

Where is the Hydrogen?

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ABSTRACT

How is hydrogen distributed among minerals and how is it bonded in their crystal structures? These are important questions, because the amount of hydrogen and the bonding configuration of hydrogen in crystalline materials governs many of that material's properties: its thermal and compressional behavior, P - T phase stability, rheology, and electrical conductivity. A reliable reconstruction of the Earth's interior, or the prediction of mineral transformations in complex industrial processes, must account for these parameters. Neutron diffraction can locate hydrogen sites in mineral structures, reveal any static or dynamic hydrogen disorder, help define the libration regime of hydrogen, and elucidate hydrogen-bonding configurations. Thus, that most elusive element for X-ray probes is perfectly detectable using neutrons.

KEYWORDS: neutron diffraction; neutron scattering; hydrous minerals; hydrogen bond; atomic disorder

INTRODUCTION

Hydrogen formed in the early universe is the most abundant element in the solar system. It constitutes 70.6 wt% of the solar system's mass, being present in the giant gaseous planets and, of course, the Sun. On Earth, hydrogen exists as water vapor in the atmosphere, as water and ice in the ocean and, on land, as supercritical fluids in volcanoes, as H₂O molecules and hydroxyls in hydrous and nominally anhydrous minerals in the Earth's crust and mantle, and

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as hydrogen “dissolved” in metallic iron in the core. Wu et al. (2018) proposed a model for the origin of Earth’s water, which included contributions from chondrites and from the solar nebula. These authors concluded that the Earth stores the majority of its hydrogen on the inside, with roughly two oceans equivalent of water in the mantle and four to five oceans in the core (FIG. 1). There is a continuous mass transfer of water between the geosphere, hydrosphere, atmosphere, and biosphere, which is promoted by a series of endogenic and exogenic phenomena, all of which govern the so-called “water cycle” or “hydrogen cycle”. Brovarone et al. (2020) and Demouchy and Bolfan-Casanova (2016) provide a description of these terrestrial water and hydrogen cycles.

Therefore, hydrogen has been one of the most investigated chemical elements over the last three centuries, especially after its recognition as an element in 1776 by Henry Cavendish. A series of experiments, coupled with atomistic simulations, have been performed over the last century to explore the stability of hydrogen over a broad range of pressures and temperatures (Goncharov 2020). Despite its chemical simplicity, solid H₂ occurs in different polymorphs in response to the different *P*–*T* conditions. However, the existence of “metallic hydrogen” under extreme conditions is still matter of debate.

Hydrogen occurs in a variety of bonding configurations, most of which are polar, that cover the whole range from purely ionic bonds (H⁺···anions) to covalent bonds (O–H, C–H, N–H) and coordinative bonds (metal–H). A comparative analysis of approximately 5,600 mineral species shows that 55%–56% of those are H-bearing minerals. In its ionic form, hydrogen can also possess a negative character and so form compounds with more electropositive metals in the form of “hydrides”. Bindi et al. (2019) discovered the first natural hydride, which was of vanadium (VH₂).

When hydrogen is bonded to a more electronegative element, it can participate in a noncovalent bond, for which the electronegative element has a lone pair, and so form a “hydrogen bond”. In the H-bonding scheme, a *donor* (*Dn*) atom is a covalently bonded atom to hydrogen, at the same time as there being an *acceptor* atom (*Ac*, a lone pair on an electron-rich acceptor atom). The hydrogen bond is directional, and its bonding energy depends on the nature of the *donor* and *acceptor* elements and the geometrical configuration: that is, the *Dn*···*Ac* distance and the *Dn*–H···*Ac* angle. Hydrogen bonds can range from being very weak (<17 kJ/mol) to very strong (170 kJ/mol) (Libowitzky and Rossman 1996). The strong hydrogen-bond network in water controls its unusual thermophysical properties, such as its unusually large specific heat, high melting point, and large surface tension.

