melt networks and fluids. These are necessary  
39 requisites to improve our understanding of deep hydrogen cycling and storage through geologic  
40 time.

41

## 42 **MEASURING HYDROGEN**

43 Despite being the most abundant element in the universe – and in part, because of its abundance –  
44 hydrogen presents challenges for quantitative measurement. At ppm levels in particular, attention  
45 should be paid to contamination by H-bearing species in an instrument vacuum, surface-adsorbed  
46 water, and organic molecules on surfaces introduced during sample preparation. Rossman (2006)  
47 provided a comprehensive review of the advantages and limitations of the many techniques used

48 for trace H analysis in NAMs and glasses, including absorption Fourier transform infrared  
49 spectroscopy (FTIR), thermogravimetric analysis (TGA), P<sub>2</sub>O<sub>5</sub> coulometry, Karl-Fischer titration,  
50 hydrogen manometry, continuous-flow mass spectrometry, nuclear reaction analysis (NRA), elastic  
51 recoil detection analysis (ERDA), proton-proton (p-p) scattering, nuclear magnetic resonance  
52 (NMR), and secondary ion mass spectrometry (SIMS). Since the time of that review, there have been  
53 major advances in instrumentation and analytical protocols for some of these techniques.

54  
55 FTIR is still the most popular of these methods, with advantages including low cost, wide  
56 availability, and low detection limits for suitably prepared samples. Moreover, FTIR provides  
57 constraints on incorporation mechanisms (structural sites and speciation) for H in minerals and  
58 glasses that none of the other techniques above besides NMR yield directly. This information can be  
59 deduced from the frequency dependence and – for anisotropic minerals – polarization of IR  
60 absorption bands (FIG. 1). SIMS has emerged as the second most frequently used technique, with  
61 improvements in detection limits afforded by advancements in instrumentation and protocol (e.g.,  
62 Mosenfelder et al. 2011). This method also offers the advantage of simultaneous measurement of  
63 other elements and isotopes, including other light elements such as fluorine that can also be  
64 incorporated at trace levels in NAMs. Furthermore, microbeam techniques such as SIMS and ERDA  
65 permit detection of H in phases such as metals or opaque minerals that cannot be readily measured  
66 using FTIR. A closely related variant of SIMS is NanoSIMS, which offers superior imaging capability  
67 and increased spatial resolution (by a factor of at least two, depending on the detection limit  
68 needed – for instance, NAMs from xenoliths can be suitably analyzed with an 8-10 μm diameter  
69 area with SIMS, or a 3-5 μm area using NanoSIMS). NanoSIMS in imaging mode can also be useful  
70 for assessing the presence of sub-micrometer to micrometer scale features – such as fluid  
71 inclusions or inclusions of hydrous phases or hydrous melt – that can skew interpretation in both  
72 natural (Mosenfelder et al. 2011) and synthetic (e.g., Liu et al. 2021) samples.

73  
74 A critical limitation of both FTIR and SIMS that is sometimes misunderstood is that neither of these  
75 techniques can yield accurate concentrations without reference to an external calibration by an  
76 independent technique, preferably on a material with a composition (and structure, particularly for  
77 FTIR) similar to the unknown. Molar absorption coefficients for bands in FTIR spectra vary for  
78 materials with different compositions. Ion yields used in SIMS for quantification fundamentally  
79 depend on the major element composition of the material being analyzed, and the magnitude of this

80 "matrix effect" is still poorly constrained for measurements of hydrogen concentration. "Absolute"  
81 techniques that have been used to empirically calibrate FTIR and SIMS include hydrogen  
82 manometry and nuclear techniques (NRA, ERDA, p-p scattering).

83  
84 Improvements in spatial resolution, data handling, and detection limits have been made in ERDA in  
85 the past 15 years (FIG. 2), and this method has been used to establish FTIR calibrations for H in  
86 some of the most important minerals in the deep Earth, including olivine (Withers et al. 2012) and  
87 its high-pressure polymorphs wadsleyite and ringwoodite (Bolfan-Casanova et al. 2018). The  
88 Withers et al. (2012) calibration results in lower hydrogen concentrations (by a factor of 0.63) in  
89 olivine compared to a previous calibration based on NRA measurements of natural olivines, which  
90 may have suffered from complications caused by sub-micrometer sized inclusions of hydrous  
91 phases (Mosenfelder et al. 2011). For the high-pressure polymorphs, in contrast, the new ERDA-  
92 based calibrations result in higher hydrogen concentrations compared to calibrations that were  
93 used in the past. These older calibrations were derived to quantify the well-known fact that  
94 absorption intensities vary with frequency of the O-H stretching vibration, but subsequent studies  
95 demonstrated that they can over- or underestimate hydrogen concentrations in non-systematic  
96 ways for different minerals (Rossman 2006). More work is needed to constrain the magnitude of  
97 the frequency dependence of IR molar absorption coefficients, which could be important for  
98 minerals like olivine with variable IR spectra encompassing a wide frequency range (FIG. 1).

