

High-pressure phase of brucite stable at Earth's mantle transition zone and lower mantle conditions

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We investigate the high-pressure phase diagram of the hydrous mineral brucite, $\text{Mg}(\text{OH})_2$, using structure search algorithms and ab initio simulations. We predict a high-pressure phase stable at pressure and temperature conditions found in cold subducting slabs in Earth's mantle transition zone and lower mantle. This prediction implies that brucite can play a much more important role in water transport and storage in Earth's interior than hitherto thought. The predicted high-pressure phase, stable in calculations between 20 and 35 GPa and up to 800 K, features MgO_6 octahedral units arranged in the anatase- TiO_2 structure. Our findings suggest that brucite will transform from a layered to a compact 3D network structure before eventual decomposition into periclase and ice. We show that the high-pressure phase has unique spectroscopic fingerprints that should allow for straightforward detection in experiments. The phase also has distinct elastic properties that might make its direct detection in the deep Earth possible with geophysical methods.

brucite | pressure | phase transition | electronic structure calculations

Water plays an important role in sustaining geological activity. For instance, water helps in lowering the mantle's melting temperature, enhancing diffusion and creep thus affecting rheology of rocks, and also influences mineral phase boundaries. Current estimates suggest that the Earth's mantle is likely to contain a mass of water equivalent to the mass of the world's oceans (1, 2). The exchange of water between the surface and deep mantle reservoirs is vital for the sustenance of surface water over geological time scales (3). Hydrous minerals stable in the hydrated oceanic crust and mantle play an important role in transporting water into the Earth's interior. Hydrated peridotite, the major mantle rock type, can be understood by considering mineral phases stable in the ternary system of $\text{MgO-SiO}_2\text{-H}_2\text{O}$ (MSH). Brucite, $\text{Mg}(\text{OH})_2$, is arguably the simplest hydrous mineral in the MSH system. Brucite is also the most important $\text{MgO-H}_2\text{O}$ binary and the most water-rich phase within the MSH ternary system.

The crystal structure of brucite consists of Mg^{2+} cations and OH^- anions arranged in layers, in an overall trigonal structure (space group symmetry $P3m1$); Fig. 1. The common ionic compound CdI_2 is the archetype crystal structure for brucite as well as for portlandite [$\text{Ca}(\text{OH})_2$] and several other transition metal hydroxides $\text{M}(\text{OH})_2$ where $\text{M} = \text{Mn, Ni, Co, Fe, Cd, etc.}$ (4–10). In brucite, the crystal structure comprises layers of edge-sharing MgO_6 polyhedra. The interaction between the layers is weak at ambient conditions, where each upward-pointing OH group is surrounded by three downward-pointing OH groups in the adjacent layer and vice versa. Under compression the H–H repulsive interactions lead to positional disordering of the protons, which are displaced from the $2d$ Wyckoff site into one of three equivalent $6i$ sites as documented from neutron diffraction studies (11, 12). Vibrational spectroscopic studies including infrared and Raman spectroscopy show a broad ν_{OH} stretching band with the appearance of additional bands upon compression. The appearance of additional bands hints at the pressure-induced frustrations of the proton (13, 14). First-principles molecular dynamics simulations

also demonstrated the proton frustrations in brucite and portlandite at high pressure (15). A first-principles study at static conditions indicated that the pressure-induced hydrogen bonding in brucite is weak or unlikely to occur within the thermodynamic stability field of brucite (16). In addition, the study also predicted that upon compression, protons may transition from a dynamic positional disorder to a static positional disorder, leading to a lowering of the trigonal symmetry to $P3$.

Layered structures similar to that of brucite are also common in group I (alkali) hydroxides. Under pressure, the alkali hydroxides tend not only to form hydrogen bonds between the layers, but undergo transitions to 3D network structures, with 0-, 1-, or 2-dimensional hydrogen-bonded sublattices (17–20). The rationale from the high-pressure behavior of those systems is that layered phases are ultimately too loosely packed to survive under pressure. The important question relevant for deep Earth geophysics is whether brucite will undergo a similar transition and densification at high pressures, and significantly deviate from a layered structure, before decomposition into MgO and H_2O occurs. The presence of such a phase would have a significant impact on whether brucite itself could be stable in the mantle transition zone and lower mantle (potentially with quite different properties than those of the known phase), as well as the relative stability of competing MSH phases. We address this question here using structure prediction methods and first-principles total energy calculations, which enable us to bypass potential difficulties in high-pressure experiments such as sample preparation or kinetic reaction barriers. In recent years, such calculations have been crucial in making important predictions of high-pressure phases relevant for solid Earth geophysics (21, 22). These have been very helpful for experimental discoveries (23). Here, we suggest that brucite transforms to a new high-pressure

Significance

Hydrous minerals help transport water deep into Earth's mantle, and form part of a cycle that regulates the sustained presence of surface water on Earth. To understand the deep-water cycle, it is crucial to study the properties of hydrous minerals under the conditions present in Earth's mantle. Brucite is one of the simplest hydrous minerals and stores significant amounts of water as hydroxyl groups. It is assumed to decompose in the mantle transition zone, but we show here that a more compact high-pressure phase is stabilized instead that pushes the stability region of brucite into the lower mantle. Brucite might be present in much larger quantities, and play a larger role in water transport and storage, than previously thought.