In this article, we describe how neutrons provide a powerful probe to detect hydrogen in the crystal structure of minerals, to reveal its bonding configuration, and to uncover the dynamics of hydrogen in minerals. This information is critical because hydrogen plays a key

role in many mineralogical, geochemical, and petrologic processes. Hydrous minerals, for example, not only provide information about the role of fluids in the Earth's crust but they also help transport water deep into Earth's mantle and so form part of the cycle that helps regulate the sustained presence of surface water on Earth. In addition, hydrous minerals have many technological applications for use as ion-exchange materials, highly selective molecular sieves, catalysts, ion conductors, and hydrogen storage materials.

COMPARISON OF X-RAY AND NEUTRON RADIATION

Bragg Scattering

The goal of Bragg-scattering, or diffraction experiments in general, is to compare diffracted intensities with possible structure-derived model intensities and to identify the best-fitting one. For powder diffraction experiments, which contain Bragg intensities at the corresponding positions of related lattice planes, $I/2\theta$ diagrams are experimentally measured. Because the samples consist of randomly distributed crystallites, the 3-D orientation information is lost. These data are affected by instrumental parameters of the diffractometer (e.g., energy resolution, angular resolution, and collimation) and by sample-specific features (e.g., crystallites, size, and texture). The Rietveld method covers all these experimental aspects and allows for a full-profile fit in each 2θ range. Single-crystal diffraction experiments preserve the angular relationship between different lattice planes, which can be especially beneficial for studies of anisotropic features, as described in the examples below.

The different ways that X-rays and neutrons interact with matter explains why detailed studies use both kinds of probes (see Ross and Cole 2021 this issue). Electromagnetic X-ray radiation interacts with the electrons, where the electronic scattering power of an atom (f_z ; the X-ray form factor) is proportional to the atomic number (Z ; its shell electrons). For this reason, heavy atoms with many electrons show a higher scattering power than light elements: this explains why hydrogen has a low scattering power, even compared with second period elements. Moreover, electrons occupy a finite volume, of the same order of magnitude as the wavelength (λ). For X-rays, atoms, including H, are not point-like scattering centers. This leads to a rapid lowering of f_z at higher scattering angles, especially for larger atoms.

In contrast, neutron radiation is based on the particle-wave duality of the neutron. Its mass is ideal for exciting oscillations of the nuclei in hard matter. Neutron radiation not only interacts with the nuclear cores but also with the magnetic moments of atoms. The neutron analogue to the X-ray form factor is the scattering length (b), the value of which depends on the specific isotope and can even vary between nuclei of the same isotope due to spin-spin interactions. If all the nuclei have the same scattering length, then they can scatter

constructively—giving rise to Bragg-like diffraction—and have a coherent (“coh”) scattering length (b_{coh}) averaged over the different nuclei, i.e., $b_{\text{coh}} = \langle b \rangle$. In the case of incoherent (“inc”) scattering, the scattering length (b_{inc}) is the root mean squared deviation of scattering lengths, i.e., $b_{\text{inc}} = (\langle b^2 \rangle - \langle b \rangle^2)^{1/2}$ (Squires 2012). For most elements, the coherent scattering length and corresponding cross section (σ_{coh}) dominates. Hydrogen is an important exception, having $b_{\text{coh}} = -3.739$ fm and $b_{\text{inc}} = 25.274$ fm (1 fm = 10^{-15} m). The incoherent scattering results in a large background that might obscure the coherent scattering, this latter being needed to determine the structure of the material. This problem can be addressed by deuterating the sample, exchanging deuterium (^2H) for the hydrogen (^1H), because deuterium has $b_{\text{coh}} = 6.671$ fm and $b_{\text{inc}} = 4.04$ fm.

