Earth and Planetary Science Letters 463 (2017) 171–177

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

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Stability of phase H in the $MgSiO_4H_2$–AlOOH–SiO_2 system

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ARTICLE INFO

Article history:
Received 8 September 2016
Received in revised form 21 January 2017
Accepted 25 January 2017
Available online xxxx
Editor: J. Brodholt

Keywords:
mantle
hydrous minerals
ab-intio calculations

ABSTRACT

The newly described hydrous phase H, $MgSiO_4H_2$, is stable to the pressures and temperatures of the Earth's lower mantle, suggesting that the Earth's lower mantle may participate in the cycling of water. We present the results of *ab initio* calculations on the stability of this phase within the phase H–δAlOOH–SiO_2 system between 20 and 60 GPa, exploring the wide pressure- and temperature stability field of this mineral. We find that hydrogen in phase H is bonded in a single well at all pressures, and only the pure phase results in pressure-induced symmetrization, while the solid solution maintains asymmetric bonding to high pressure. Substitutions on octahedral sites are locally charge-balanced by H. Furthermore, small amounts of Al + H in SiO_2 stabilize the $CaCl_2$-structure of SiO_2 to pressures as low as 20 GPa while phase H and δAlOOH form an ideal mixture at all pressures considered. The resulting structure is stable relative to the anhydrous assemblage of the Earth's lower mantle by 16–19 kJ/mol. In alumina-rich phase H this increases the stability of the mineral by ~800 K relative to the pure substance, making it potentially stable under lower mantle temperatures along typical geotherms.

1. Introduction

The storage and cycling of water in the mantle has a significant control of seismic wavespeeds, material deformation, and melting temperatures. While some regions of the mantle may be able to store in excess of 1 wt% water in nominally anhydrous phases, none of the major minerals of the lower mantle appear to be able to accommodate as much as those of the transition zone (e.g. Panero et al., 2015). Therefore, any significant storage of water in the Earth's lower mantle must happen through minor hydrous phases.

Phase D, $Mg_2SiO_4(OH)_4$ is stable to ~45 GPa and ~1700 K (Frost and Fei, 1998; Shieh et al., 1998), with the potential to carry water into the lower mantle only in extremely cold regions. The aluminous end member of phase D, $Al_2SiO_4(OH)_2$, however, is stable to higher temperatures at the very top of the lower mantle (Pamato et al., 2015), in which the high-temperature stability is possibly due to stabilization from configurational entropy arising from Al–Si disorder. $CaCl_2$-structured δAlOOH is stable for all pressures of the lower mantle (Sano et al., 2008) and potentially stable to average mantle temperatures as well. At ~10 GPa SiO_2 transforms to the rutile-structured tetragonal stishovite ($P4_2/mnm$) characterized by octahedrally-coordinated silica. SiO_2 subsequently transforms to the $CaCl_2$-structure at ~45 GPa (*Pnnm*) via a Landau transition due to a rotation of the octahedra (Andrault et al., 1998). This structural transition enhances the solubility of $Si^{4+} = Al^{3+} + H^+$ defects in silica-rich systems and is likely an additional mechanism for carrying water into the lower mantle in silica-saturated regions (Panero and Stixrude, 2004). However, minerals such as aluminous phase D and minerals on the δAlOOH–SiO_2 join are unlikely to be stable in a mafic, pyrolitic mantle.