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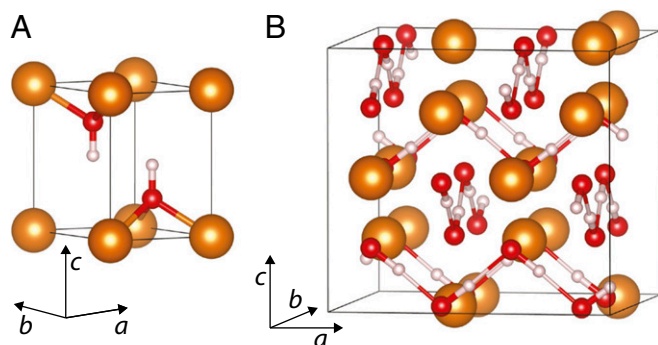


Fig. 1. (A) Low-pressure phase of brucite with $P\bar{3}m1$ space group symmetry. (B) High-pressure phase of $Mg(OH)_2$ with tetragonal $P4_12_12$ space group symmetry. Both the structures are drawn to the same scale at $P = 20$ GPa. Gold (red, white) spheres denote Mg (O, H) atoms. Hydrogen bonds in the tetragonal phase are indicated by thin lines.

phase at conditions relevant to subducting slabs in the mantle transition zone and lower mantle, i.e., pressures of ~ 20 GPa and temperatures of ~ 800 K.

Results

Our density-functional calculations give excellent agreement for the structural parameters of brucite ($P\bar{3}m1$) with experimental data at $P = 1$ atm (Table 1). They also correctly reproduce the pressure-induced stabilization of hydrogen bond formation and static proton disorder, in the form of the $P\bar{3}$ phase (16) (Fig. 2, Upper). For those two known brucite phases, decomposition into periclase (MgO) and ice-VIII is then calculated to occur at 18 and 21 GPa, respectively, i.e., in the Earth mantle transition zone. This agrees reasonably well with thermodynamic modeling based on the measured P - V - T equation of state for brucite, which estimated a decomposition pressure of 27 GPa at $T = 300$ K (24). Note that brucite has been compressed significantly beyond this pressure, likely due to kinetic barriers in the decomposition reaction (24, 25).

Our crystal structure prediction runs, however, revealed a candidate for a high-pressure phase of $Mg(OH)_2$ with tetragonal space group symmetry ($P4_12_12$), which is energetically more stable than both known modifications above 17 GPa (Fig. 2, Upper). With the appearance of a high-pressure phase, the thermodynamic stability limit of $Mg(OH)_2$ (toward decomposition into MgO and ice) is shifted to significantly higher pressures: by 8 GPa in the ground state, from 21 to 29 GPa. This delays the decomposition of $Mg(OH)_2$ from the lower part of the mantle transition zone (the pressure region 13–21 GPa) (26) deep into the lower mantle. The stability of the tetragonal $Mg(OH)_2$ phase is unaffected by the choice of exchange-correlation functional or the inclusion of zero-point effects (ZPEs). For instance, using the van der Waals density-functional approach (vdW-DF) with the optB88 functional (27–30), which includes dispersion interactions based on the electronic density, instead of the semilocal Perdew–Burke–Ernzerhof (PBE) functional, we find tetragonal $Mg(OH)_2$ to be stable from 18 to 27 GPa. When ZPEs are included with the PBE functional, tetragonal $Mg(OH)_2$ is stable from 19 to 33 GPa.

We used the quasi-harmonic approximation to estimate the Gibbs free energies of the relevant phases and construct the finite-temperature phase diagram of $Mg(OH)_2$. To that end, we included the vibrational contribution to the entropy of each phase, which results in

$$F(T, V) = E_0(V) + k_B T \int_0^\infty g(\omega) \ln \left[2 \sinh \left(\frac{\hbar \omega}{2k_B T} \right) \right] d\omega,$$

where $g(\omega)$ is the phonon density of states obtained from finite displacement calculations. As shown in Fig. 2 (Lower), this results in a large stability field for the tetragonal $Mg(OH)_2$ phase, up to $T = 800$ K at 30 GPa, where it forms a triple point with brucite (in the $P\bar{3}$ model) and the decomposition into MgO + ice-VIII. This triple point corresponds to a depth of ~ 800 km, in the upper reaches of the lower mantle, and approaches cold geothermal gradients estimated for subducting slabs (23, 31, 32) and the melting line of ice (33, 34). We included in this phase diagram the calculated geotherm for old and rapidly descending slabs as a solid blue line (32). This should serve as a low-temperature