Thus, X-rays and neutrons yield different, but complementary, information in diffraction experiments. X-rays reveal the electron density in a crystal and, thus, they can potentially reveal information on chemical bonding; neutrons uncover exact atomic positions. This is especially true for polar X–H bonds determined using X-ray diffraction, as the valence-only charge density of hydrogen is polarized toward the heavier atom, resulting in the systematic underestimation of X–H distances. In addition, neutrons provide advantages over X-rays in studies of other light elements, such as lithium and beryllium. There is also another important aspect: local effects can have an impact on the spatial distribution of the scattered neutrons. One of the most prominent is the Debye–Waller factor—also known as the *temperature factor* or *atomic displacement parameter*—which describes the damping effect on Bragg intensities caused by oscillations of the atoms around their time- and space-averaged positions in a crystal. It is common for light elements, such as hydrogen, to show anharmonic effects. Thus, their constant nuclear scattering lengths for neutrons are of great advantage. It allows measurements with high statistics up to high momentum transfer, where anharmonic effects on the scattered intensities are more pronounced. Another process that can affect the intensities is absorption. For X-rays, penetration depths are usually in the range of a few microns to less than 1 mm, which limits diffraction experiments to sample diameters of typically below 0.3 mm. Conversely, thermal neutrons show, for most elements, penetration depths of several centimeters, meaning that large and complex sample environments can be easily accessed (see Chakoumakos and Parise 2021 this issue). On the other hand, neutron diffraction typically requires larger samples than those used for X-ray diffraction, which can present a significant challenge.

Beyond Bragg Scattering

Hydrogen is commonly involved in the formation of complex static and dynamic disorder. The Bragg diffraction experiments discussed above produce a structural model based on the projection of the whole crystal into a single average unit cell, which is assumed to follow strict translational symmetry in real space. However, all the diffuse scattering that arises from

static and dynamic disorder, order on a short length scale, complex correlated defect structures, or even amorphous atomic arrangements is neglected. Scattering terms due to these phenomena are often found as weak contributions to the background or as small intensity variations of the Bragg intensities. If information from Bragg scattering is complemented by that emerging from disorder phenomena, then *total scattering* techniques arise, and these can probe the *total electron density* in real space. A full discussion of total scattering methods goes beyond the scope of this article, and the reader is referred to Keen (2001) and Egami and Billinge (2012) for more details.

Inelastic/Quasi-Elastic Scattering

Although this article focuses mainly on neutron diffraction, both inelastic neutron scattering and quasi-elastic neutron scattering offer additional, powerful tools by which to investigate hydrogen in minerals. Inelastic neutron scattering and quasi-elastic neutron scattering provide information about hydrogen bonding within minerals and mineral surfaces, as well as dynamical information of how hydrogen “moves” in a structure. For example, inelastic neutron scattering came into use to investigate interlayer H₂O molecules, hydroxyl groups, and hydrogen bonding in a variety of phyllosilicates and clay minerals (e.g., Cygan et al. 2015). Wang et al. (2014) determined the vibrational density of states of strongly H-bonded interfacial water on surfaces of metal oxides using inelastic neutron scattering. Understanding the structure and properties of water at metal oxide–water interfaces is of special importance because they determine and control specific chemical processes, such as catalysis or mineral growth and dissolution. The inelastic neutron scattering method can also provide insights about the behavior of molecular H₂O in confined environments, as described below.

The quasi-elastic neutron scattering method offers a way to gain insights into the diffusion of hydrogen within materials and its transport mechanisms, i.e., by measuring the rates of the rotational and translational diffusional motions of bulk H₂O molecules. Stack et al. (2021) described how quasi-elastic neutron scattering is applied to explore the diffusional dynamics at mineral–H₂O interfaces and to investigate the mobility of H₂O confined in a great variety of both organic and inorganic H₂O-containing materials. Furthermore, the method has also been applied to study water mobility and fluid movement through porous rocks, a process that influences such fields as contaminant remediation, CO₂ storage, and oil recovery.

