Revision 1

Crystal chemistry of dense hydrous magnesium silicates:

The structure of Phase H, MgSiH$_2$O$_4$, synthesized at 45 GPa and 1000 °C

LUCA BINDI,[1,2*] MASAYUKI NISHI,[3,4] JUN TSUCHIYA,[3,4] TETSUO IRIFUNE[3,4]

[1] Dipartimento di Scienze della Terra, Università di Firenze, Via La Pira 4, I-50121 Firenze, Italy
[2] CNR - Istituto di Geoscienze e Georisorse, sezione di Firenze, Via La Pira 4, I-50121 Firenze, Italy
[3] Geodynamics Research Center, Ehime University, Matsuyama 790-8577, Japan
[4] Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo 152-8550, Japan

ABSTRACT

The crystal structure of the dense hydrous magnesium silicate Phase H, MgSiH$_2$O$_4$, synthesized at 45 GPa and 1000 °C, was investigated by single-crystal X-ray diffraction. Although showing a deterioration process under the X-ray beam, the compound was found to be orthorhombic, space group *Pnnm* (CaCl$_2$-type structure), with lattice parameters *a* = 4.733(2), *b* = 4.3250(10), *c* = 2.8420(10) Å, *V* = 58.18(3) Å^3 and *Z* = 1. The structure was refined to R_1 = 0.0387 using 53 observed reflections [2σ(*I*) level]. Magnesium and silicon were found to be disordered at the same octahedral site (with a mean bond distance of 1.957 Å). Hydrogen was not located in the difference Fourier maps but it is very likely disordered at a half-occupied 4*g* position. The centrosymmetric nature of the structure of Phase H is examined in relation to that reported for pure *δ*-AlOOH at ambient conditions (non-centrosymmetric, *P*2$_1$*nm*), and the possibility that these two compounds can form a solid solution at least at high pressure is discussed.

KEYWORDS: Phase H, dense hydrous magnesium silicates, lower mantle, crystal structure, synthesis

INTRODUCTION

Dense hydrous magnesium silicates (DHMS) play an important role in the transportation of water into the deep mantle by the subduction of oceanic slabs. Until recently, phase D has been considered to be the highest pressure form of DHMS (Frost and Fei 1998; Shieh et al. 1998). However, Tsuchiya (2013) and Nishi et al. (2014) found that phase D

36 transforms to a new dense hydrous silicate, Phase H, at pressures above ~48 GPa. Phase H in

37 the descending slab may deliver a significant amount of water to the deepest part of the lower

38 mantle thus influencing the structure and dynamics of the deep mantle.

39 On the basis of an *in situ* energy-dispersive X-ray diffraction study Nishi et al. (2014)

40 found that the reflections of phase H at ambient conditions could be indexed with an

41 orthorhombic cell with $a \approx 4.7$, $b \approx 4.3$, $c \approx 2.8$ Å. However, the quality of the collected X-ray

42 diffraction patterns was not enough to allow the detailed structure of Phase H to be reliably

43 determined (see Nishi et al. 2014). Therefore, these authors limited their study to report either

44 $P2_1nm$ (by analogy with the δ-AlOOH structure; Suzuki et al. 2000; Komatsu et al. 2006) or

45 $P2/m$ (as inferred from theoretical calculations; Tsuchiya 2013) as possible space groups, with

46 a preference for the orthorhombic symmetry. Electron diffraction measurements with a

47 transmission electron microscope also failed to obtain the structural data because of rapid

48 amorphization of the sample during observations. In order to determine the detailed structure

49 of phase H, different techniques in the analyses of the recovered sample are required.

50 Here we report the results of a structural study of Phase H by single-crystal X-ray

51 diffraction on fragments directly extracted from the run products synthesized at 45 GPa and

52 1000 °C. The structure and the space group of Phase H have been unequivocally identified

53 and considerations on the possible $MgSiH_2O_4 - AlAlH_2O_4$ solid solution at high pressures are

54 reported.