Table 1. Crystallographic data of $Mg(OH)_2$ phases

Phase	Pressure	Lattice constants	Atomic positions
$P\bar{3}m1$ (Exp)	1 atm	$a = b = 3.150 \text{ \AA}$, $c = 4.770 \text{ \AA}$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Mg(0,0,0) O(1/3, 2/3, 0.220) H(1/3, 2/3, 0.413)
$P\bar{3}m1$ (DFT)	1 atm	$a = b = 3.182 \text{ \AA}$, $c = 4.801 \text{ \AA}$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Mg(0, 0, 0) O(1/3, 2/3, 0.217) H(1/3, 2/3, 0.419)
$P\bar{3}$	10 GPa	$a = b = 5.310 \text{ \AA}$, $c = 4.383 \text{ \AA}$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Mg1(0, 0, 0) Mg2(1/3, 2/3, -0.018) O(-0.006, -0.336, -0.239) H(-0.070, -0.365, -0.451)
$P4_12_12$	20 GPa	$a = b = 8.178 \text{ \AA}, c = 7.549 \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$	Mg1(0.380, 0.380, 0) Mg2(-0.130, -0.130, 0) Mg3(-0.370, 0.120, 0.5) O1(-0.120, 0.372, 0.266) O2(0.370, -0.122, 0.266) O3(-0.122, 0.120, 0.016) O4(0.372, -0.370, 0.016) H1(-0.126, -0.477, 0.404) H2(0.381, 0.227, 0.404) H3(0.227, 0.129, 0.154) H4(-0.477, -0.378, 0.154)

Optimized crystal structures of various brucite phases, from ground-state DFT-PBE calculations. First row gives experimental results for the $P\bar{3}m1$ phase at $P = 1$ atm from powder neutron diffraction (12).

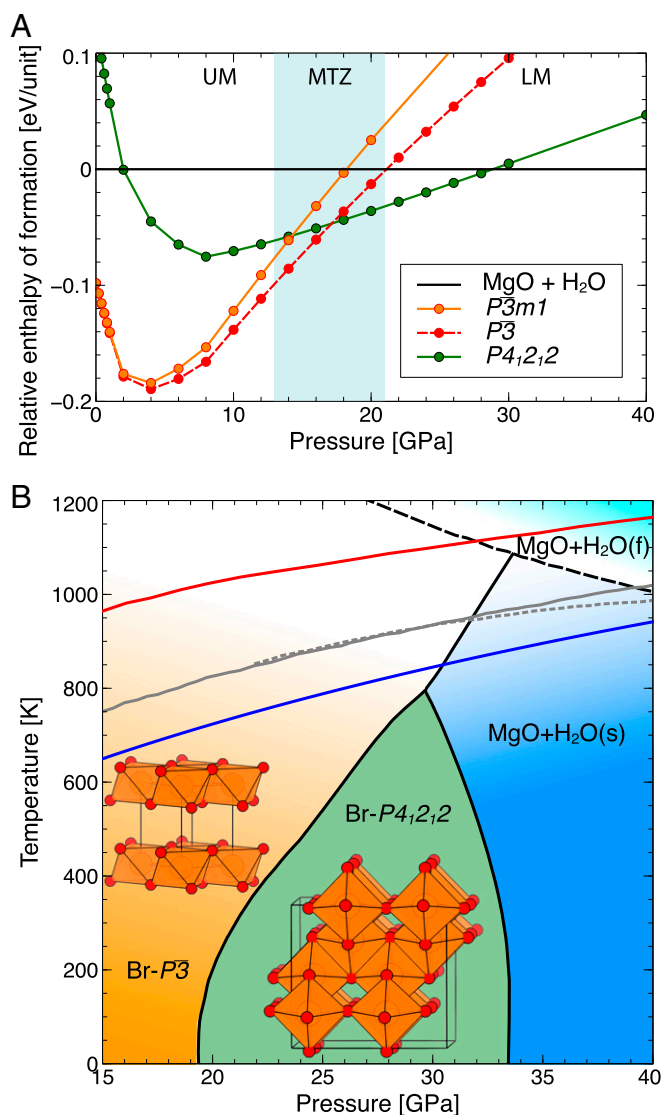


Fig. 2. Thermodynamic phase diagram of $\text{Mg}(\text{OH})_2$. (A) Ground-state enthalpies of formation of various $\text{Mg}(\text{OH})_2$ phases, relative to decomposition into MgO and ice-VIII. The light-blue band represents the pressures relevant for the mantle transition zone (MTZ), upper- (UM) and lower (LM) mantle. (B) Computationally derived thermodynamic phase diagram for $\text{Mg}(\text{OH})_2$. Also shown are a parameterized high-temperature decomposition curve (dashed black line) (24), cold and typical slab geotherms (blue and red solid lines) (23, 32), and ice melting lines (solid and dotted gray lines) (33, 34).

boundary for mantle slab geotherms (we extrapolated the data from ref. 32 beyond 20 GPa in a power expansion). We did not consider nuclear quantum effects in the construction of the phase diagram. Those can play an important role in aqueous systems (35) and might affect the phase transition pressures in the low-temperature region in particular if the protons' chemical environment differs significantly across the respective phases. There is some indication (see below) that the hydrogen bonds in tetragonal $\text{Mg}(\text{OH})_2$ are stronger than in brucite.