HYDROGEN IN MINERAL STRUCTURES: BONDING CONFIGURATION, LIBRATION, AND DISORDER

Structurally Incorporated H₂O in Minerals

Neutron experiments have been extensively used to study hydrous minerals and have played a crucial role in improving our understanding of the chemical and physical properties of crystalline minerals (Gies 2009). In the Earth sciences, the adjective “hydrous” is commonly used for all the mineral species that contain either hydroxyl groups or H₂O molecules. Below, we use case studies from two different mineral groups, with differently bonded H₂O, to illustrate the different ways that molecules interact with natural crystalline materials. These include examples of heteropolyhedral microporous framework compounds with “confined” H₂O and of cyclosilicates with “ultraconfined” H₂O.

Microporous Frameworks with “Confined” H₂O

There are several microporous frameworks containing H₂O. The most studied are the zeolites, which have H₂O molecules confined in channels: these molecules are hydrogen-bonded to the oxygen atoms of the aluminosilicate framework and/or to each other. Zeolites have attracted interest mostly for their use as molecular sieves, but they have also been proposed as hydrogen storage materials, forming the basis for a new field of technologically important compounds: the zeolitic imidazolate frameworks. Many neutron diffraction experiments have been carried out on zeolites, revealing details of the hydrogen bonding and showing that the confined H₂O molecules in these open-framework materials are usually *weakly bonded* (Gies 2009). In contrast, there have been far fewer studies of heteropolyhedral microporous frameworks in which the H₂O molecules are *strongly bonded*. Among those, it is worth noting two dimorphs: epididymite, which is orthorhombic (space group *Pnma*), and eudidymite, which is monoclinic (space group *C2/c*) and having ideal formula Na₂Be₂Si₆O₁₅·H₂O (H₂O ~4 wt%).

Gatta et al. (2008) performed a reinvestigation of the structure of these two dimorphs by single-crystal neutron diffraction at 298 K. The structure of these minerals is built on topologically different frameworks made by SiO₄ and BeO₄ tetrahedra. Sodium atoms are located in small cavities (~4–5 Å) and bonded to oxygen atoms of the tetrahedral framework and H₂O molecules. The structure refinements allowed Gatta and colleagues to unambiguously locate all the H sites. The configuration of the H₂O molecules and hydrogen bonds in epididymite and eudidymite are shown in FIGURE 2. In epididymite, two strong hydrogen bonds occur with the framework oxygen atoms. The unique H₂O molecule appears to be significantly bent, having an H–O_{Dn}–H angle of ~102°, compared to ~106° in the (ideal) water molecule. This value is unusually low, although still in the range of the H–O_{Dn}–H angles in solid-state materials. The configuration of the H₂O molecules and hydrogen bonding in

eudidymite is even more complex. As shown in FIGURE 2, two symmetry-related and mutually exclusive O_{Dn} sites occur (with site occupancy 50%) at only 0.37 Å apart, giving two statistically distributed configurations of the H_2O molecule in the eudidymite structure. The $H1-O_{Dn}-H2$ angle is $\sim 104^\circ$, slightly less compressed than in epididymite. The (static) position disorder of H_2O in eudidymite can be ascribed to the fact that if the molecules were at the center of the channel, then the $H\cdots O$ distances would be too long and the $H-O_{Dn}-H$ angle would be far from an energetically favorable configuration. The strong hydrogen bonding in these dimorphs and the arrangement of H_2O molecules in the small channels of epididymite and eudidymite control their physical and chemical properties. For example, the temperature of dehydration is unusually high ($T > 800^\circ C$), and the heat capacities and entropies are generally higher than those found for zeolites (Geiger et al. 2010).

Cyclosilicates with "Ultraconfined" H_2O

Molecular H_2O is a common constituent of cyclosilicates that have 1-D channels. This is the case of beryl and cordierite. Beryl is a nominally anhydrous mineral that has the ideal formula $Al_2Be_3Si_6O_{18}$. However, alkali cations (Cs, Rb, K, Na) and H_2O molecules can occur within the six-membered ring channels along [001]. Many single-crystal X-ray diffraction and vibrational spectroscopy experiments have shown how H_2O , along with alkali cations, are located in the ~ 4.9 Å diameter channels running parallel to [001] (see Gatta et al. 2006 and references therein). Because the confinement of H_2O is largely 1-D and the diameter of the confining channel (≤ 5 Å) is not much bigger than that of the confined molecule (diameter of H_2O is ~ 2.75 Å), the H_2O in beryl is usually referred to as being "ultraconfined".