55

56 EXPERIMENTAL

57 **Synthesis**

58 Synthesis experiments were conducted using a 1,500-t multi-anvil apparatus

59 (MADONNA-II) at Ehime University (Matsuyama, Japan). We used sintered diamond anvils

60 with a truncated edge length of 1.5mm as the second-stage anvils. The sample was loaded into

61 a gold capsule. The sample assembly was composed of sintered $(Mg,Cr)O$ and MgO pressure

62 media, with a cylindrical $LaCrO_3$ heater, and a molybdenum electrode. Temperature was

63 monitored by a $W_{97}Re_3$-$W_{75}Re_{25}$ thermocouple. The pressure media and a heater were dried at

64 1000°C for 3 hours before assembling the high-pressure cell. Details of the sample assembly

65 are shown in the supplementary information by Nishi et al. (2014). We used the $MgSiH_2O_4$

66 composition as starting material, which is prepared from $Mg(OH)_2$ brucite and SiO_2 silica

2

67   powders in a 1:1 molar ratio. The sample was compressed to 45 GPa at room temperature.

68   Then the temperature was increased to 1000 °C and held constant for 6 h. Phase H prevailed

69   in the run product being accompanied by trace amounts of $MgSiO_3$ perovskite (Fig. 1).

Strategy for the X-ray data collection
70

71   Two crystals were hand-picked under a reflected light microscope from the run product

72   MII201H (Fig. 1), mounted on a 0.008 mm diameter carbon fiber and examined with an

73   Oxford Diffraction Xcalibur 3 diffractometer (X-ray Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å)

74   equipped with a Sapphire 2 CCD detector. After some minutes of X-ray exposure, intensity

75   decrease and broadening of the reflections belonging to Phase H were observed. Such an

76   intensity decay of Phase H during the data collection was attributed to a progressive

77   amorphization process. Under the electron beam, the amorphization was quite immediate

78   (Nishi et al. 2014). Under the X-ray beam, the process was slower, but, in the end (after ~140

79   minutes), a total disappearance of the reflections was noticed. However, the unit-cell

80   parameters obtained for the first two crystals of Phase H using the very low number of

81   collected reflections yielded to an orthorhombic cell with $a \approx 4.7$, $b \approx 4.3$, $c \approx 2.8$ Å, in

82   agreement with the observations of Nishi et al. (2014) at ambient conditions.

83   At this point, a third small crystal ($24 \times 35 \times 41$ μm) was selected and tested taking into

84   account the observed deterioration process (see Table 1 for details). The crystal was found to

85   be composed of Phase H and gold in a proportion roughly estimable to be 95/05, respectively.

86   Trace amounts of perovskite (Fig. 1) were not detected. The Phase H deterioration was

87   estimated by careful measurements of selected strong reflections belonging to Phase H (i.e.,

88   110, 011 and 121) and the strong 220 reflection belonging to the Au structure (which does not

89   show interferences with the reflections of Phase H). In other words, gold was used as internal

90   standard (as this material does not undergo the deterioration process), and the frames where

91   these reflections occurred (Fig. 2) were collected for 21 times during the entire data

92   collection. The Ewald sphere was collected up to $\theta_{max} \approx 27°$ with 99.8% completeness, which

93   is a very satisfactory result given the observed deterioration and the size of the crystal. The

94   number of independent reflections was sufficient to identify the correct space group and begin

95   the structure determination (see below).

3

96   Intensity integration and standard Lorentz-polarization corrections were done with the

97   *CrysAlis* RED (Oxford Diffraction 2006) software package. The program ABSPACK of the

98   *CrysAlis* RED package (Oxford Diffraction 2006) was used for the absorption correction.

99

100   **RESULTS AND DISCUSSION**

101   **Space group determination and structure solution**

102   The orthorhombic unit-cell values obtained for Phase H using only the X-ray reflections

103   collected in the first 60 minutes (to avoid the use of reflections affected by deterioration

104   effects) are $a = 4.733(2)$, $b = 4.3250(10)$, $c = 2.8420(10)$ Å. No deviation from 90° was

105   observed by refining the unit cell without symmetry constraints. The observed reflection

106   conditions are the following: $0kl$: $k+l = 2n$, $h0l$: $h+l = 2n$, $h00$: $h = 2n$, $0k0$: $k = 2n$, and $00l$: $l =$

107   $2n$, thus leading to the choice of *Pnnm* or *Pnn*2 as possible space groups. The statistical tests

108   on the distribution of $|E|$ values ($|E^2\text{-}1| = 0.952$) strongly indicated the presence of an