The tetragonal $\text{Mg}(\text{OH})_2$ phase ($P4_12_12$) is very different from the low-pressure layered phase (Fig. 1; see Table 1 for structural data). The high-pressure phase forms a 3D network of edge-sharing MgO_6 octahedral units. In fact, the phase (when ignoring protons) is isostructural with the anatase- TiO_2 crystal structure, but with MgO_6 octahedral units that are less distorted compared with the TiO_6 octahedral units in anatase (Fig. 2, Lower, Inset).

The protons are located in channels in between the MgO_6 polyhedral units. Alternatively, the crystal structure can be characterized by zigzag hydrogen-bonded $\text{O}-\text{H}\cdots\text{O}-\text{H}$ chains running along the a and b directions, and which are lying in the bc and ac planes, respectively. In the ground state, the $\text{O}-\text{H}$ vectors order antiferroelectrically (Fig. 1), but it is very likely that proton disorder sets in at finite temperatures. The major structural differences compared with the low-pressure phase of brucite suggest that there are significant kinetic barriers to transform from the layered phase into the tetragonal phase (just as for the decomposition), which would explain why the transition has not been observed in room-temperature experiments to pressures well into the predicted pressure stability region of the tetragonal phase.

The pressure-volume relation for brucite ($P3$) can be described by a Birch-Murnaghan equation of state with equilibrium volume $V_0^{P3} = 41.68 (\pm 0.09) \text{ \AA}^3$, bulk modulus $K_0^{P3} = 43.4 (\pm 1.1) \text{ GPa}$, and its pressure derivative $K_0'^{P3} = 5.39 (\pm 0.10)$. In contrast to brucite, the 3D network of MgO_6 polyhedra in tetragonal $\text{Mg}(\text{OH})_2$ allows for a substantially more compact packing with $V_0^{P4_12_12} = 38.06 (\pm 0.07) \text{ \AA}^3$, $K_0^{P4_12_12} = 67.3 (\pm 1.6) \text{ GPa}$, and $K_0'^{P4_12_12} = 4.91 (\pm 0.09)$. At 1 bar the tetragonal phase is 8.67% smaller than brucite, and stiffer by $\sim 55\%$. At 20 GPa, where tetragonal $\text{Mg}(\text{OH})_2$ has the lower enthalpy, it is 3.8% more compact than the brucite ($P3$) phase.

Although the tetragonal phase is denser compared with the brucite phase, at 1 bar the full elastic stiffness tensor reveals significant anisotropy. The principal stiffness components are related as $c_{11}^{P4_12_12} \sim 1.5 \times c_{33}^{P4_12_12}$, $c_{12}^{P4_12_12} \geq c_{13}^{P4_12_12}$, and the shear stiffness components are related as $c_{44}^{P4_12_12} \geq c_{66}^{P4_12_12}$ (Fig. 3). At zero pressure (i.e., 1 bar), the Hill-averaged bulk ($K_{\text{Hill}}^{P4_12_12}$) and shear ($G_{\text{Hill}}^{P4_12_12}$) moduli are 69.5 and 55.4 GPa, respectively, for the tetragonal $\text{Mg}(\text{OH})_2$ phase. This is significantly stiffer than the bulk (K_{Hill}^{P3}) and shear (G_{Hill}^{P3}) moduli for the trigonal phase, 46.7 and 36.4 GPa, respectively (36). The compressional (V_P) and shear (V_S) sound velocities for the tetragonal phase are also faster compared with the trigonal phase (Fig. 3).

In addition to changes in the velocities, brucite and tetragonal $\text{Mg}(\text{OH})_2$ have quite distinct elastic anisotropy. At low pressures (~ 0 GPa), the brucite phase has significant V_P - and V_S -elastic anisotropy, 57 and 46%, respectively. In comparison, tetragonal $\text{Mg}(\text{OH})_2$ has modest V_P - and V_S -elastic anisotropies of 20% and 13%, respectively (Fig. 4). At higher pressures, as the layered nature of the compound becomes less pronounced, the elastic anisotropy in brucite reduces, with the V_P elastic anisotropy decreasing at a faster rate than the V_S anisotropy. In other words, the pressure derivative of C_{33} is greater than the pressure derivative of C_{11} , i.e., $dC_{11}/dP < dC_{33}/dP$. For tetragonal $\text{Mg}(\text{OH})_2$ at higher pressure, the V_P elastic anisotropy reduces and remains fairly constant over the pressure range that corresponds to the entire upper mantle, transition zone, and lower mantle. The S-wave elastic anisotropy for tetragonal $\text{Mg}(\text{OH})_2$, on the other hand, increases almost linearly upon compression beyond 5 GPa. In this phase, the pressure derivative of C_{11} is slightly greater than the pressure derivative of C_{33} , i.e., $dC_{11}/dP > dC_{33}/dP$. In addition, even though the octahedral network in the tetragonal phase is 3D, hydrogen bonds that additionally constrain the elastic response are essentially confined along the a and b directions. The predicted anisotropies could provide another diagnostic test for the presence of tetragonal $\text{Mg}(\text{OH})_2$ in the deep mantle, but need to be accompanied by an understanding of the rheological parameters including the slip systems, the combined elastic anisotropy and lattice preferred orientation to relate these calculated numbers to the seismic anisotropy observed in the deep mantle and in subduction zone settings.