Two single-crystal neutron diffraction experiments performed by Artioli et al. (1993) and Gatta et al. (2006) revealed two different H_2O configurations that appear to be controlled by the weight fraction of H_2O and alkali cations (i.e., the channel content). First, the H_2O /alkali-rich beryls (i.e., $H_2O + Na_2O + Cs_2O > 3$ wt%) show a configuration of the H_2O with the oxygen site on the 6-fold axis and hydrogens distributed around the 6-fold axis with the $H\leftrightarrow H$ vector lying on a plane parallel to (001) (type-II H_2O) (FIG. 3). Second, for the H_2O /alkali-poor beryls ($H_2O + Na_2O + Cs_2O < 1.5$ wt%) the O site lies on the 6-fold axis and the H sites are distributed in six equivalent positions around the axis, with the $H\leftrightarrow H$ vector oriented almost parallel to [001] (i.e., at $\sim 4^\circ$ from [001]) (type-I H_2O) (FIG. 3). No evidence of interaction could be inferred via hydrogen bonding between H_2O molecules and framework oxygens in either beryl configuration. In the presence of H_2O , there is only a weak interaction with alkali cations lying along the channels.

Additional experiments based on inelastic neutron scattering, quasi-elastic neutron scattering, dielectric spectroscopy, and density functional theory *ab initio* simulations, were later performed on beryl and revealed a new state of H_2O within the mineral (Anovitz et al.

2013; Kolesnikov et al. 2016). There is a novel “quantum tunneling state” of the H₂O molecule that is confined in the ~4.9 Å channels of beryl. In this state, the oxygen and hydrogen atoms of the water molecule are “delocalized” and are, therefore, simultaneously present in all six symmetrically equivalent positions in the channel at the same time, an effect that can only occur in quantum mechanics.

Hydroxyl (OH⁻) in Minerals

The majority of the so-called “hydrous minerals” contain hydroxyl (OH⁻) groups rather than H₂O molecules. Here, we focus on one of the most common groups of minerals of the Earth’s crust: the phyllosilicates. These minerals reveal differing bond configurations that control, in part, their physical properties.

Phyllosilicates

Among phyllosilicates, talc and muscovite represent two examples in which the hydrogen-bond configuration is rather unusual. Talc occurs as a natural product of metamorphism or of the hydrothermal alteration of Mg-rich ultramafic rocks, and its ideal chemical formula is Mg₃Si₄O₁₀(OH)₂. Talc is also one of the most important industrial minerals, because of its low coefficient of friction, chemical inertness, and hydrophobicity. It contains ~5 wt% H₂O. The crystal structure of talc consists of a sheet of linked [MgO₄(OH)₂] octahedra (“O”), sandwiched between two sheets of SiO₄ tetrahedra (“T”) combined to six-member rings, giving the so-called “T–O–T” layered structure (FIG. 4). The T–O–T layers are charge neutral, held together by weak van der Waals attractive forces, resulting in the extreme softness of this mineral. The crystal structure of the 1T_c-talc (space group $C\bar{1}$) was reinvestigated by single-crystal neutron diffraction at 20 K (Gatta et al. 2013) and within the framework of a multimethodological study in which the thermal and compressional behavior were also investigated. Neutron structure refinement revealed an unusual hydrogen-bonding scheme in talc, shown in FIGURE 4, with one *donor* site and three *acceptors*, i.e., a trifurcated configuration. The three acceptors belong to the six-membered ring of tetrahedra juxtaposed to the octahedral sheet (FIG. 4). The O_{Dn}–H vector is perpendicular to the octahedral sheet. The vibrational regime of the proton site appears to be only slightly anisotropic. With such a configuration (i.e., long O_{Dn}⋯O_{Ac} distances, low O_{Dn}–H⋯O_{Ac} angular values), the hydrogen bonds are very weak in energy.

