**LETTER**

**Partition of Al between Phase D and Phase H at high pressure: Results from a simultaneous structure refinement of the two phases coexisting in a unique grain**

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**ABSTRACT**

The crystal structure of the two dense hydrous magnesium silicates Phase D, MgSiH$_2$O$_6$, and Phase H, MgSiH$_2$O$_8$, synthesized at 45 GPa and 1000 °C and coexisting in the same micrometer-sized grain, was investigated by single-crystal X-ray diffraction to study the preferential partition of Al between the two structures. In agreement with the literature, Phase D was found to be trigonal, space group $P3_1/m$, with lattice parameters $a = 4.752(2)$ Å, $c = 4.314(2)$ Å, $V = 84.37(6)$ Å$^3$ ($R_I = 0.020$), and Phase H was found to be orthorhombic, space group $Pnnm$, with lattice parameters $a = 4.730(2)$ Å, $b = 4.324(2)$ Å, $c = 2.843(2)$ Å, $V = 58.15(5)$ Å$^3$ ($R_I = 0.024$). The estimated proportion (vol%) of the two phases from the refinement is 27.2$\_\text{Phase D} - 73$ Phase H. The analysis of the geometric details of the two structures shows that Phase D hosts almost all the Al available, whereas Phase H is nearly identical to pure MgSiH$_2$O$_6$. Overexposed electron-microprobe X-ray maps of the same grain used for the X-ray diffraction study together with WDS spots on the two phases confirmed the structural results. Thus, our results suggest that when Phase D and Phase H coexist, Al is strongly partitioned into Phase D at the expense of coexisting Phase H. At pressure above ~50 GPa, where Phase D is no longer stable, Phase H is able to incorporate the high aluminum contents present in hydrous peridotitic compositions in the deep lower mantle and be stabilized at the expense of Phase D and magnesium silicate perovskite.

**Keywords:** Phase D, Phase H, aluminum, dense hydrous magnesium silicates, lower mantle, crystal structure, synthesis

**INTRODUCTION**

Dense hydrous magnesium silicates (DHMS) play a crucial role in the delivery of a significant amount of water to the lower mantle by the subduction of oceanic slabs thus influencing the structure and dynamics of the deep Earth. Until recently, Phase D, MgSiH$_2$O$_6$, has been considered to be the highest-pressure phase among the DHMS (Frost and Fei 1998; Shieh et al. 1998). However, Tsuchiya (2013) and Nishi et al. (2014) found that at pressures above ~50 GPa, Phase D transforms to a new dense hydrous silicate, MgSiH$_2$O$_8$, labeled Phase H. The crystal structure of Phase H has been recently investigated by Bindi et al. (2014) by means of single-crystal X-ray diffraction and its stability field, in relation to the hydrous AlOOH component, has been studied in detail by Ohira et al. (2014) and Ohtani et al. (2014). These Authors hypothesized the MgSiH$_2$O$_8$–AlAlH$_2$O$_8$ (Al-Phase H) solid solution as potentially the most important hydrous phase present under deep lower mantle conditions.

The key role of Al in expanding the stability of DHMSs at higher temperatures has been also demonstrated for Phase D independently by Ghosh and Schmidt (2014) and by Pamato et al. (2015). The incorporation of high amounts of Al in the structure of Phase D makes this phase stable at temperatures extending to over 2000 °C at 26 GPa (Pamato et al. 2015), implying that subducted oceanic crust could be a significant long-term water reservoir in the convecting lower mantle.

Both Phase D and Phase H have been proven to host Al replacing Mg in solid solution. However, no structural studies have been carried out on the two phases in coexistence to study the preference of Al for one at high pressure. Electron microprobe studies alone could be affected by large uncertainties in the identification of the phases given the very small size and the close chemical formulas.

Here we report the fortuitous recovery of a single micrometer-sized grain in a run product synthesized at 45 GPa and 1000 °C exhibiting an intergrowth of Phase D and Phase H. This grain gave us the chance to study the partition of Al in the two phases by simultaneous structure refinements of the two phases.

**EXPERIMENTAL METHODS**

**Synthesis**

Synthesis experiments were conducted using a 1500-t multi-anvil apparatus (MADONNA-II) at Ehime University (Matsuyama, Japan). We used sintered diamond anvils with a truncated edge length of 1.5 mm as the second-stage anvils. The sample was loaded into a gold capsule. The sample assembly was composed of sintered (Mg,Cr)O and MgO pressure media, with a cylindrical LaCrO$_3$ heater, and a molybdenum electrode. Temperature was monitored by a W-Re-W-Re$_2$ thermocouple. The pressure media and the heater were dried at 1000 °C for 3 h before assembling the high-pressure cell. Details of the sample assembly are shown in the supplementary information of Nishi et al. (2014). The experiment was performed in...