99  
100 Technical improvements are also in progress for p-p scattering, which has the advantage of  
101 revealing the 3-dimensional distribution of hydrogen in thin samples. This capability could be used  
102 to detect hydrous inclusions in samples and is effective for discriminating against surface  
103 contamination (Weis et al. 2018). Another, more commonly used technique in geoscience is Raman  
104 spectroscopy. Raman is a particularly powerful technique for characterizing hydrogen speciation in  
105 fluid inclusions (e.g., Vlasov et al. 2023) and H<sub>2</sub>O concentrations in melt inclusions (Thomas et al.  
106 2006) that are not exposed at the surface of a mineral. The introduction of higher power lasers has  
107 also made it more feasible to quantify hydrogen in NAMs (e.g., Thomas et al. 2015; Martinek and  
108 Bolfan-Casanova 2021), although this method can be difficult to apply accurately owing to  
109 variations in laser power and other instrumental factors that need to be carefully controlled.  
110 Nevertheless, Raman can be especially useful for small phases with high H contents that are difficult  
111 to measure otherwise, simultaneously providing site-specific information analogous to that

112 provided by FTIR.

113

## 114 **HYDROGEN IN MANTLE MINERALS**

### 115 *Upper mantle*

116 Hydrogen in deep-seated minerals is most commonly incorporated as hydroxyl ( $\text{OH}^-$ ), although  
117 other mechanisms involving structurally bound  $\text{H}_2\text{O}$ , various configurations of H bonded to C (in  
118 diamonds; Vangu et al. 2023) or N (as  $\text{NH}_4^+$ ), and even neutral  $\text{H}_2$  molecules (Yang et al. 2016) can  
119 also be relevant. Structural sites for  $\text{OH}^-$  are well defined for hydrous phases such as amphibole, but  
120 in NAMs the sites can vary considerably even for a single mineral. This variation can provide clues  
121 to the physical conditions at which the mineral last equilibrated. Hydrogen in NAMs can be  
122 incorporated via coupled substitution with other elements, or in association with intrinsic point  
123 defects such as vacancies in cation sites.

124

125 Taking olivine as an example, FIGURE 1 illustrates most of the IR absorption bands commonly  
126 observed in natural and synthetic crystals that have not been otherwise attributed to fluid  
127 inclusions or inclusions of hydrous phases such as serpentine. The comparison demonstrates that  
128 absorption bands in natural crystals can be reproduced in experiments. Moreover, the stark  
129 difference between spectra of two different natural olivines derived from the mantle implies that no  
130 single incorporation mechanism can be called upon to explain all the bands. Indeed, the structural  
131 sites responsible for the different absorptions in these samples are still vigorously debated, with  
132 proposed mechanisms including vacancies in octahedral or tetrahedral sites balanced by  
133 protonation of oxygen atoms, coupled substitutions with  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  in octahedral sites paired with  
134 vacancies in adjacent octahedral sites, coupled substitution with  $\text{Ti}^{4+}$  or  $\text{Fe}^{3+}$  in octahedral sites  
135 balanced by hydrogen in tetrahedral vacancies, and various coupled substitutions of hydrogen with  
136 fluorine or boron.

137

138 More effort has been invested into olivine than any other NAM for the purpose of studying the  
139 effects of pressure, temperature, oxygen fugacity, and other thermodynamic parameters (e.g., silica  
140 activity,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  fugacity) on hydrogen incorporation. In theory, spectral characteristics and  
141 overall H content could be used to infer conditions of formation for mantle samples, but

142 discrepancies among studies prevent consensus on an overall thermodynamic law. Some of these  
143 discrepancies can be attributed to the use of different analytical methods and calibrations, but some  
144 are probably related to incomplete approach to equilibrium caused by slow diffusion kinetics.  
145 Hydrogen diffusion mechanisms in olivine and other NAMs have been intensely investigated and  
146 are more complex than originally thought, with complications caused by different diffusion rates for  
147 and intersite-reaction between different defects (Padrón-Navarta et al. 2014; Jollands et al. 2019).  
148 Thus, the distribution of point defects in the starting material can lead to a metastable OH<sup>-</sup> pattern  
149 in FTIR spectra, if there is insufficient time in the experiment to reach true equilibrium.

