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1 **Hydrogen in the Deep Earth**

2 Jed L. Mosenfelder¹, H el ene Bureau², and Anthony C. Withers³

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), P₂O₅ 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 H₂O 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 (OH^-), although
117 other mechanisms involving structurally bound H_2O , various configurations of H bonded to C (in
118 diamonds; Vangu et al. 2023) or N (as NH_4^+), and even neutral H_2 molecules (Yang et al. 2016) can
119 also be relevant. Structural sites for 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 Al^{3+} or Fe^{3+} in octahedral sites paired with
134 vacancies in adjacent octahedral sites, coupled substitution with Ti^{4+} or 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, H_2O and 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⁻ 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 H₂O.

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 H₂O (up to ~3 wt% H₂O; 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 H₂O; 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% H₂O) 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% H₂O, if H associated with Al³⁺ or Fe³⁺ replaces Si⁴⁺ 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 (CaSiO₃ 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 δ -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 ~ 9 GPa. Earlier
216 experiments revealed low storage capacities for hydrogen in this SiO₂ polymorph, primarily tied to
217 the presence of Al³⁺ impurities. However, an "ultrahydrous" form of stishovite containing weight-
218 percent levels of H₂O can be synthesized at low temperatures (350-550 °C, at ~ 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 CaCl₂-structured
221 SiO₂ 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 Al³⁺ and H⁺ 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 (Tschauner 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 H₂ and H₂O 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 H₂O or OH⁻ groups
259 has been overturned by experiments (Hirschmann et al. 2012) demonstrating that molecular H₂ 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 H₂ 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 H₂O and OH⁻ groups depend on melt composition and overall hydrogen content, but
273 this new work demonstrates previously unseen complexities in bands attributed to the OH⁻ groups