Tetragonal $\text{Mg}(\text{OH})_2$ is an ionic compound. A topological analysis of the electron density based on Bader's quantum theory of atoms in molecules (37) suggests partial atomic charges of +1.61/−0.80 electrons for Mg^{2+} and OH^- ions, respectively, at 20 GPa. This is very similar to the partial charges of +1.65/−0.82 electrons in

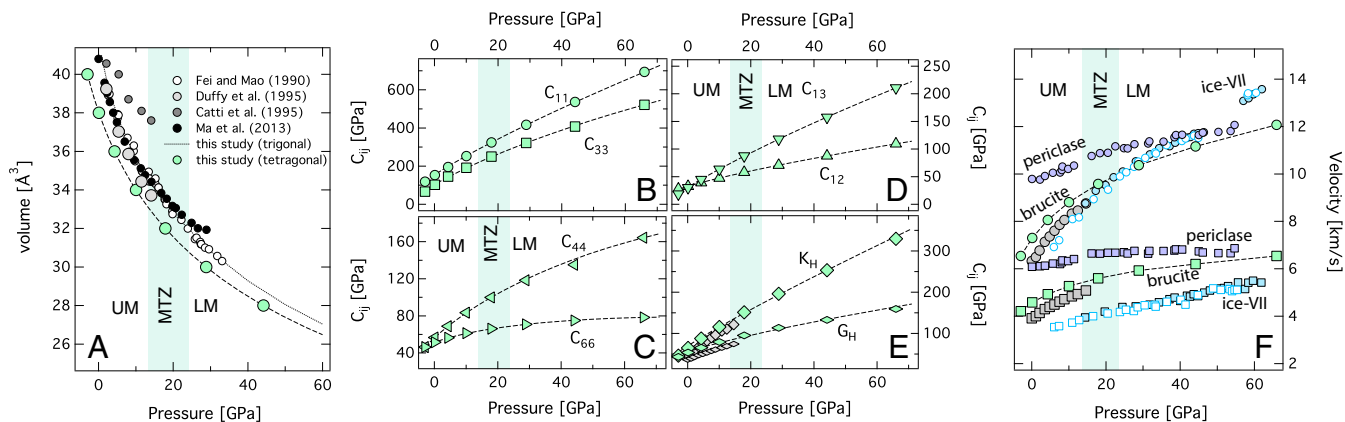


Fig. 3. Equation of state, elasticity, and sound velocity of $\text{Mg}(\text{OH})_2$. (A) Plot of volume as a function of pressure. Green symbols and thin dotted line refer to the $P4_12_12$ - and $P\bar{3}$ - $\text{Mg}(\text{OH})_2$ phases, respectively. The dashed line gives the finite strain fit to the $P4_12_12$ phase. Experimental results are shown in filled light gray (single-crystal X-ray diffraction); dark gray (powder neutron diffraction); black and white symbols (synchrotron-based powder X-ray diffraction), from refs. 12, 14, 24, 25. (B–D) The full elastic stiffness tensor components, and (E) Hill-averaged bulk (K_H) and shear (G_H) moduli for tetragonal $\text{Mg}(\text{OH})_2$ as function of pressure. (F) Calculated compressional/shear sound-wave velocities (circles/squares) for tetragonal $\text{Mg}(\text{OH})_2$ (light-green symbol). Gray symbols refer to the experimentally determined sound velocity of brucite (36). Experimental data are given for the decomposition products periclase (MgO) (filled blue symbols) (63) and ice-VII (filled light-blue symbols): compression; white symbols: decompression) (50).

brucite ($P\bar{3}$) at the same pressure. The high-pressure phase does, however, feature stronger hydrogen bonds, as the structural rearrangement in $P4_12_12$ results in much shorter hydrogen-bonded separations: at 20 GPa, $d_{\text{O}\dots\text{O}}$ is 1.62 Å, compared with 1.87 Å in the $P\bar{3}$ phase. As a consequence, the covalent O–H bonds are somewhat extended and arguably weakened in the $P4_12_12$ phase. At 20 GPa, the hydroxyl bond length d_{OH} is ~ 1.01 Å for $P4_12_12$ compared with 0.98 Å in the $P\bar{3}$ phase.