150

151 A further complication is that "solubility" experiments in simple systems (e.g., one or two mineral  
152 phases plus fluid) cannot be used to accurately model the storage capacities of NAMs in natural  
153 peridotites or other rocks, because the presence of multiple phases changes water fugacities as a  
154 result of varying dissolution of chemical species into the coexisting fluid, melt, or supercritical fluid.  
155 Consequently, studies constraining H contents and partitioning between multiple NAMs (olivine,  
156 orthopyroxene, clinopyroxene, and garnet) and coexisting hydrous melts at high pressure are  
157 critical for determining the overall H storage capacity of the mantle and the influence of hydrogen  
158 on the onset of partial melting (e.g., Novella et al. 2014). These studies reveal that H storage  
159 capacity in olivine goes up with increasing depth, while storage capacity in pyroxenes declines with  
160 increasing depth as a result of decreasing Al solubility with increasing pressure. Furthermore, the H  
161 storage capacity of garnets with pyrope-rich compositions relevant to the mantle is much lower  
162 than other NAMs, despite the fact that grossular-rich crustal garnets can contain wt% levels of H<sub>2</sub>O.

163

164 Recent improvements in analytical techniques (FIG. 2) have facilitated quantification of H contents  
165 in diamonds, revealing H to be the second major impurity in between N and B (Vangu et al. 2023).  
166 Although diamonds are minor phases in the mantle, they can be used to place constraints on parent  
167 metasomatic fluids. Combined investigations of hydrogen in host diamonds and their fluid and solid  
168 inclusions (e.g., Pearson et al. 2014; Tschauner et al. 2018; Weiss et al. 2022) from cratons, the  
169 transition zone and the lower mantle thus could constitute a powerful strategy to characterize  
170 hydrogen cycling in the deep Earth (Novella et al. 2024 this issue).

171

172 ***Transition zone***

173 The dominant phases in the mantle transition zone between 410 and 660 km depth are the high-  
174 pressure polymorphs of olivine (wadsleyite and ringwoodite) and majoritic garnet, with minor  
175 amounts of clinoenstatite or akimotoite depending on pressure, temperature, and whole-rock  
176 composition. It has been recognized for over 30 years from theoretical and experimental studies  
177 that wadsleyite and ringwoodite could be significant hosts for hydrogen. Experiments demonstrate  
178 that they can incorporate weight percent levels of H<sub>2</sub>O (up to ~3 wt% H<sub>2</sub>O; e.g., Bolfan-Casanova et  
179 al. 2018), far beyond the amounts that can be stored in olivine and other NAMs at lower pressures.  
180 Significantly lower, but non-trivial amounts of hydrogen can be incorporated in majorite (up to  
181 ~1000 ppm H<sub>2</sub>O; e.g., Thomas et al. 2015), clinoenstatite, and akimotoite. The importance of these  
182 phases as carriers for hydrogen in the deep Earth has now been field tested by the discovery of a  
183 hydrous ringwoodite inclusion (containing ~1.5 wt% H<sub>2</sub>O) in diamond (Pearson et al. 2014),  
184 proving that at least locally the transition zone is a rich hydrous reservoir in the deep Earth.

185 Recognition of the capacity of the transition zone to store more hydrogen than the upper mantle  
186 has spurred numerous attempts to constrain its actual hydrogen content using seismology and  
187 electrical conductivity. Furthermore, the low velocity zone above the 410 km seismic discontinuity  
188 can be conveniently explained as a consequence of dehydration melting caused by the upwelling of  
189 hydrated transition zone material. This low velocity zone in turn forms a source for hydrated melts  
190 that can ascend further once they become buoyant, balancing the influx of water into the transition  
191 zone from subducting slabs. Geophysical and geochemical implications of a "wet" transition zone  
192 are explored later in this issue.

193

## 194 ***Lower mantle***

195 Deeper still in the Earth, potentially the most important carrier for hydrogen is bridgmanite, the  
196 perovskite-structured polymorph of orthopyroxene that comprises ~80% of the mantle below the  
197 transition zone. Unfortunately, experimental studies on hydrogen incorporation in bridgmanite are  
198 highly contradictory. Some studies have suggested this mineral can incorporate as much as 0.1-0.2  
199 wt% H<sub>2</sub>O, if H associated with Al<sup>3+</sup> or Fe<sup>3+</sup> replaces Si<sup>4+</sup> in the structure (e.g., Fu et al. 2019).  
200 However, other studies (e.g., Liu et al. 2021) have measured much lower or completely negligible H  
201 concentrations and proposed that other measurements by SIMS or FTIR were compromised by the  
202 presence of hydrous phases or melt, either as inclusions in bridgmanite or on grain boundaries  
203 between crystals. This concern may also apply to claims of relatively high hydrogen concentrations  
204 in periclase (or ferropericlase) and davemaoite (CaSiO<sub>3</sub> perovskite), the next most prevalent



205 minerals in the lower mantle.

206

207 If bridgmanite and other NAMs comprising the bulk of the lower mantle can't incorporate  
208 significant hydrogen, the best candidates for transporting hydrogen into the deepest parts of the  
209 Earth may be dense hydrous magnesium-aluminum silicates (such as phase D and phase H, with  
210 variable Al contents), aluminous or ferric phases (such as  $\delta$ -AlOOH and the high-pressure  
211 polymorphs of FeOOH), or solid solutions between these phases (e.g., Nishi et al. 2017; Ishii et al.  
212 2022). These high-pressure phases are unstable along average mantle adiabats but can be stable  
213 within cold subducting slabs.