274 (FIG. 3). In peridotitic glasses, two bands at 4400 and 4270 cm⁻¹ are observed, as opposed to the
275 single band between ~4500 to 4400 cm⁻¹ 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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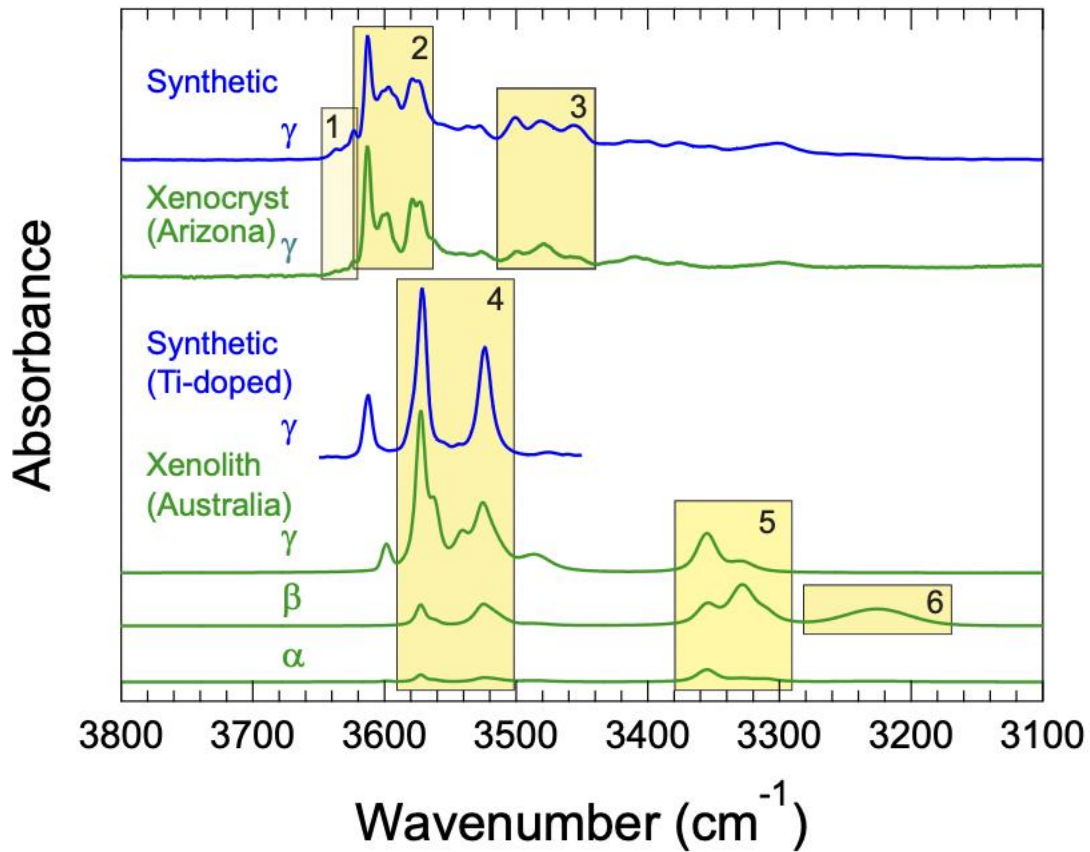
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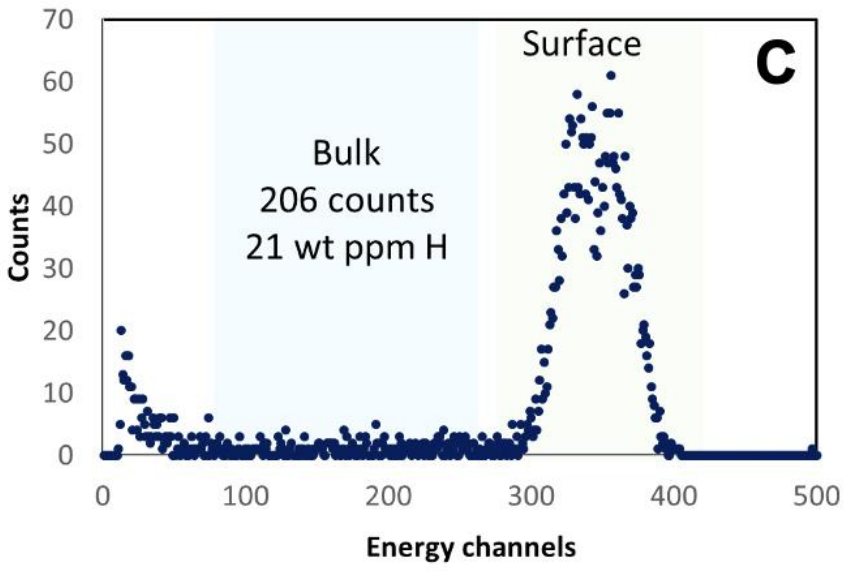
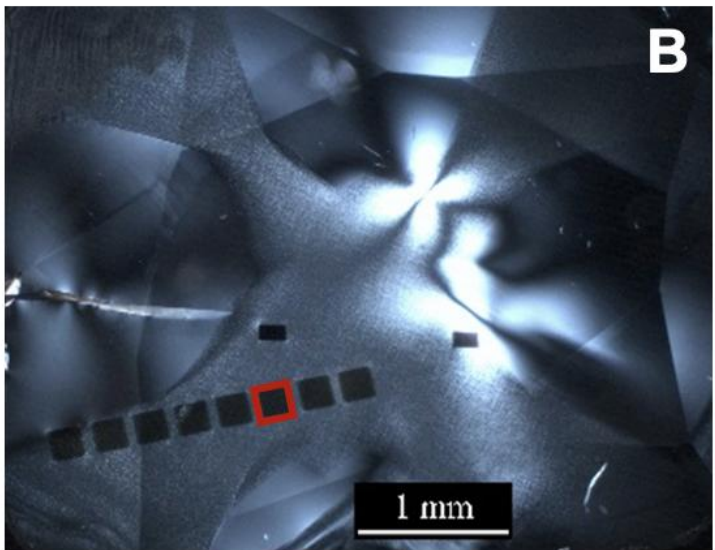
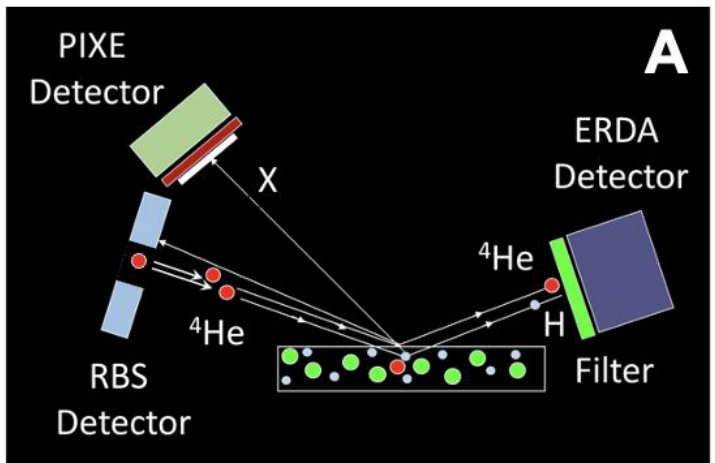
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389 **FIGURE 1.** Mid-infrared spectra of olivine, illustrating the rich diversity of O-H absorption bands in
 390 natural and synthetic crystals. Spectra are arbitrarily scaled and offset for the sake of comparison.
 391 Greek letters refer to the 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⁺ substituting for Si⁴⁺; 3) three H⁺ substituting for Si⁴⁺, with Fe²⁺ in a
 398 nearby octahedral site oxidized to Fe³⁺; 4) two H⁺ substituting for Si⁴⁺, with Ti⁴⁺ in a nearby
 399 octahedral site; 5) H⁺ in a vacant octahedral site, with a trivalent cation (e.g., Al³⁺, Cr³⁺, or Fe³⁺) in an
 400 adjacent octahedral site; 6) two H⁺ 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° . 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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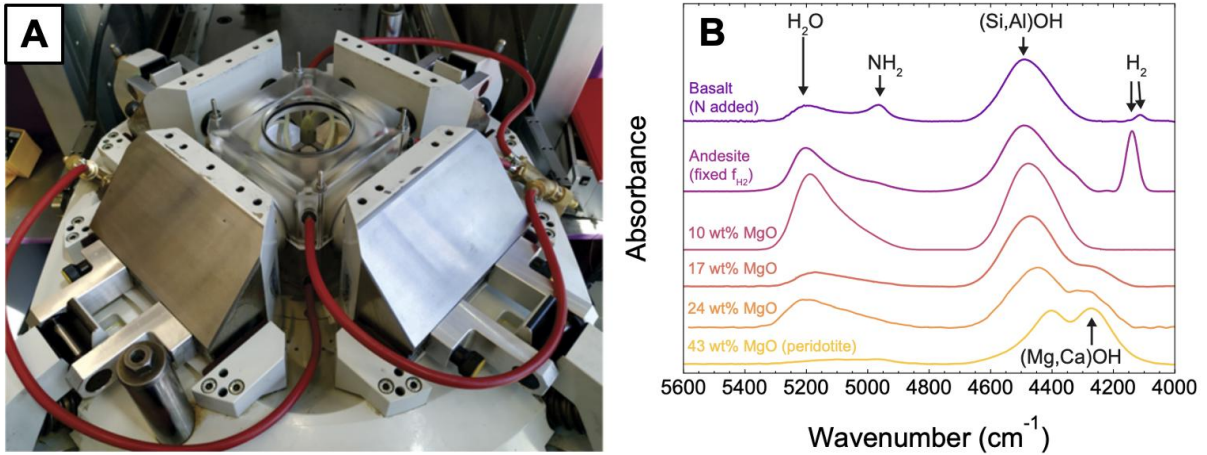
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 425 **FIGURE 3 (A)** Multi-anvil apparatus used to recover glasses quenched from highly depolymerized
 426 melts at high pressure (Bondar et al. 2022). Rapid quenching is achieved by modifying the anvil
 427 setup in two ways: 1) the device is cooled 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 $H/10^6 \text{ Si}$, which is the same unit), while mineralogists and petrologists use
 446 "wt% H_2O " or "wt. ppm H_2O ". 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 " $\mu\text{g/g}$ " (equivalent to wt. ppm), as preferred currently
 453 by most geochemists. For silicate phases, the articles in this issue use "wt% H_2O " or "ppm H_2O by
 454 weight" (=wt. ppm H_2O). 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 ($\text{Mg}_{1.8}\text{Fe}_{0.2}\text{SiO}_4$), the conversion factor from
 458 $\mu\text{g/g}$ H_2O (or wt. ppm H_2O) to $H/10^6 \text{ Si}$ is $0.1119 \times (147 \text{ g/mol}) / (1 \text{ Si per formula unit}) = 16.45$.

