$FeSiO_4H_2$ stabilized at subducting slab conditions: A geologically viable water carrier into the Earth's lower mantle

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Hydrous minerals hold the key to unlocking the enduring mystery of the water cycle deep inside the Earth. Tremendous efforts have been devoted to identifying geologically viable minerals meeting stringent pressure-temperature-density stability requirements for descent into deep Earth, and such pursuits remain active. Here, we identify two hydrous iron silicates, α- and β-$FeSiO_4H_2$, formed by a reaction of Earth-abundant $FeSiO_3$ and H_2O and stabilized at the pressure-temperature conditions in cold subducting slabs. These phases have a sufficiently high density for a stable descent into the Earth's lower mantle, and then decompose to release water after reaching equilibrium with the mantle geotherm. Moreover, $Mg(Fe)SiO_4H_2$ solutions are found to be more stable than the pure substances and can serve as effective carriers to transport substantial amounts of water to lower-mantle regions via the cold subduction zones. These findings establish a viable and robust material basis for the deep-Earth water cycle, with major implications for elucidation of many prominent geological processes.

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I. INTRODUCTION

Water (H_2O) has tremendous influence on the physical and chemical properties of the Earth's constituent compositions [1–3]. The knowledge about the transport of water into the Earth's interior is crucial to understanding its evolution and dynamics. It was estimated that a large amount of water ($\sim 10^{11}$ kg/yr) is continuously transported into the Earth's interior through subduction zones, while only a fraction of the water degasses to the Earth's surface [4,5]. This imbalance indicates that a large amount of water is delivered and stored in the Earth's interior by deep, global water circulation [6–11]. The transition zone is known to be a major water reservoir [12,13]. There is also evidence of significant amounts of water stored in the lower mantle; for example, the phenomenon of partial melting that offers a reasonable interpretation of the observed low-velocity regions near the top of the lower mantle and at the core-mantle boundary can occur only in the presence of abundant water [14].

It is widely accepted that water is carried into the Earth's interior by hydrous minerals in the uppermost of the descending cold plate [15,16]. Extensive past studies focused on various dense hydrous magnesium silicates, such as phase A ($Mg_7Si_2O_{14}H_6$), phase E ($Mg_2SiO_6H_4$), superhydrous phase B ($Mg_{10}Si_3O_{18}H_4$), phase D ($MgSi_2O_6H_2$), and phase H ($MgSiO_4H_2$) [17–27], as potential deep-Earth water carriers [28]. However, these dense hydrous magnesium silicates are not fully compatible with the stability requirements in the geologically relevant environments, as some dissociate into an assemblage of nominally anhydrous phases plus water at the lower-mantle pressure and temperature conditions (<1500 km) [16], while all of them possess lower density compared to the preliminary reference Earth model (PREM) data. When these low-density hydrous minerals are located at the uppermost of the subducting slab, one possible scenario might arise, wherein low-density hydrous minerals may undergo upward transportation through geological activities, encompassing diapirs [29–32]. As a result, certain portions of the low-density hydrous minerals have the potential to be recycled to the overriding plate instead of being further transported into the deep interior of the Earth. Recently, several hydroxide phases [e.g., δ-AlOOH and $Ca(OH)_2$] and their solid solutions with hydrous silicates were found stable in a wider pressure-temperature stability range [27,33–39], and these hydrous minerals were proposed as potential carriers to transport water into the lower-mantle depths. However, challenges remain in finding more minerals with high gravitational stability and Earth abundance that have a major impact on water transport into the deep lower mantle [40]. Therefore, finding geologically viable carriers for deep water circulation remains an outstanding problem that requires new insights and further exploration from materials physics perspectives.