The recently predicted and confirmed phase H, $MgSiO_4H_2$ (Tsuchiya, 2013; Ohtani et al., 2014), has a similar structure to δAlOOH ($P2_1nm$ to *Pnnm*) with a monoclinic distortion of the space group $P2/m$ or *Pnnm* (Nishi et al., 2014; Bindi et al., 2014). *Ab initio* structural calculations predict that phase H has alternating chains of edge-sharing Mg-octahedra and Si-octahedra that lie parallel to the *c*-axis. The chains alternate along both *a*- and *b*-axis, sharing corners, and leaving interconnected octahedral void spaces. The H atoms lie in these void spaces, along the shortest diagonal. Each hydrogen atom is bonded to one oxygen atom that is part of three octahedra: two edge sharing Si-octahedra and one corner-linked Mg-octahedron. The hydrogen bonds form with an oxygen atom opposite the bonded one within the octahedral void that is also part of three octahedra: two edge sharing Mg-octahedra and one corner-linked Si-octahedron. As with δAlOOH, pressure induced shortening of the O–O distance along the OH..O bond leads to symmetrization of the hydrogen bonds at 25 GPa. While the end-member composition of phase H has a

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http://dx.doi.org/10.1016/j.epsl.2017.01.033
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limited pressure stability of ~60 GPa, experiments in aluminum-bearing systems, however, reveal that the stability of phase H may be significantly broader (Ohira et al., 2014; Walter et al., 2015; Nishi et al., 2014). As with phase D, increased thermal stability may arise from configurational entropy due to disordering on the octahedral sites. Therefore, the stability of phase H in the lower mantle may be significantly expanded with solid solutions in the $MgSiO_4H_2$–δAlOOH–SiO_2 system.

Therefore, we investigate the effect of composition on the stability of phase H in the $MgSiO_4H_2$–δAlOOH–SiO_2 ternary using ab initio calculations treating each intermediate composition in a statistical sense, considering the multiple configurations of each cation and hydrogen between 20 and 60 GPa.

2. Methods

First-principles calculations were performed using the projector augmented wave method (PAW) (Kresse and Joubert, 1999) of the density functional theory as implemented in the Vienna Ab-initio Simulation Package (VASP) package (Kresse and Furthmüller, 1996; Kresse and Joubert, 1999). We employ the generalized-gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (Perdew et al., 1996) formulation for exchange-correlation part, with a kinetic energy cutoff of 800 eV. End member, defect-free calculations were performed with a 4 × 4 × 4 **k**-points Monkhorst and Pack grid such that the convergence in enthalpy is better than 0.001 eV per formula-unit across the pressure range of the calculations. Or the calculations inside the ternary, with defect structures, we use 2 × 3 × 2 supercell, containing between 72 and 96 atoms. The electronic density is sampled in the reciprocal space on grids of 2 × 2 × 2 **k**-points mesh to achieve better than 0.004 eV convergence in enthalpy.

We choose a grid of compositions spanning the entire SiO_2–δAlOOH–$MgSiO_4H_2$ ternary in steps of 20 mol%; two more points, at 10–90 mol% are added along the δAlOOH–SiO_2 binary at 20 GPa, for a total of 31 compositions at 20 GPa and 29 compositions at 40 and 60 GPa. For each composition the cations are randomly distributed on the octahedral sites. We calculated at least 10 such randomly generated structures at 20, 40, and 60 GPa representing more than 900 configurations. H atoms are also randomly distributed in the structure over all potential OH bonding sites. As there is only a single cation site in SiO_2 or δAlOOH, we do not consider disordering in these end member compositions: a suite of 5 randomly generate hydrogen configurations for δAlOOH all relax to identical structures for all pressures between 20 and 60 GPa. However, as both Mg and Si are in octahedral sites in phase H, we do not assume *a priori* that this structure is fully ordered.

10 configurations of a single composition, $Al_8Mg_6Si_{10}O_{48}H_{20}$ (1/3 δAlOOH–1/2 phase H–1/6 SiO_2-stishovite), were also calculated at 80, 100, 120, 140, and 160 GPa to examine the effects of pressure on the hydrogen bonding. The total number of structural relaxations therefore represents nearly 1000 independent calculations.