459

To:	wt% H_2O	$\mu\text{g/g}$ H_2O or wt ppm H_2O	$H/10^6\text{Si}$	at ppm H	wt ppm H
From:					
wt% H_2O	1	10^4	$1119 \text{ M}/\text{N}_{\text{Si}}$	$1119 \text{ M}/\text{N}$	1119
$\mu\text{g/g}$ or wt ppm H_2O	10^{-4}	1	$0.1119 \text{ M}/\text{N}_{\text{Si}}$	$0.1119 \text{ M}/\text{N}$	0.1119
$H/10^6\text{Si}$	$8.937 \times 10^{-4} \text{ N}_{\text{Si}}/\text{M}$	$8.937 \text{ N}_{\text{Si}}/\text{M}$	1	$\text{N}_{\text{Si}}/\text{N}$	$\text{N}_{\text{Si}}/\text{M}$
at ppm H	$8.937 \times 10^{-4} \text{ N}/\text{M}$	$8.937 \text{ N}/\text{M}$	$\text{N}/\text{N}_{\text{Si}}$	1	N/M
wt ppm H	8.937×10^{-4}	8.937	$\text{M}/\text{N}_{\text{Si}}$	M/N	1
M = molecular mass of one mineral formula unit; N_{Si} = Si per formula unit, N = atoms per formula unit					

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