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Hydrous wadsleyite crystal structure up to 32 GPa

Fei Wang[1,2,*], Elizabeth C. Thompson[3,†], Dongzhou Zhang[4,‡], Jingui Xu[4], Ercan E. Alp[5], and Steven D. Jacobsen[1,§]

[1]Department of Earth and Planetary Sciences, Northwestern University, Evanston, Illinois 60208, U.S.A.
[2]Bayerisches Geoinstitut, University of Bayreuth, 95447 Bayreuth, Germany
[3]Department of Earth and Environmental Systems, The University of the South, Sewanee, Tennessee 37383, U.S.A.
[4]Hawai'i Institute of Geophysics and Planetology, School of Ocean and Earth Science and Technology, University of Hawai'i at Manoa, Honolulu, Hawaii 96822, U.S.A.
[5]Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439 U.S.A.

Abstract

Hydroxylation of wadsleyite, β-$(Mg,Fe)_2SiO_4$, is associated with divalent cation defects and well known to affect its physical properties. However, an atomic-scale understanding of the defect structure and hydrogen bonding at high pressures is needed to interpret the influence of water on the behavior of wadsleyite in the mantle transition zone. We have determined the pressure evolution of the wadsleyite crystal symmetry and structure, including all O···O interatomic distances, up to 32 GPa using single-crystal X-ray diffraction on two well-characterized, Fe-bearing (Fo_{90}) samples containing 0.25(4) and 2.0(2) wt% H_2O. Both compositions undergo a pressure-dependent monoclinic distortion from orthorhombic symmetry above 9 GPa, with the less hydrous sample showing a larger increase in distortion at increased pressures due to the difference in compressibility of the split M3 site in the monoclinic setting arising from preferred vacancy ordering at the M3B site. Although hydrogen positions cannot be modeled from the X-ray diffraction data, the pressure evolution of the longer O1···O4 distance in the structure characterizes the primary hydrogen bond length. We observe the hydrogen-bonded O1···O4 distance shorten gradually from 3.080(1) Å at ambient pressure to about 2.90(1) Å at 25 GPa, being still much longer than is defined as strong hydrogen bonding (2.5–2.7 Å). Above 25 GPa and up to the maximum pressure of the experiment at 32.5 GPa, the hydrogen-bonded O1···O4 distance decreases no further, despite the fact that previous spectroscopic studies have shown that the primary O-H stretching frequencies continuously drop into the regime of strong hydrogen bonding (<3200 cm^{-1}) above ~15 GPa. We propose that the primary O1-H···O4 hydrogen bond in wadsleyite becomes highly nonlinear at high pressures based on its deviation from frequency-distance correlations for linear hydrogen bonds. One possible explanation is that the hydrogen position shifts from being nearly on the long O1-O4 edge of the M3 site to a position more above O1 along the *c*-axis.

Keywords: Wadsleyite, mantle transition zone, hydrogen bond, water