The structure of muscovite, which has the ideal composition KAl₂(Si₃Al)O₁₀(OH,F)₂, is more complex. Muscovite is a dioctahedral mica with “T–O–T” layers connected by interlayer cations (mainly K). The presence of Al as the principal octahedral cation generates an octahedral layer in which 2/3 of the three potential octahedral sites are populated (FIG. 4). This, in turn, leads to a different H location and hydrogen-bonding configuration compared to talc. A series of studies based on neutron diffraction methods were devoted to muscovite

(see Gatta et al. 2011 and references therein). Gatta et al. (2011), using single-crystal neutron diffraction analysis, collected diffraction data at 295 K and 10 K on a $2M_1$ -muscovite and provided high-quality structure refinements with all the atomic sites (including H) modelled anisotropically. In addition to showing that a trifurcated hydrogen-bonding scheme occurs, in which the three interactions are very weak, the refinements proved that only one independent H site occurs in the structure of muscovite, with no evidence of static or dynamic disorder, which was previously a matter of controversy. The neutron refinements also revealed details not easily determined by X-ray diffraction. They showed, for example, that the atomic displacement ellipsoid of hydrogen has a pronounced anisotropy and that a disordered Si/Al distribution occurs on the two independent tetrahedral sites.

The details of the hydrogen environment in muscovite and talc were only revealed by neutron diffraction. The results were important in understanding the physico-chemical and elastic properties of the minerals. Specifically, different orientations of the $O_{Dn}-H$ vector in phyllosilicates can play an important role in their compressional and thermal expansion behavior, which are notably anisotropic.

Nominally Anhydrous Minerals

Other rock-forming minerals, which usually occur in their anhydrous form, can incorporate hydrogen at a significant level. Neutron diffraction experiments reveal how hydrogen is incorporated in such minerals, thereby determining their hydrogen storage capacity. This is especially important in studies of the Earth's interior, because even trace amounts of hydrogen in a mineral structure can affect the propagation of seismic wave velocities and rheological properties of mantle minerals (e.g., Karato 2006).

Silicate garnets are important constituents of the Earth's crust and mantle. Hydroxyl can be incorporated in garnets and other materials via the so-called "hydrogarnet substitution", in which SiO_4^{4-} is replaced by four OH^- . Lager et al. (1987) performed seminal time-of-flight powder neutron diffraction experiments on the hydrogarnet katoite, $Ca_3Al_2(O_4H_4)_3$, at 300 K, 200 K, and 100 K. Rietveld structure refinements on the deuterated sample elucidated the positions and anisotropic displacement tensor of the (unique) H site (FIG. 5). Lager and colleagues found that the displacement ellipsoid (which represents magnitudes and directions of vibration of an atom, due to the always-present atomic motion) has a pronounced anisotropy, even at 100 K. Weak hydrogen bonds, having a bifurcated configuration, occur with oxygen vertices of the tetrahedron and act as *donors* and *acceptors*. Recently, Kyono et al. (2019) investigated the stability of katoite in situ at high pressures and temperatures using neutron diffraction. They discovered that katoite remains hydrated up to 850 °C and 8 GPa, suggesting that this mechanism might transport "water" into the Earth's mantle.