Within the phase H–δAlOOH–SiO_2 ternary, we calculate the partition function for each composition and pressure,

$$Z = \sum_i e^{-\beta E_i} \tag{1}$$

where E_i is the energy of configuration i, and β is $(k_B T)^{-1}$. The probability of each state is therefore a function of both the energy of the state as well as the temperature,

$$P_i = \frac{1}{Z} e^{-\beta E_i} \tag{2}$$

The ensemble average energy at that composition is then calculated directly from the partition function,

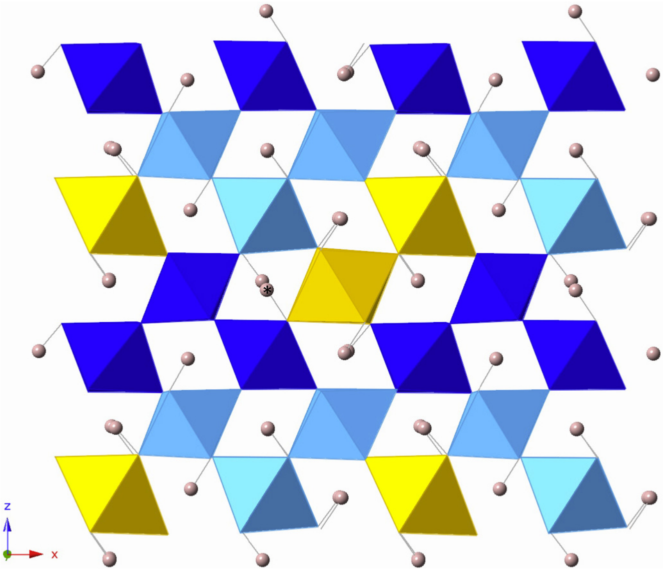

Fig. 1. Relaxed structure of one configuration of $Al_8Mg_6Si_{10}O_{48}H_{20}$ (1/3 δAlOOH–1/2 phase H–1/6 SiO_2-stishovite) at 20 GPa viewed normal to the (101) plane, in which MgO_6 units are yellow, SiO_6 units are dark blue, and AlO_6 units are light blue. H is pink with an average bond length of 1.05 Å and average hydrogen bond length of 1.39 Å, forming linear bonds across the octahedral vacancies in the [101] direction. The relaxed hydrogen positions avoid the bridging O atoms between SiO_6 octahedra. The hydrogen atom marked with an $*$ is the one represented in Fig. 3a. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$\langle E \rangle = \sum_i E_i P_i \tag{3}$$

and lattice constants weighted similarly according to the energy partition function. For two compositions for which we perform 20+ configurations at 20 GPa, selecting 10-configuration subsets from these calculations show that $\langle E \rangle$ varies by less than 2 kJ/mol, which we adopt as the precision of the calculations, and therefore establish that 10 configurations is sufficient to sample a representative portion of the configuration space.

We treat the configurational entropy as a counting of microstates in which each octahedral site is independent and hydrogen atoms are associated with Mg- and Al-octahedra, avoiding the Si octahedra, consistent with the static relaxation of the randomly generated configurations.

We neglect the effects of compositional variations in the vibrational component of the entropy and define and work with the "configurational" Gibbs free energy of mixing,

$$G_{\mathrm{mix}} = \left(\langle E \rangle - \mathrm{TS}\right) - (\alpha G_{\mathrm{A}} + \beta G_{\mathrm{B}} + \gamma G_{\mathrm{C}}) \tag{4}$$

where α, β, and γ are the relative proportions of the end member compositions A, B, and C.

3. Results

3.1. Structural results

Within the phase H–δAlOOH–SiO_2 ternary, we find structural consistency across all relaxed structures, in which randomly generated configurations relax with octahedral coordination for each Mg, Si, and Al cation with H extending between corners of neighboring octahedra with near 180° O–H..O. As expected based on charge considerations, in each configuration with excess silica, the hydrogen relaxes to an oxygen associated with Al- or Mg-octahedra (Fig. 1), avoiding neighboring SiO_6 units.

Along the δAlOOH–SiO_2 binary at 20 GPa, the inclusion of just 16.7% δAlOOH into stishovite ($2Si^{4+} = 2(Al^{3+} + H^+)$) causes an