The changes in the hydrogen bonding lead to significant differences in the vibrational properties, which should make detection of the high-pressure phase quite straightforward. In Fig. 5, we show calculated O–H stretch modes of the different phases as a function of $d_{\text{O}\dots\text{O}}$ distance, compared with an empirical functional relation established from experimental spectroscopic data on hydrous minerals (38). Calculated frequencies for the $P\bar{3}m1$ and $P\bar{3}$ phases, as has been noted before (39, 40), give good

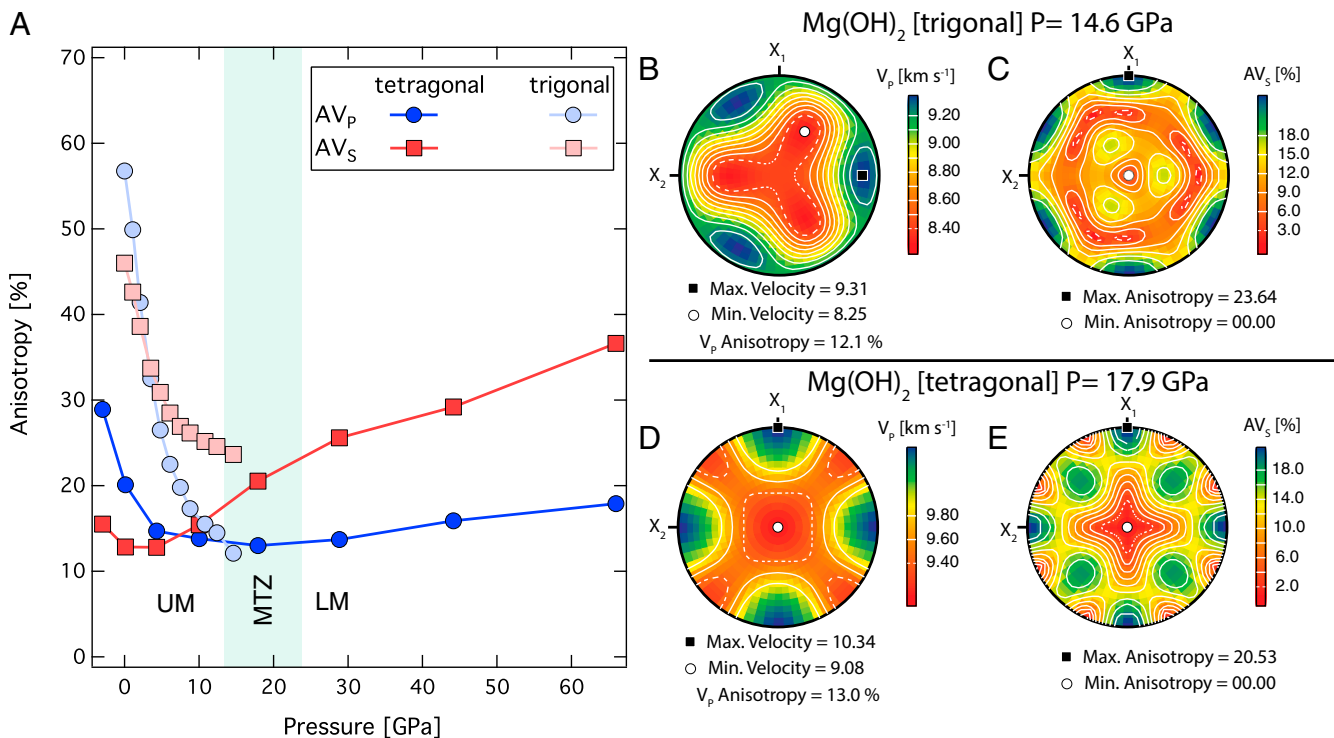


Fig. 4. Elastic anisotropy of $\text{Mg}(\text{OH})_2$. (A) Plot of P-wave anisotropy (AV_p , blue) and S-wave anisotropy (AV_s , red) as a function of pressure. The light and dark color symbols correspond to trigonal (brucite) and tetragonal $\text{Mg}(\text{OH})_2$, respectively. (B and D) show the stereographic projection of the P-wave velocity variations across the orthogonal directions for both phases. (C and E) show the stereographic projection of the S-wave anisotropy variations across the orthogonal directions for both phases. The orthogonal coordinates X_1 and X_2 are shown in the stereographic projections. The X_3 axis is perpendicular to both X_1 and X_2 axes. The color shadings are in inverse logarithmic scales. The minimum and maximum velocity directions for tetragonal $\text{Mg}(\text{OH})_2$ along the X_3 and X_1 axes coincide with the extremal C_{33} and C_{11} elastic constants, respectively.