Two high-pressure polymorphs of olivine are wadsleyite and ringwoodite. Both polymorphs are major minerals of the Earth's transition zone and may also serve as a large internal reservoir for hydrogen. Recently, a natural transition-zone ringwoodite, containing at least 1.4 wt% of H₂O, was discovered as an inclusion in diamond (Pearson et al. 2014). Subsequently, single-crystal neutron diffraction experiments elucidated the storage capacity of hydrogen in wadsleyite and ringwoodite (Purevjav et al. 2016, 2018): these experiments determined how the hydrogen exchange mechanisms are quite different in the two polymorphs. In wadsleyite, there is only one oxygen site (out of four) that is available to be exchanged by OH⁻ (Purevjav et al. 2016). In ringwoodite, however, a hydrogen can exchange not only with the Mg or Fe in the octahedra but also with the Si in the tetrahedra (by substitutions as $1\text{Mg}^{2+} + 1\text{Si}^{4+} \leftrightarrow 6\text{H}^+$, $2\text{Mg}^{2+} + 1\text{Si}^{4+} \leftrightarrow 8\text{H}^+$, or $4\text{Mg}^{2+} + 1\text{Si}^{4+} \leftrightarrow 12\text{H}^+$, requiring vacant Mg and Si sites) (Purevjav et al. 2018). Therefore, ringwoodite has a larger “water” capacity in the lower half of the transition zone compared to that of wadsleyite in the upper half of the transition zone. The difference is a vital clue towards understanding why these dense mantle minerals show distinctly different softening behaviors after hydration.

CONCLUDING REMARKS

In this article, we have shown the benefits of using neutron scattering techniques, especially diffraction, for the location of the hydrogen sites in a mineral (even with concentration of a few thousands ppmw), the description of the static or dynamic disorder of hydrogen sites, the libration of hydrogen through a full description of the displacement tensor from the center of gravity, and the hydrogen-bonding configuration in minerals. This, in turn, provides the essential information needed to model the physical and chemical properties of the hydrogen-bearing minerals in either natural or industrial contexts. A mineral's thermal or compressional behavior, its *P-T* phase stability, and its leaching or catalytic activity are all influenced by the hydrogen-bonding scheme. Past limitations, due to the experimental need to use large crystal volumes or masses of polycrystalline samples, have been largely overcome by more powerful or more diverse neutron sources and instruments.

We hope that this article will further stimulate the mineralogical community's interest in developing and making greater use of the range of currently available neutron-based techniques.

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FIGURE CAPTIONS

FIGURE 1 Water circulation into the Earth's deep interior. FIGURE KINDLY PROVIDED BY M. NISHI.

FIGURE 2 (LEFT) Configuration of the H₂O molecules and H bonds in the structure of epididymite. **(RIGHT)** Configuration of the H₂O molecules and H bonds in the structure of eudidymite. Displacement ellipsoids probability factor is 50%. In reality, each H₂O is bonded to extra-framework Na sites (not shown). COMPLETE STRUCTURE MODELS IN GATTA ET AL. (2008).

FIGURE 3 (A) Photo of the mineral beryl. **(B)** Schematic configuration of the H₂O orientation in beryl. In H₂O/alkali-rich beryl, oxygen atoms lie on the 6-fold axis, hydrogen atoms and H-H vectors lie on (001) (type-II H₂O). **(C)** In H₂O/alkali-poor beryl, oxygen atoms lie on the 6-fold axis, H-H vectors are oriented almost parallel to [001] (type-I H₂O). Colors: O sites in red; H sites in yellow.

FIGURE 4 (LEFT) Hydrogen-bonding configuration in talc based on the structural models at 20 K. FROM GATTA ET AL. (2013). **(RIGHT)** Hydrogen-bonding configuration in muscovite based on the structural models at 20 K. FROM GATTA ET AL. (2011). Displacement ellipsoids probability factor is 50%. The "T-O-T" layers are parallel to (001).

FIGURE 5 (A) Crystal structure of the hydrogarnet Ca₃Al₂(O₄H₄)₃ viewed down [111]. BASED ON THE NEUTRON STRUCTURE REFINEMENT OF LAGER ET AL. (2005). **(B)** Configuration of the ("empty") 4(OH)⁻ tetrahedron (O in red spheres, H in yellow ellipsoids). Tetrahedron edge length is ~ 3 Å. Displacement ellipsoids probability factor is 50%.