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Bridgmanite (Mg, Fe)SiO_3 is considered the most abundant mineral in Earth's lower mantle, and it was thought to have very low water storage capacities [41,42]. Previous studies revealed that the presence of Fe, which is an increasingly more abundant element at greater depths, may significantly change the stability of silicates and their water solubility [43–47]. An important issue, therefore, is whether $FeSiO_3$ can react with water to form hydrous phases at relevant pressure and temperature conditions. In this paper, we address this issue by evaluating the stability of H_2O-saturated $FeSiO_3$ under pressure, using an advanced structure prediction method in conjunction with first-principles calculations. Our search found two Fe-bearing hydrous silicate phases that are stable at a wide range of pressures (18–61 GPa) and temperatures (<1450 K). Moreover, these hydrous Fe silicates have a consistently notable higher density compared to the PREM data, giving them superior gravitational stability during a descent into the lower-mantle depths. The stability at the pressure-temperature-density conditions of the subducting slabs makes $FeSiO_4H_2$ a geologically viable carrier for transporting significant amounts of water into the Earth's deep interior.

II. COMPUTATIONAL DETAILS

To identify stable $FeSiO_4H_2$ phases, we employed an advanced structure search method and its same name code CALYPSO [48–51], which has been successfully employed in predicting the crystal structures of a variety of multiple-component minerals [34,36,52]. We carried out variable-cell calculations at 20, 50, and 100 GPa with one to four formula units per simulated cell, where 60% lowest enthalpy structures were retained to produce the next-generation structures by a particle swarm optimization algorithm and the remaining 40% structures were randomly generated under the symmetry constraint. Our *ab initio* calculations were performed in the framework of density-functional theory within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [53], as implemented in the VASP code [54]. The all-electron projector augmented-wave (PAW) method [55] was adopted with $3p^63d^74s^1$, $3s^23p^2$, $2s^22p^4$, and $1s^1$ treated as valence electrons for Fe, Si, O, and H atoms, respectively. The GGA+U approach [56] was used to describe the correlation effects among the localized Fe $3d$ electrons, adopting the recently proposed values for the on-site Coulomb interaction $U = 5.0$ eV and Hund's coupling $J = 0.8$ eV [39,57]. The plane-wave basis set cutoff energy of 1000 eV and Monkhorst-Pack Brillouin zone sampling grid of $2\pi \times 0.03$ Å^{-1} were used to ensure an enthalpy convergence of better than 1 meV/atom. To establish the pressure-temperature phase diagram, we calculated the Gibbs free energy in the framework of a quasiharmonic approximation as implemented in the PHONOPY code [58]. We simulated the Gibbs free energy of liquid water using the thermodynamic properties and equations of states [see Supplemental Material (SM) [59]].

III. RESULTS AND DISCUSSION

Our structure search yielded two Fe-based hydrous silicate phases, α- and β-$FeSiO_4H_2$ (see Table S1 for detailed structural information [59]). The α-$FeSiO_4H_2$ is in an antiferromagnetic ordering (Fig. S1) with the space group of $P2_1/c$. The crystal lattice parameters are $a = 5.12$ Å, $b = 4.69$ Å, $c = 9.36$ Å, $\alpha = \gamma = 90^\circ$, and $\beta = 96.9^\circ$ at 20 GPa. This structure is similar to that of δ-AlOOH, where Al is replaced by Fe and Si atoms, which are octahedrally coordinated with six O atoms [Fig. 1(a)]. The SiO_6 and FeO_6 octahedrons are connected by edge or vertex sharing, and H atoms occupy SiO_6 and FeO_6 octahedral interstices and bond with O atoms to form OH dipoles in the crystal lattice. The β-$FeSiO_4H_2$ phase also adopts an antiferromagnetic ordering with the same space group, and its crystal lattice parameters are $a = 4.77$ Å, $b = 9.13$ Å, $c = 4.67$ Å, $\alpha = \gamma = 90^\circ$, and $\beta = 85.1^\circ$ at 40 GPa. While β-$FeSiO_4H_2$ retains the main structural features of α-$FeSiO_4H_2$ [Fig. 1(b)], the octahedrons formed by SiO_6 and FeO_6 in β-$FeSiO_4H_2$ are only connected by vertex sharing, leading to denser packing. These structures of $FeSiO_4H_2$ do not contain symmetric hydrogen bonds, in contrast to many hydrous minerals stable at lower-mantle pressure conditions (e.g., $MgSiO_4H_2$, FeOOH, and AlOOH), which all contain symmetric hydrogen bonds.