accounts of existing experimental data: in $P\bar{3}m1$, the O–H stretch frequency is almost independent of pressure (i.e., independent of the $d_{O\cdots O}$ distance), whereas the $P\bar{3}$ phase reproduces the softening of the O–H stretch modes due to increased hydrogen bonding under pressure. Note that in Fig. 5 we have shifted the axes of computed against experimental frequencies by 100 cm^{-1} to account for the anharmonicity of the O–H stretch (40). The hydrogen bonding is much more pronounced in the tetragonal phase, and as a consequence its O–H stretch frequencies are significantly redshifted, about 400 cm^{-1} relative to the $P\bar{3}$ phase, and also show a more rapid decrease upon compression. At 20 GPa, where tetragonal $\text{Mg}(\text{OH})_2$ should become stable at low temperatures, $\nu_{\text{OH}} = 2,840 \dots 3,140\text{ cm}^{-1}$ in our calculations, whereas the $P\bar{3}$ phase at the same pressure has $\nu_{\text{OH}} = 3,540 \dots 3,670\text{ cm}^{-1}$. The stretch mode frequencies of tetragonal $\text{Mg}(\text{OH})_2$ at low pressures (large $d_{O\cdots O}$ distance) are significantly lower than the correlation from ref. 38 suggests; however, under compression, in the region of its stability, the calculated modes are in quite good agreement with the empirical relation.

In Fig. 5 (*Inset*), we visualize the relation between $d_{O\cdots O}$ and the covalent bond length d_{OH} for tetragonal $\text{Mg}(\text{OH})_2$. We find that hydrogen bond symmetrization occurs around 100 GPa, which is much higher than in the hydrous phases $\delta\text{-AlOOH}$, phase D [$\text{MgSi}_2\text{O}_4(\text{OH})_2$], and phase H (MgSiO_4H_2), where symmetrization is seen around 30–40 GPa (41–43). Whereas nuclear quantum effects can significantly reduce the symmetrization pressure (in ice, for instance, from ~ 100 down to 65 GPa) (44, 45), we do not expect tetragonal $\text{Mg}(\text{OH})_2$ to feature symmetric hydrogen bonds in its region of thermodynamic stability.

Discussion

Our first-principles calculations suggest that upon compression, the hydrous mineral brucite will transform to a dense phase with a 3D network structure, before eventual decomposition into periclase (MgO) and ice-VII (H_2O). The phase is found to be stable at pressure–temperature conditions that correspond to cold subducting slabs in the Earth’s mantle transition zone and lower mantle. It is possible that configurational disorder, on the proton

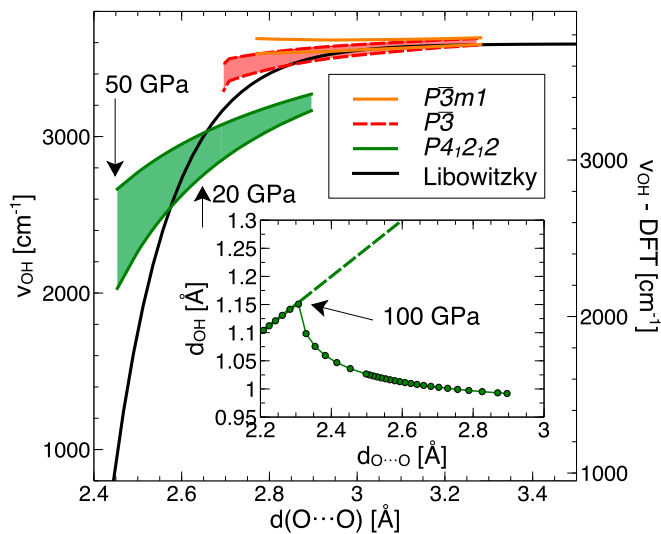


Fig. 5. Hydrogen bonding in $\text{Mg}(\text{OH})_2$. Calculated O–H stretch frequencies in the low- and high-pressure phases of $\text{Mg}(\text{OH})_2$, as function of hydrogen-bonded distance $d_{O\cdots O}$. Also shown is a correlation curve based on ambient pressure data for various hydrous phases including minerals (38). The red and green shaded region indicates the complete range of modes for the $P\bar{3}$ and $P4_12_12$ phases, respectively. (*Inset*) Plot of d_{OH} vs. $d_{O\cdots O}$ for tetragonal $\text{Mg}(\text{OH})_2$. The hydrogen bond symmetrization ($d_{\text{OH}} = 1/2 d_{O\cdots O}$) occurs at 100 GPa. Note that calculated frequencies are red-shifted by 100 cm^{-1} with respect to the functional fit.