214

215 Another phase relevant in subducting slabs is stishovite, stable at pressures above  $\sim 9$  GPa. Earlier  
216 experiments revealed low storage capacities for hydrogen in this SiO<sub>2</sub> polymorph, primarily tied to  
217 the presence of Al<sup>3+</sup> impurities. However, an "ultrahydrous" form of stishovite containing weight-  
218 percent levels of H<sub>2</sub>O can be synthesized at low temperatures (350-550 °C, at  $\sim 10$  GPa; Spektor et  
219 al. 2016). This ultrahydrous stishovite is also stable at higher temperatures and pressures and  
220 comparable amounts of hydrogen may also be incorporated in the higher-pressure CaCl<sub>2</sub>-structured  
221 SiO<sub>2</sub> polymorph (e.g., Lin et al. 2022). However, the exact amounts are subject to large uncertainties  
222 as they are primarily based on density functional theory (DFT) calculations and/or calculations  
223 from X-ray diffraction (XRD) data combined with extrapolated equations of state for the  
224 ultrahydrous phase. Furthermore, coupled substitution of Al<sup>3+</sup> and H<sup>+</sup> becomes increasingly feasible  
225 at more extreme conditions (Ishii et al. 2022). Thus, stishovite and its higher-pressure polymorphs,  
226 with a wide combined pressure-temperature stability, could facilitate transport of hydrogen from  
227 the upper mantle all the way down to the core-mantle boundary. Dehydration, melting, and/or  
228 reaction with liquid iron to form iron hydride phases would then likely occur at the thermal  
229 boundary layer next to the outer core (Lin et al 2022).

230

## 231 **HYDROGEN IN FLUIDS AND MELTS**

232 Aqueous fluids and hydrous melts are key transport agents for hydrogen in the Earth. At certain  
233 pressures and temperatures in the upper mantle, fluids and melts become miscible (supercritical),  
234 with important geophysical and geochemical implications (e.g., Mibe et al. 2007). Advances in  
235 analytical techniques and high-pressure instrumentation are opening up new avenues for studying

236 deep-seated fluids and hydrous melts. For instance, synchrotron XRD enabled the discovery of Ice-  
237 VII inclusions in diamonds that were trapped at pressures as high as 25 GPa (Tschauer et al.  
238 2018). This finding supports the inference from hydrous ringwoodite in diamond (Pearson et al.  
239 2014) that localized regions of the transition zone (and possibly the top of the lower mantle) are  
240 hydrated. More broadly, the application of a battery of microanalytical techniques including FTIR,  
241 Raman, electron microprobe analysis, and electron microscopy assisted by focused ion-beam  
242 sample preparation has enabled thorough characterization of complex fluid inclusions in natural  
243 lithospheric diamonds, as reviewed by Weiss et al. (2022).

244

245 On the experimental side, progress in understanding the speciation of fluids in the deep Earth is  
246 exemplified by studies of synthetic fluid inclusions (Vlasov et al. 2023). This work demonstrates  
247 immiscibility between H<sub>2</sub> and H<sub>2</sub>O at high pressures, which potentially has important implications  
248 for the overall oxidation of the mantle early in Earth's evolution and diamond growth in super-  
249 reducing environments in the modern Earth (Vlasov et al. 2023). Although technically still very  
250 difficult, high-pressure experiments using synchrotron XRD (in a large volume press; Mibe et al.  
251 2007) and other in situ techniques (e.g., spectroscopic observations in diamond anvil cells) have  
252 also made remarkable progress in directly observing supercritical behavior in deep fluids and  
253 melts.

254

255 Decades of research have gone into understanding the dissolution mechanisms of hydrogen in  
256 glasses quenched from melts at high pressure, but recent advances reveal new complexities with  
257 important implications for the geochemical evolution of the Earth. The prevailing wisdom that  
258 hydrogen dissolves in geologically relevant melts primarily as either molecular H<sub>2</sub>O or OH<sup>-</sup> groups  
259 has been overturned by experiments (Hirschmann et al. 2012) demonstrating that molecular H<sub>2</sub> can  
260 be a dominant species at high pressure and low oxygen fugacity (FIG. 3). Furthermore, a wealth of  
261 new experimental studies (e.g., Grewal et al. 2020) have revealed that low oxygen fugacities  
262 promote complexing of hydrogen with carbon and nitrogen. The solubility of H<sub>2</sub> and various C-H  
263 and N-H species (example shown in FIG. 3) in melts as a function of thermodynamic variables is a  
264 complex topic beyond the scope of this paper, but the recognition of these incorporation  
265 mechanisms has critical implications for the distribution of volatiles in planetary bodies and their  
266 degassing and redox evolution following magma ocean formation and solidification (e.g.,  
267 Hirschmann et al. 2012; Grewal et al. 2020).