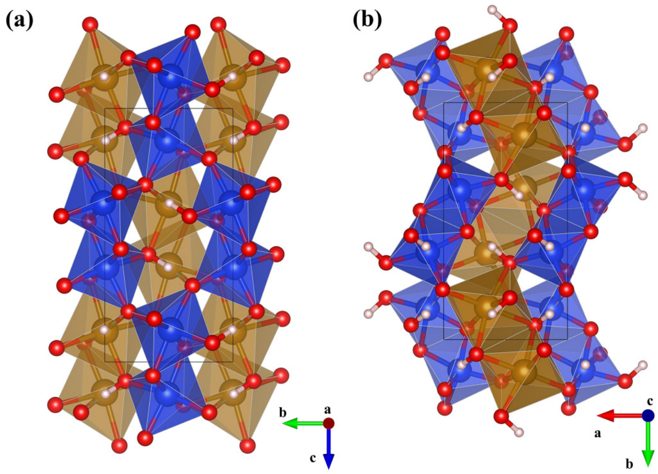

FIG. 1. The crystal structure of (a) α-$FeSiO_4H_2$ and (b) β-$FeSiO_4H_2$. The Fe, Si, O, and H atoms are represented by brown, blue, red, and pink spheres, respectively.

To evaluate the stability of $FeSiO_4H_2$, we constructed a four-component convex hull, which takes into account all known stable compounds formed by Fe, Si, O, and H elements. The convex hull results (Figs. S2 and S3) show that $FeSiO_4H_2$ remains stable when many decomposing reaction paths are taken into account. We also considered various related minerals in assessing the stability of $FeSiO_4H_2$ with respect to decomposition at high pressures [Figs. 2(a) and S4]. In the current stability assessment, we considered only the minerals known to be major components in the Earth, including Fe_2O_3, FeO, SiO_2, $FeSiO_3$, Fe_2SiO_4, and H_2O. Our calculations show [Fig. 2(a)] that α-$FeSiO_4H_2$ becomes energetically more favorable above 18 GPa, then transforms at 35 GPa into β-$FeSiO_4H_2$, which remains stable up to ∼61 GPa, before decomposing to $FeSiO_3$ and H_2O. Furthermore, calculated phonon spectra show no imaginary modes in the pressure range of 18–61 GPa (Fig. S6), confirming the dynamic stability of $FeSiO_4H_2$ in the entire pressure range where it is energetically stable.