and/or cation sites [for instance by forming $(\text{Mg}, \text{Fe}, \text{Ca})(\text{OH})_2$], stabilizes tetragonal $\text{Mg}(\text{OH})_2$ at higher temperatures. It is also known that brucite and gibbsite [$\text{Al}(\text{OH})_3$] have similar structures and can form mixed layered double hydroxides (46). A high-pressure phase of gibbsite exists, $\delta\text{-Al}(\text{OH})_3$, comprising a 3D structure of corner-sharing AlO_6 octahedra (47, 48). It is thus conceivable that elevated temperatures stabilize a high-pressure solid solution $(\text{Mg}_{1-x}\text{Al}_x)(\text{OH})_{2+x}$ with a more complex 3D network structure, or a tetragonal structure $[(\text{Mg}_{1-x}\text{Al}_x)(\text{OH})_2]^{x+}$ balanced by an appropriate anion presence, e.g., $(\text{A}^-)_x$. Any incorporation of Al^{3+} in high-pressure $\text{Mg}(\text{OH})_2$ is also likely to enhance its thermal stability: Recent studies on aluminum incorporation in phase-D [$\text{Al}_2\text{SiO}_4(\text{OH})_2$] have shown that it enhances its thermal stability significantly (49). Thus, dense tetragonal $\text{Mg}(\text{OH})_2$ together with other dense hydrous phases could act as an efficient carrier of water in cold subduction slabs. The emergence of this more stable compound at the edge of the $\text{MgO}\text{-H}_2\text{O}\text{-SiO}_2$ phase diagram has implications for the relative stability of more complex MSH phases at similar conditions.

We find that the tetragonal $\text{Mg}(\text{OH})_2$ phase follows conventional high-pressure paradigms in that a layered structure is replaced by a more compact 3D structure upon compression—the unexpected result is that this transition occurs (consistently in our calculations) before the decomposition reaction becomes favorable. Besides being more compact, this phase is significantly stiffer than known brucite, which could lead to characteristic seismic signatures. A transition from the trigonal to the tetragonal phase is likely to be marked by an enhancement in both P- and S-wave velocity. Under further compression, as tetragonal $\text{Mg}(\text{OH})_2$ decomposes to a mixture of MgO and H_2O (ice) around 30 GPa, the P-wave velocity is likely to enhance whereas the S-wave velocity is likely to decrease, owing to significantly lower S-wave velocity for ice-VII at high pressure (50). In combination (Fig. 3), both effects provide for a distinct test of the presence of the denser tetragonal phase of $\text{Mg}(\text{OH})_2$ in cold subduction zones. However, it is very likely that the magnitude of the velocity discontinuity owing to the dissociation of tetragonal $\text{Mg}(\text{OH})_2$ might be smeared by the presence of additional chemical components, which in turn is likely to stabilize other hydrous phases.

Tetragonal $\text{Mg}(\text{OH})_2$ also features significantly stronger hydrogen bonds and weaker covalently bound hydroxyl groups compared with the trigonal phase, which we predict to lead to a very different spectroscopic signature, and could also result in qualitatively different proton diffusion behavior at elevated temperatures. The weaker covalent O–H bonds are likely to reduce the temperature where proton diffusivity sets in, and further stabilize the tetragonal phase over the trigonal phase at high temperature. On the other hand, due to the anatase-like structure of tetragonal $\text{Mg}(\text{OH})_2$, protons can diffuse along 1D channels of the MgO_6 polyhedral network, whereas in the low-pressure trigonal phase they can diffuse in 2D wells between MgO_6 sheets. This is likely to significantly influence proton-induced electrical conductivity of the high-pressure phase of $\text{Mg}(\text{OH})_2$. At the base of the mantle transition zone, several thermodynamic processes occur that might induce partial melting, as documented in seismological observations (2, 51). First, the dissociation of high-pressure $\text{Mg}(\text{OH})_2$ and other dense hydrous magnesium silicates such as phase-H (23) and phase-D (52) release water, which is likely to reduce the solidus of the lower mantle and lead to partial melting. In addition, it is known that there is a drastic reduction in the water storage capacity between the mantle transition zone minerals and lower mantle minerals, which also helps in reduction of the lower mantle solidus and thus helps in initiating partial melting in the lower mantle. Both processes may occur simultaneously and need to be understood to gain detailed insight into the deep Earth water budget.

Methods

We performed density-functional theory (DFT) calculations in conjunction with the projector augmented wave method and plane-wave basis sets as implemented in

the Vienna Ab initio Simulation Package (53–55). Plane-wave cutoffs of $E_c = 800$ eV and k-point sampling densities of $20/\text{\AA}^{-1}$ were found to give sufficiently converged energies and forces. Electronic exchange–correlation energies are approximated with the PBE generalized gradient functional (56), and geometries were optimized until remaining forces on the atoms were smaller than 1 meV/\AA .

Crystal structure predictions were then run at 20, 50, and 100 GPa, with two and four formula units per unit cell, and using approaches based on evolutionary algorithms and the particle swarm optimization method as implemented in the XtalOpt and CALYPSO packages (57, 58). Around 600 structures were optimized in each search run. Phonon dispersions and densities of state were obtained with the finite displacement method using the PHON program and appropriate supercells of the relevant structures, with central difference displacements of $\pm 0.02 \text{ \AA}$ and up to 640 atoms (59).

We applied $\pm 1\%$ strains to accurately determine the stresses in the limit of small strain (60). The elastic constants c_{ij} were obtained from the stress–strain relation,

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