109   inversion center, thus suggesting the choice of the space group *Pnnm*. The position of the

110   cation (Mg/Si) was determined by means of direct methods (Sheldrick 2008). A least-squares

111   refinement on F^2 using this position and isotropic temperature factor produced an R_1 factor of

112   0.074. Three-dimensional difference Fourier synthesis yielded the position of the remaining

113   oxygen atom. The program SHELXL (Sheldrick 2008) was used for the refinement of the

114   structure. The occupancy of the cation site was left free to vary (Si vs. vacancy) and led to an

115   electron number of 12.94(8). Such a value is very close to a $Mg_{0.50}Si_{0.50}$ site population (mean

116   electron number = 13) and thus, in order to reduce the number of free variables, the

117   occupancy was fixed to this distribution. Neutral scattering curves for Mg, Si, and O were

118   taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974). At

119   this point, a careful examination of the difference Fourier maps (ΔF), did not allow the

120   precise location for the H atom. Notwithstanding, the first peak in the ΔF (0.64 e$^-$ Å^{-3}) was at

121   coordinates 0.475, 0.042, 0 (Wyckoff position 4g), at about 1.0 Å from the oxygen atom, but

122   it was not included in the refined model. At the last stage, with isotropic atomic displacement

123   parameters for all atoms, the residual value settled at $R_1 = 0.0387$ for 53 observed reflections

124   [2σ(I) level] and 5 parameters and at $R_1 = 0.0729$ for all 73 independent reflections. The ratio

125   between the number of observed reflections and the refined parameters is adequate (53/5 =

126   10.6).

4

127   Calculated X-ray powder-diffraction pattern, computed with the atomic coordinates and

128 occupancies obtained in this study (Table 2), is given in Table 3 together with the measured

129 pattern obtained by Nishi et al. (2014) at 42 GPa and 1000°C. Table 4[1] lists the observed and

130 calculated structure factors.

Description of the structure

132   The structure of Phase H was found to be topologically identical to that of $CaCl_2$ (Fig.

133 3). The tetragonal symmetry of the rutile-type structure is broken by the mutual rotation of the

134 strands of octahedra. The cations (Mg and Si) were found to be disordered at the origin of the

135 unit cell (Wyckoff position $2a$), whereas the oxygen atom was found to be in a $4g$ position

136 (Table 2). The mean octahedral metal-oxygen distance of 1.957 Å is in good agreement with

137 the calculated value for $^{VI}[Mg\text{-}O]_{0.50}$ + $^{VI}[Si\text{-}O]_{0.50}$ of 1.94 Å (taking into account the ionic

138 radii; Shannon 1976) and that obtained considering the average octahedral bond value of

139 MgO_6 and SiO_6 polyhedra in the structure of $MgSiO_3$ ilmenite (1.94 Å; Horiuchi et al. 1982).

140 Interestingly, Komatsu et al. (2011), by means of neutron diffraction studies at ambient

141 conditions, found that the Tschermak $Si^{4+} + Mg^{2+} \leftrightarrow 2Al^{3+}$ substitution does not induce either

142 an enlargement of the orthorhombic unit-cell [V = 56.375(1) and 56.217(1) Å^3 for δ-AlOOH

143 and δ-(Al$_{0.86}$Mg$_{0.07}$Si$_{0.07}$)OOH, respectively] or a lengthening of the octahedral bond distances

144 (1.923 and 1.922 Å, respectively). On the contrary, we noticed a considerable increase of the

145 unit-cell volume [58.18(3)] and of the M-O distance (1.957 Å) passing from the pure Al- to

146 the (MgSi)-compound.

147   The quality of the diffraction data did not allow to locate with confidence the position

148 of the hydrogen atom. However, the first peak in the ΔF was at coordinates 0.475, 0.042, 0

149 (Wyckoff position $4g$), and this position is in excellent agreement with that found by Komatsu

150 et al. (2011) for the *Pnnm* structure of δ-(Al$_{0.86}$Mg$_{0.07}$Si$_{0.07}$)OOH [i.e., 0.4835(11), 0.0401(9),

151 0]. If we assume that the position found for hydrogen in Phase H is real (with a 50%

152 occupancy), the following hydrogen bonding system is obtained: O–H = 1.01 Å, H–O = 1.45

153 Å, O···O = 2.461(4) Å and O–H–O = 178.9°.