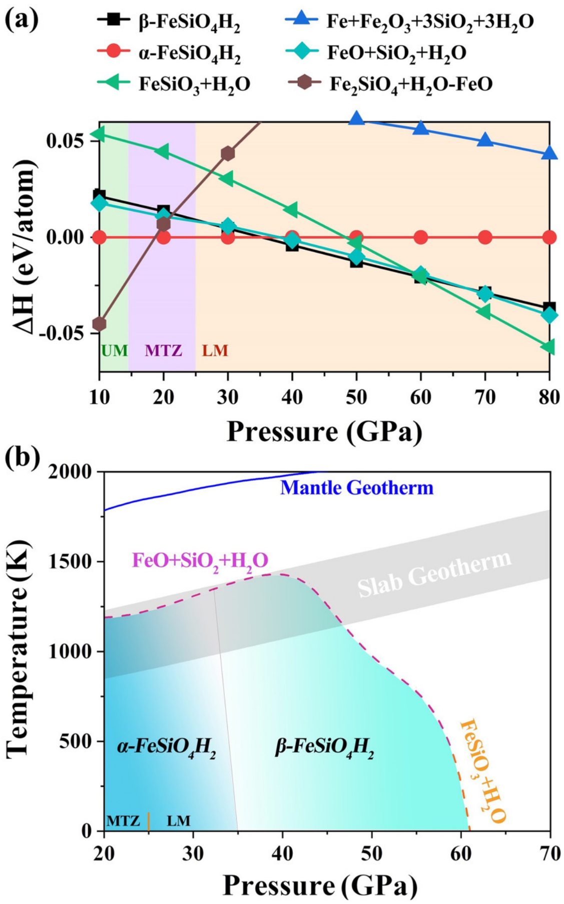

FIG. 2. (a) Calculated enthalpy as a function of pressure of β-$FeSiO_4H_2$, Fe + Fe_2O_3 + 3SiO_2 + 3H_2O, FeO + SiO_2 + H_2O, $FeSiO_3$ + H_2O, and Fe_2SiO_4 + H_2O-FeO measured relative to α-$FeSiO_4H_2$. Negative relative enthalpy indicates that $FeSiO_4H_2$ is stable in the pressure ranges of 18–61 GPa, which spans the pressures in the upper mantle (UM), mantle transition zone (MTZ), and lower mantle (LM), as indicated by the distinct color-shaded zones. (b) The pressure-temperature phase diagram of $FeSiO_4H_2$. The boundary between α- and β-$FeSiO_4H_2$ phases is shown by the gray solid line. Purple and orange dashed lines represent the dissociation boundary where $FeSiO_4H_2$ decomposes into FeO + SiO_2 + H_2O and $FeSiO_3$ + H_2O, respectively. The gray zone represents the geothermal conditions of the subducting slab, while the blue line indicates the geothermal conditions of the mantle. The pressure boundary of the mantle transition zone (MTZ) and the lower mantle (LM) is about 25 GPa, as indicated at the bottom of the panel.

Dense hydrous silicates are known to be thermodynamically stable at pressure-temperature conditions relevant to the subducting slabs, which are lower compared to those along the normal mantle geotherm. To examine the stability fields of $FeSiO_4H_2$, we calculated its Gibbs free energy, especially along the following two possible routes for the dissociation of $FeSiO_4H_2$ involving several minerals known to be among the most abundant in the Earth's mantle and H_2O as reactants:

$$FeSiO_4H_2 = FeSiO_3 + H_2O, \tag{1}$$

$$FeSiO_4H_2 = FeO + SiO_2 + H_2O. \tag{2}$$

Water turns into a liquid phase at elevated temperatures, so we simulated the Gibbs free energy of liquid water using the thermodynamic properties and equations of states from previous work [59]. Results in Fig. 2(b) show that α-$FeSiO_4H_2$ is stabilized up to $\sim$35 GPa at 0 K, and a thermal stability of α-$FeSiO_4H_2$ is achieved at 20, 25, 30, and 32 GPa around 1190, 1230, 1310, and 1350 K, respectively, indicating a positive Clapeyron slope. The threshold pressure for the phase transition from α- to β-$FeSiO_4H_2$ decreases as the temperature rises. Meanwhile, the β-$FeSiO_4H_2$ phase spans a wider pressure-temperature stability field, from 32 to 61 GPa and up to 1450 K. The threshold temperature for the thermal stability of the $FeSiO_4H_2$ phases first increases with rising pressure, then decreases steeply when pressure exceeds 40 GPa, which is similar to the behavior of phase H $MgSiO_4H_2$ under pressure [24–26].

To further assess the structural stability of the hydrous Fe silicates, we performed *ab initio* molecular dynamics simulations to evaluate the mean-square displacements (MSDs) (Fig. S7), which indicate that all the atoms in α-$FeSiO_4H_2$ at 20 GPa and 1000 K and β-$FeSiO_4H_2$ at 40 GPa and 1500 K fluctuate within a small range around the equilibrium positions, indicating that these atoms remain near their lattice sites. These MSD results offer compelling evidence for the structural stability of $FeSiO_4H_2$ at pertinent high-pressure high-temperature conditions.

The existence of lower-mantle water reservoirs hinges on the availability of hydrous minerals that can transport water into the lower mantle without premature dehydration. Our calculations show that the $FeSiO_4H_2$ phases are thermodynamically stable at pressures from 18 to 61 GPa and temperatures up to 1450 K. The temperature for the dissociation boundary of $FeSiO_4H_2$ is lower than those of a typical mantle geotherm and, as a result, these hydrous Fe silicates cannot form the basis for long-term water storage in the lower mantle. It is, however, important to note that $FeSiO_4H_2$, which accommodates a much larger amount of water ($\sim$12 wt %) than the water carriers in the transition zone ($\sim$1–3 wt % water in wadsleyite and ringwoodite) [13,64], can serve as an effective, albeit transient, water carrier deep into the lower mantle via the transport of cold subducting slabs.