268

269 The development of a new rapid-quenching multi-anvil technique (FIG. 3) has facilitated study of  
270 previously unquenchable depolymerized melts, including peridotitic glasses that are directly  
271 relevant to the lower mantle (Bondar et al. 2023). It has long been known that the relative  
272 proportions of H<sub>2</sub>O and OH<sup>-</sup> groups depend on melt composition and overall hydrogen content, but  
273 this new work demonstrates previously unseen complexities in bands attributed to the OH<sup>-</sup> groups  
274 (FIG. 3). In peridotitic glasses, two bands at 4400 and 4270 cm<sup>-1</sup> are observed, as opposed to the  
275 single band between ~4500 to 4400 cm<sup>-1</sup> in more polymerized glasses. These bands are  
276 interpreted to represent (Si,Al)-OH and (Ca,Mg)-OH species, respectively, whereas the single band  
277 is interpreted to represent only (Si,Al)-OH. The appearance of new species in increasingly  
278 depolymerized glasses and the frequency shifts will require further work to determine the  
279 absorption coefficients for the bands and establish a solubility law at very high pressures that is  
280 more relevant to melting in the deep Earth. Ultimately, this finding will have critical implications for  
281 modeling not only water-fluxed formation of ultramafic melts, but hydrogen solubility in magma  
282 oceans, which influences planetary degassing (e.g., Hirschmann et al. 2012).

283

## 284 **CONCLUSION**

285 The study of hydrogen in the deep Earth will continue to advance via improvements in  
286 experimental instrumentation, analytical techniques, and quantitative modeling, only some of  
287 which we have been able to cover here. For instance, we have almost completely ignored DFT-  
288 based, first-principles predictions of hydrogen incorporation mechanisms and storage capacities at  
289 high pressures and temperatures. These studies will inevitably play an increasingly important role  
290 as computing power grows. On the analytical side, an example of an emerging and promising  
291 technique is atom probe tomography (APT), which can be used to hone in on the atomic scale to  
292 identify hydrogen incorporation mechanisms. Confident application of APT to NAMs will require  
293 overcoming technical limitations (particularly high H backgrounds) with commercially available  
294 instruments (Chen et al. 2023). Developments in high-pressure experimentation can also be  
295 expected to enable further strides in constraining how hydrogen is recycled and stored in the deep  
296 Earth. These developments include both "offline" instrumentation advances in obtaining higher  
297 pressures with larger samples, and "online" combination of high-pressure techniques with in situ  
298 analytical probes (e.g., synchrotron radiation), allowing the study of hydrogen incorporation in  
299 materials while circumventing any chemical or structural modifications caused by quenching.