---

[1] For a copy of Table 4, document item AMxxxxx, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site at http://www.minsocam.org.

Considerations on the MgSiH$_2$O$_4$ – AlAlH$_2$O$_4$ join

We have here demonstrated that Phase H retains its centrosymmetricity (being derived from the original rutile-type structure) and that it crystallizes with the CaCl$_2$-type structure, *Pnnm* space group. The previously inferred space group, *P*2$_1$*nm*, cannot be assumed because of the presence of additional systematic absences (i.e., 0*kl*: *k+l* = 2*n*+1 and 0*k*0: *k* = 2*n*+1) beside those typically due to that space group. The non-centrosymmetric *Pnn*2 space group has to be discarded as well, since there is no structural reasons to remove the inversion center. Analogously, Komatsu et al. (2011) pointed out that the *Pnnm* model is more appropriate than the *Pnn*2 model previously reported (Kudoh et al. 2004) to describe the structure of *δ*-(Al$_{0.86}$Mg$_{0.07}$Si$_{0.07}$)OOH. This is because it is unlikely that the ordering of the minor Mg/Si cations substituting for Al along the *c* axis causes the loss of the mirror plane perpendicular to *c* axis. The main reason for the eventual breaking of the mirror plane would be represented by the desymmetrization of the H atom position. However, no split into two H positions was observed by Komatsu et al. (2011) for *δ*-(Al$_{0.86}$Mg$_{0.07}$Si$_{0.07}$)OOH, and the previous *Pnn*2 model reported by Kudoh et al. (2004) was found to be identical to a centrosymmetric description of the structure (see discussion in Komatsu et al. 2011).

The only reasonable decrease of symmetry for the structure of Phase H would be toward the monoclinic subgroup *P*2/*m*, which would allow the ordering of Mg and Si into two different octahedra (Tsuchiya 2013). However, this model seems unlikely at least at ambient conditions or at H*P*-H*T* because it would imply a distortion giving rise to a monoclinic β angle different from 90° (i.e., 93°; Tsuchiya 2013) and, more importantly, would lead to an increase of diffraction lines in the powder pattern not observed in either synchrotron X-ray powder diffraction experiments (Nishi et al. 2014) or by single-crystal investigations (this study).

The crystal structure of pure *δ*-AlOOH has been proved to be non-centrosymmetric, space group *P*2$_1$*nm* (Komatsu et al. 2006). The presence of Mg and Si substituting for Al (even in very low amounts) was observed to provoke the *P*2$_1$*nm* → *Pnnm* transition (Komatsu et al. 2011). We have here demonstrated that Phase H, with pure MgSiH$_2$O$_4$ stoichiometry, crystallizes in the *Pnnm* space group. Thus, it seems that when cations with different valence states (i.e., Mg^{2+}, Al^{3+} and Si^{4+}) become disordered at the octahedral sites, a fluctuation of the hydrogen positions occurs in order to keep the charge neutrality. Such a disordered

6

185 distribution of hydrogen is considered the crystallographic breaker for the symmetry change

186 (Komatsu et al. 2011). These considerations, together with the fact that the structure of pure δ-

187 AlOOH was found to undergo a phase transition to *Pnnm* at $P > 8\text{-}9$ GPa (Sano-Furukawa et

188 al. 2008; Kuribayashi et al. 2014), imply that $MgSiH_2O_4$ and $AlAlH_2O_4$ could form a

189 complete solid solution at high pressure, likely acting therefore as a fundamental water

190 reservoir in the deep mantle.

191

196

197

198

199   REFERENCES CITED

200 Downs, R.T., Bartelmehs, K.L., Gibbs, G.V., and Boisen, M.B.Jr. (1993) Interactive software

201   for calculating and displaying X-ray or neutron powder diffractometer patterns of

202   crystalline materials. American Mineralogist, 78, 1104-1107.

203 Frost, D.J., and Fei, Y. (1998) Stability of phase D at high pressure and high temperature.

204   Journal of Geophysical Research, 103, 7463-7474.

205 Horiuchi, H., Hirano, M., Ito, E., and Matsui, Y. (1982) $MgSiO_3$ (ilmenite-type): single

206   crystal X-ray diffraction study. American Mineralogist, 67, 788-793.