Thermodynamic stability is a widely considered key requirement for minerals to serve as potential water carriers into the deep Earth. Meanwhile, another equally important but less considered requirement is gravitational stability, having an influence on the depth to which hydrous minerals descend into the deep Earth's interior alongside the subducting slab. In the uppermost of the subducting slab, a portion of hydrous minerals with densities smaller than that of PREM [65] (Fig. 3) have the potential to form diapirs, which may facilitate the return of some subducting materials to the overriding plate [29–32]. In this crucial regard, $FeSiO_4H_2$ has the notable advantage of possessing clearly a higher density compared to that of the PREM, making it superior in gravitational stability for descent into the deep lower-mantle regions.

The subducting slab is composed of ocean sediments, basaltic oceanic crust, and the peridotitic mantle. The composition of the peridotitic mantle is similar to that of the normal mantle, where magnesium silicates are prevalent, while the ocean sediments and basaltic oceanic crust

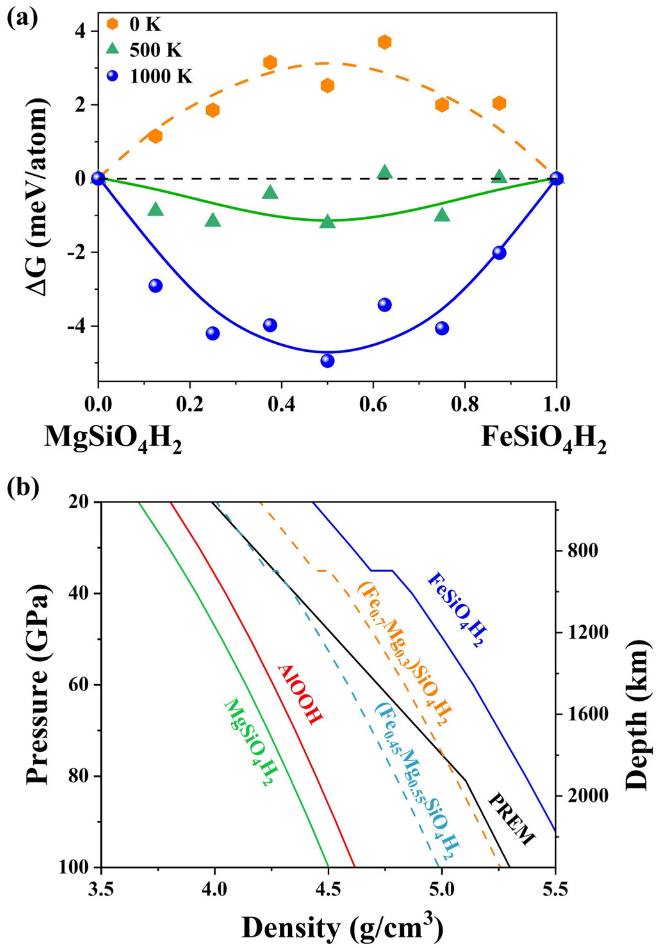

FIG. 3. (a) Gibbs free energies of $Fe_xMg_{1-x}SiO_4H_2$ relative to those of pure substances $MgSiO_4H_2$ and $MgSiO_4H_2$ at 35 GPa and 0, 500, and 1000 K. (b) Density of hydrous minerals AlOOH, $MgSiO_4H_2$, $FeSiO_4H_2$, $(Fe_{0.45}Mg_{0.55})SiO_4H_2$, and $(Fe_{0.7}Mg_{0.3})SiO_4H_2$ compared with that of Earth's mantle according to the preliminary reference Earth model [65].