300

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304

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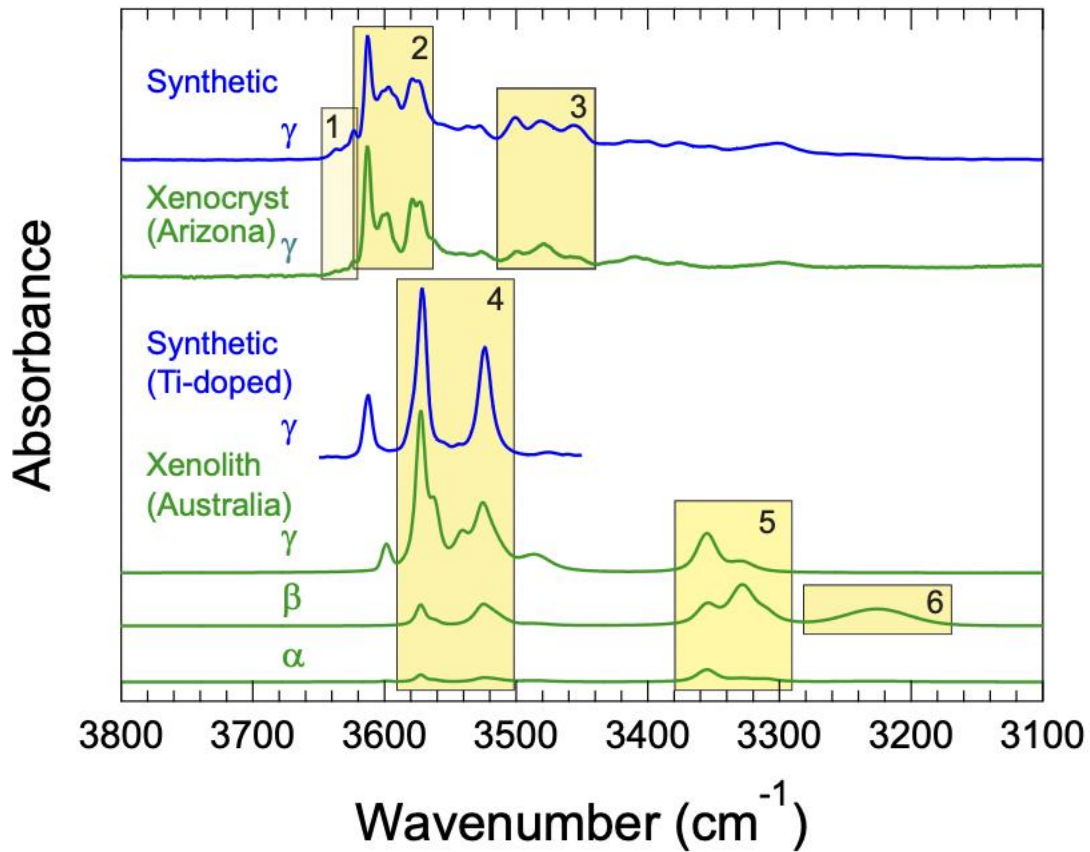
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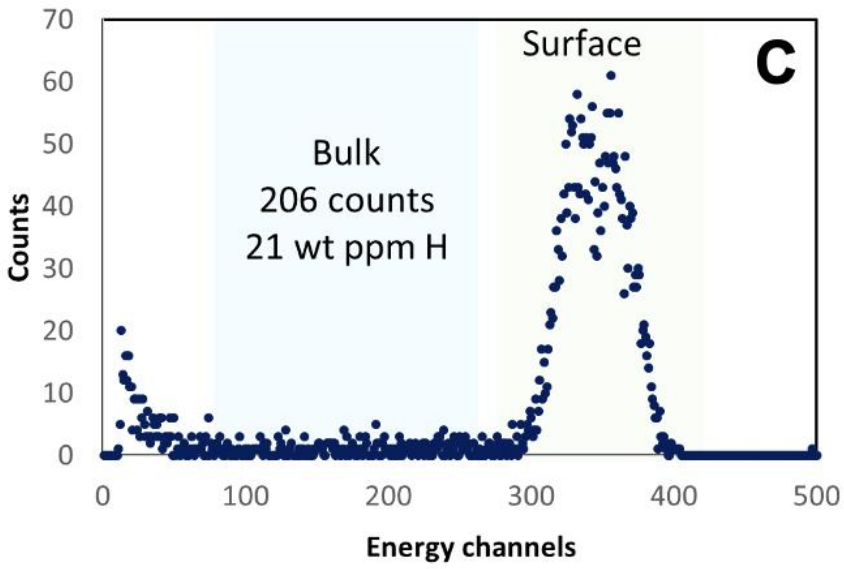
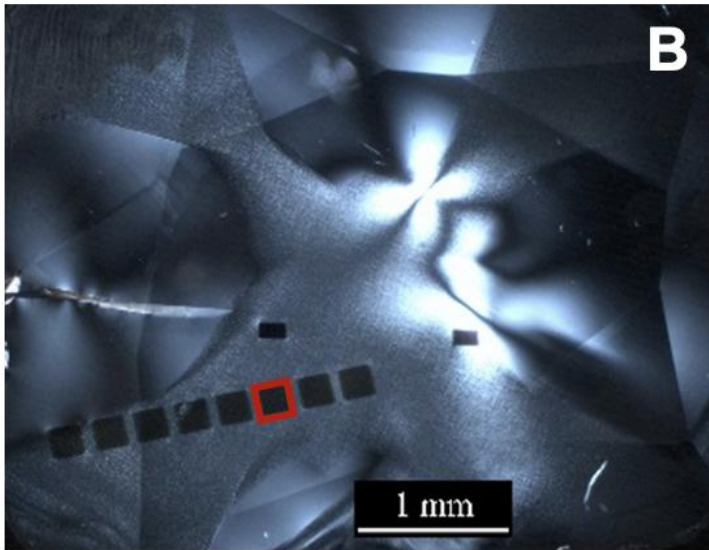
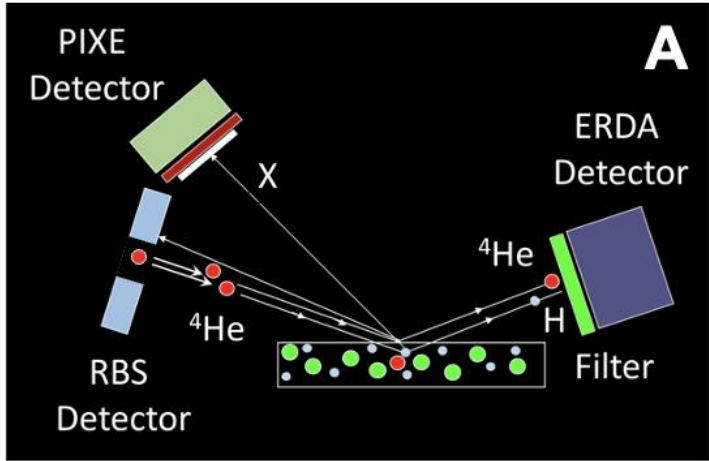
## Figures