207 Ibers, J.A., and Hamilton, W.C., Eds. (1974) *International Tables for X-ray Crystallography*,

208   vol. IV, 366p. Kynock, Dordrecht, The Netherlands.

209 Komatsu, K., Kuribayashi, T., Sano, A., Ohtani, E., and Kudoh, Y. (2006) Redetermination of

210   the high-pressure modification of AlOOH from single-crystal synchrotron data. Acta

211   Crystallographica, E62, i216-i218.

212 Komatsu, K., Sano-Furukawa, A., and Kagi, H. (2011) Effects of Mg and Si ions on the

213   symmetry of δ-AlOOH. Physics and Chemistry of Minerals, 38, 727-733.

214 Kudoh, Y., Kuribayashi, T., Suzuki, A., Ohtani, E., and Kamada, T. (2004) Space group and
215   hydrogen sites of δ-AlOOH and implication for hypothetical high-pressure form of
216   Mg(OH)$_2$. Physics and Chemistry of Minerals, 31, 360-364.

217 Kuribayashi, T., Sano-Furukawa, A., and Nagase, T. (2014) Observation of pressure-induced
218   phase transition of δ-AlOOH by using single-crystal synchrotron X-ray diffraction
219   method. Physics and Chemistry of Minerals, 41, 303-312.

220 Nishi, M., Irifune, T., Tsuchiya, J., Tange, Y., Nishihara, Y., Fujino, K., and Higo, Y. (2014)
221   Stability of hydrous silicate at high pressures and water transport to the deep lower
222   mantle. Nature Geoscience, 7, 224-227.

223 Oxford Diffraction (2006) *CrysAlis* RED (Version 1.171.31.2) and ABSPACK in *CrysAlis*
224   RED. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

225 Sano-Furukawa, A., Komatsu, K., Vanpeteghem, C.B., and Ohtani, E. (2008) Neutron
226   diffraction study of *δ*-AlOOH at high-pressure and its implication symmetrization of the
227   hydrogen bond. American Mineralogist, 93, 1558-1567.

228 Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic
229   distances in halides and chalcogenides. Acta Crystallographica, A32, 751-767.

230 Sheldrick, G.M. (2008) A short history of SHELX. Acta Crystallographica, A64, 112-122.

231 Shieh, S.R., Mao, H-K., Hemley, R.J., and Ming, L.C. (1998) Decomposition of phase D in
232   the lower mantle and the fate of dense hydrous silicates in subducting slabs. Earth and
233   Planetary Science Letters, 159, 13-23.

234 Suzuki, A., Ohtani, E., and Kamada, T. (2000) A new hydrous phase *δ*-AlOOH synthesized at
235   21 GPa and 1000 °C. Physics and Chemistry of Minerals, 27, 689-693.

236 Tsuchiya, J. (2013) First principles prediction of a new high-pressure phase of dense hydrous
237   magnesium silicates in the lower mantle. Geophysical Research Letters, 40, 4570-4573.

238

239

240

241

242

243

244

FIGURE CAPTIONS

245

246 FIGURE 1. Back scattered electron image of the run product MII201H synthesized at 45 GPa

247 and 1000 °C. White small dots are the gold derived from capsule. Scale bar is

248 indicated.

249 FIGURE 2. A frame showed in different moments of the data collection (after 5, 90 and 150

250 minutes, respectively) evidencing the progressive broadening and decrease of

251 intensity of the reflections belonging to Phase H. The insets in the first two panels

252 refer to the diffraction profile of a reflection belonging to Phase H (up) and a

253 reflection belonging to the gold structure (down). In the last panel (right) no

254 reflections belonging to Phase H are present, thus indicating the total amorphization

255 of the compound.

256 FIGURE 3. The crystal structure of Phase H down [001]. The horizontal direction is the *a* axis.

257 Grey polyhedra refer to (Mg,Si)-O octahedra; white circles refer to oxygen atoms,

258 whereas the hydrogen atoms (small black circles) have been tentatively drawn at

259 the Wyckoff position 4*g* (0.475, 0.042, 0) and bonded (dashed lines) to oxygen.

260 The fact that hydrogen is half occupied does impede the formation of the unrealistic

261 H–H distance of 0.43 Å.

262