(uppermost of the subducting slab) possess an Fe-rich environment [66,67]. Additional, previous investigations have provided compelling evidence supporting the presence of Fe-rich minerals in the Mg-rich environment interior of the Earth [68–72]. It is therefore likely that Fe incorporated hydrous mineral $Mg(Fe)SiO_4H_2$ will form in the uppermost layer of the subducting slab. To assess the viability of this scenario, we evaluated the Gibbs free energy for the formation of solid solutions of $MgSiO_4H_2$ and $FeSiO_4H_2$ at pertinent pressure-temperature conditions. It is noted that configurational entropy exerts a dominant influence on the thermodynamic stability in solution systems, while the electronic and vibrational entropies have negligible contributions [73–75]. We calculated the relative Gibbs free energy (ΔG) defined by

$$\Delta G = \Delta H - TS_{\mathrm{conf}}, \tag{3}$$

$$\Delta H = H_{\mathrm{Fe}_x\mathrm{Mg}_{1-x}\mathrm{SiO_4H_2}} - xH_{\mathrm{FeSiO_4H_2}} - (1-x)H_{\mathrm{MgSiO_4H_2}}, \tag{4}$$

where T and S_{conf} in Eq. (3) are the temperature and configurational entropy of the $Fe_xMg_{1-x}SiO_4H_2$ solution, and the three terms on the right-hand side in Eq. (4) are enthalpies of the solution, $MgSiO_4H_2$ and $FeSiO_4H_2$, respectively. The calculated ΔG is negative for the solution in a full range of Fe/Mg ratios [Fig. 3(a)], indicating the stability of $Mg(Fe)SiO_4H_2$ at rising temperatures.

We further evaluated the gravitational stability of $Mg(Fe)SiO_4H_2$ solutions. The results in Fig. 3(b) show that the density of $Fe_{0.45}Mg_{0.55}SiO_4H_2$ becomes comparable to that of PREM at pressures corresponding to the depths of the mantle transition zone and the uppermost zone of the lower mantle; increasing Fe content in $Fe_{0.7}Mg_{0.3}SiO_4H_2$ extends its gravitational stability at depths further inside the lower mantle. These results demonstrate that Fe-rich $Mg(Fe)SiO_4H_2$ solutions, serving as potential carriers in the uppermost of the subducting slab, are likely to restrain their involvement in the formation of diapirs and have a great advantage to transport water into the Earth's deep lower mantle. The Fe-poor $Mg(Fe)SiO_4H_2$ solutions might exist in the peridotitic mantle of a subducting slab and carry water in the deep interior of the Earth for its good thermodynamic stability under subducting slab conditions.

Geological studies suggest a nearly dry bridgmanite-dominated environment in vast lower-mantle regions [41]. This scenario stems from a lack of known hydrous minerals that can be stabilized in the deep lower-mantle geotherm conditions [24–27]. There is, however, experimental evidence showing that Al could enhance the thermal stability of hydrous magnesium silicates [76,77]. For example, it was observed that Al-bearing phase H $MgSiO_4H_2$ remains stable at pressure and temperature conditions corresponding to the depths greater than 2600 km in the subducting slab [76,77]. One may expect that the same phenomenon could occur in Al incorporated $FeSiO_4H_2$ given its structural similarity with hydrous magnesium silicate. An expanded range of thermodynamic stability combined with the gravitational stability makes hydrous Fe silicates geologically viable water carriers into the deep lower mantle.

IV. CONCLUSION

In summary, we have pursued a rational design idea leading to the identification of hydrous iron silicates as geologically viable water carriers into the Earth's lower mantle, based on the consideration of both thermodynamic and gravitational stabilities of the targeted minerals together with their Earth abundance as key criteria. We employed a crystal structure search in conjunction with first-principles energetic calculations to predict two distinct structural phases of $FeSiO_4H_2$ that are stabilized in the pressure range of 18–61 GPa and temperatures up to ~1450 K. The superior gravitational stability and favorable thermodynamic stability make $FeSiO_4H_2$ a promising carrier to transport this hydrous mineral in subducting slabs and then release water deep into the lower mantle. Our study also suggests that a wide range of hydrous Fe/Mg silicates may serve as a viable and robust material basis for the water cycle in the Earth's deep interior, with major implications for understanding the evolution of constituent compositions in deep Earth.

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