388

389 **FIGURE 1.** Mid-infrared spectra of olivine, illustrating the rich diversity of O-H absorption bands in  
 390 natural and synthetic crystals. Spectra are arbitrarily scaled and offset for the sake of comparison.  
 391 Greek letters refer to the optical direction that was parallel to the E-vector of the polarized beam  
 392 for each spectrum. A strong correspondence is apparent for the spectra of synthetic olivine  
 393 (recovered from 3 GPa and 1250 °C; Withers et al. 2012) and a xenocryst from Buell Park, Arizona.  
 394 Spectra for a xenolithic olivine from Mount Gambier, South Australia more closely resemble spectra  
 395 of synthetic forsterite doped with Ti at 2 GPa and 1400 °C (Padrón-Navarta et al. 2014). Shaded  
 396 regions denote bands with the following possible interpretations: 1) coupled H-F defects in  
 397 tetrahedral sites; 2) four H<sup>+</sup> substituting for Si<sup>4+</sup>; 3) three H<sup>+</sup> substituting for Si<sup>4+</sup>, with Fe<sup>2+</sup> in a  
 398 nearby octahedral site oxidized to Fe<sup>3+</sup>; 4) two H<sup>+</sup> substituting for Si<sup>4+</sup>, with Ti<sup>4+</sup> in a nearby  
 399 octahedral site; 5) H<sup>+</sup> in a vacant octahedral site, with a trivalent cation (e.g., Al<sup>3+</sup>, Cr<sup>3+</sup>, or Fe<sup>3+</sup>) in an  
 400 adjacent octahedral site; 6) two H<sup>+</sup> in an octahedral site.

401





403 **FIGURE 2.** Elastic Recoil Detection Analysis (ERDA). **(A)** Principle of ERDA. An incident  $3 \times 3 \mu\text{m}^2$   
404 beam of  $^4\text{He}^+$  at 2.8 MeV and 500 pA is scanned on the sample with a grazing angle of  $30^\circ$ . Three  
405 detections are simultaneously performed: particle induced X-ray emission (PIXE), Rutherford  
406 backscattering (RBS), and ERDA. More details are available in Withers et al. (2012); Bolfan-  
407 Casanova et al. (2018); and Vangu et al. (2023). **(B)** Optical picture of an asteriated diamond  
408 (Sorbonne University Collection) with two growth sectors, corresponding to octahedral  
409 (transparent areas) and cuboid (opaque gray, central star) crystal growth. The dark squares are  
410 areas analyzed by ERDA, resulting in formation of a thin graphite surface. The square outlined in  
411 red corresponds to the ERDA spectrum in (C). **(C)** Typical ERDA spectrum for a nominally  
412 anhydrous mineral, obtained in the cuboid sector of the diamond in (B). The large peak (green  
413 shaded area) results from surface contamination, while the bulk region (blue) corresponds to H  
414 contained in the sample. The 206 counts obtained in this energy range correspond to a  
415 concentration of 21 wt ppm H with a relative uncertainty of 12% (Vangu et al. 2023).

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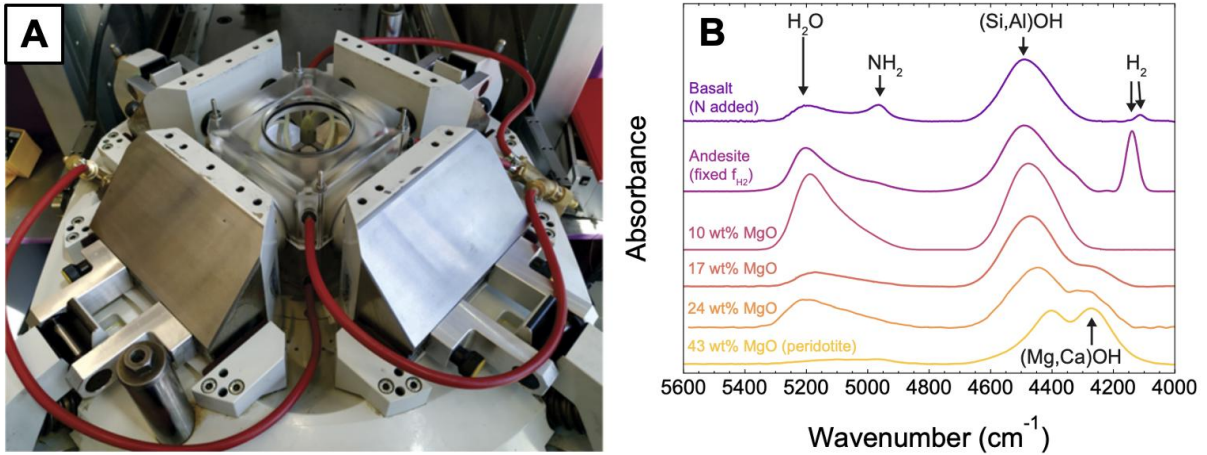
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 425 **FIGURE 3 (A)** Multi-anvil apparatus used to recover glasses quenched from highly depolymerized  
 426 melts at high pressure (Bondar et al. 2022). Rapid quenching is achieved by modifying the anvil  
 427 setup in two ways: 1) the device is cooled by circulating coolant through the volume enclosed by  
 428 the plastic box that can be seen in the center of the photograph; 2) the multi-anvil cell assembly is  
 429 redesigned to maximize heat transfer from the sample to the cooled exterior of the solid pressure  
 430 medium. **(B)** Near infrared spectra of glasses quenched at high pressures, demonstrating different  
 431 solubility mechanisms for hydrogen in melts. Top spectrum is an Fe-free basalt synthesized at 1.2  
 432 GPa at low  $f_{O_2}$ , with added nitrogen; this glass contains  $NH_2^-$  groups and  $H_2$  in addition to  $H_2O$  and  
 433  $OH^-$  groups. Second spectrum from the top is an andesitic glass recovered from 2.6 GPa, at low  $f_{O_2}$   
 434 and fixed  $f_{H_2}$  (Hirschmann et al. 2012). The other four glasses (Bondar et al. 2022) illustrate the  
 435 effect of increasing depolymerization (with increasing MgO content) on shifting the peak position of  
 436 the (Si,Al)OH band to the right, and emergence of a new band at lower frequency attributed to  
 437 (Mg,Ca)OH. For comparison, spectra are arbitrarily scaled, offset, and corrected for background  
 438 associated with an  $Fe^{2+}$  band at higher frequency (wavenumber) and/or the fundamental O-H  
 439 stretching vibration at lower frequency.

440

441 **SIDEBAR**

442

443 The use of different units in the literature for specifying hydrogen concentrations can lead to  
 444 confusion. Typically, geophysicists in the field of rock mechanics specify an atomic concentration  
 445 using "ppm H/Si" (or H/10<sup>6</sup> Si, which is the same unit), while mineralogists and petrologists use  
 446 "wt% H<sub>2</sub>O" or "wt. ppm H<sub>2</sub>O". Others yet may prefer to specify hydrogen as at. ppm H or OH,  
 447 without ratioing to Si concentration (which would obviously be inapplicable to materials such as  
 448 diamond or oxide minerals). Usage of a weight-based unit for minerals facilitates convenient  
 449 comparison to the convention most commonly used for glasses, as well as other elemental  
 450 concentrations (as listed in a table of microprobe data, for instance). However, some authors  
 451 casually use the unit "ppm" without stating whether they mean atomic or wt. ppm. This problem is  
 452 conveniently circumvented by using the unit "μg/g" (equivalent to wt. ppm), as preferred currently  
 453 by most geochemists. For silicate phases, the articles in this issue use "wt% H<sub>2</sub>O" or "ppm H<sub>2</sub>O by  
 454 weight" (=wt. ppm H<sub>2</sub>O). To aid the reader in following the literature, a table for converting from  
 455 one unit to another is provided below.

456

457 As an example, for a typical mantle olivine composition (Mg<sub>1.8</sub>Fe<sub>0.2</sub>SiO<sub>4</sub>), the conversion factor from  
 458 μg/g H<sub>2</sub>O (or wt. ppm H<sub>2</sub>O) to H/10<sup>6</sup> Si is 0.1119 × (147 g/mol) / (1 Si per formula unit) = 16.45.

459

To:	wt% H <sub>2</sub> O	μg/g H <sub>2</sub> O or wt ppm H <sub>2</sub> O	H/10 <sup>6</sup> Si	at ppm H	wt ppm H
From:					
wt% H <sub>2</sub> O	1	10 <sup>4</sup>	1119 M/N <sub>Si</sub>	1119 M/N	1119
μg/g or wt ppm H <sub>2</sub> O	10 <sup>-4</sup>	1	0.1119 M/N <sub>Si</sub>	0.1119 M/N	0.1119
H/10 <sup>6</sup> Si	8.937×10 <sup>-4</sup> N <sub>Si</sub> /M	8.937N <sub>Si</sub> /M	1	N <sub>Si</sub> /N	N <sub>Si</sub> /M
at ppm H	8.937×10 <sup>-4</sup> N/M	8.937N/M	N/N <sub>Si</sub>	1	N/M
wt ppm H	8.937×10 <sup>-4</sup>	8.937	M/N <sub>Si</sub>	M/N	1
M = molecular mass of one mineral formula unit; N <sub>Si</sub> = Si per formula unit, N = atoms per formula unit					

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