Compressibility and thermal expansion of hydrous ringwoodite with 2.5(3) wt% H₂O

Yu Ye, 1,* David A. Brown, 2 Joseph R. Smyth, 3 Wendy R. Panero, 3 Steven D. Jacobsen, 4 Yun-Yuan Chang, 4 Joshua P. Townsend, 4 Sylvia-Monique Thomas, 4† Erik H. Hauri, 5 Przemyslaw Dera, 6 and Daniel J. Frost 7

1 Department of Physics, University of Colorado at Boulder, Boulder, Colorado 80309, U.S.A. 2 Department of Geological Sciences, University of Colorado at Boulder, Boulder, Colorado 80309, U.S.A. 3 School of Earth Sciences, Ohio State University, Columbus, Ohio 43210, U.S.A. 4 Department of Earth and Planetary Sciences, Northwestern University, Evanston, Illinois 60208, U.S.A. 5 Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Road NW, Washington, D.C. 20015, U.S.A. 6 Bayerisches Geoinstitut, Universität Bayreuth, D95440 Bayreuth, Germany

ABSTRACT

Ringwoodite (γ-Mg₃SiO₅) is the stable polymorph of olivine in the transition zone between 525–660 km depth, and can incorporate weight percent amounts of H₂O as hydroxyl, with charge compensated mainly by Mg vacancies (Mg⁺⁺ = 2H⁺), but also possibly as (Si⁴⁺ = 4H⁺) and Mg⁺⁺ + 2H⁺ = Si⁵⁺. We synthesized pure Mg ringwoodite containing 2.5(3) wt% H₂O, measured by secondary ion mass spectrometry (SIMS), and determined its compressibility at 300 K by single-crystal and powder X-ray diffraction (XRD), as well as its thermal expansion behavior between 140 and 740 K at room pressure. A third-order Birch-Murnaghan equation of state (BM3 EOS) fits values of the isothermal bulk modulus K₀ = 159(7) GPa and (dK₀/dP)₀₋₀ = K’ = 6.7(7) for single-crystal XRD; K₀ = 161(4) GPa and K’ = 5.4(6) for powder XRD, with K₀ = 160(2) GPa and K’ = 6.2(3) for the combined data sets. At room pressure, hydrous ringwoodite breaks down by an irreversible unit-cell expansion above 586 K, which may be related to dehydration and changes in the disorder mechanisms. Single-crystal intensity data were collected at various temperatures up to 736 K, and show that the cell volume V(cell) has a mean thermal expansion coefficient αᵥ₀ = 40(4) × 10⁻⁶/K (143–736 K), and 29(2) × 10⁻⁶/K (143–586 K before irreversible expansion). V(Mg) have αᵥ values of 41(3) × 10⁻⁶/K (143–736 K), and V(Si) have αᵥ values of 20(3) × 10⁻⁶/K (143–586 K) and 132(4) × 10⁻⁶/K (586–736 K). Based on the experimental data and previous work from ²⁸Si NMR, we propose that during the irreversible expansion, a small amount of H⁺ cations in Mg sites transfer to Si sites without changing the cubic spinel structure of ringwoodite, and the substituted Si⁴⁺ cations move to the normally vacant octahedral site at (½, ½, ½), including new SIMS data on this and several Mg-ringwoodite samples from previous studies, we summarize volume-hydration data and show that the Mg²⁺ = 2H⁺ dominates up to about 2 wt% H₂O, where a discontinuity in the volume vs. H₂O content trend suggests that other hydration mechanisms become important at very high H₂O contents.

Keywords: Compressibility, hydrous ringwoodite, irreversible thermal expansion

INTRODUCTION

For a pyrolite-model upper mantle composition (Anderson 2007; Ringwood 1966), ringwoodite-(Mg,Fe)SiO₄ dominates the mineralogy of the lower transition zone from 525 to 660 km depth. At 525 km depth, wadsleyite transforms to ringwoodite at about 1790 K, whereas at 660 km depth, ringwoodite breaks down into perovskite plus ferropericlase (Mg,Fe)O at about 1873 K (e.g., Ito and Katsura 1989). Ringwoodite has the cubic spinel structure (Fd₃m), with Mg in the octahedral site (½, ½, ½), and Si in the tetrahedral site (1/8, 1/8, 1/8), with little or no site disorder at 300 K as supported by the ²⁸Si NMR study of Stebbins et al. (2009a). The most hydrous ringwoodite could contain up to about 3 wt% H₂O (e.g., Kohlastedt et al. 1996), and a ²⁸Si NMR spectroscopic study by Stebbins et al. (2009b) demonstrated that the most H⁺ substitution occurs at the Mg site, whereas the presence of short Si-H distance indicated a significant, although minor amount of Si-OH (silanol) groups.

Hydration increases the molar volume of ringwoodite (e.g., Inoue et al. 1998; Smyth et al. 2003) and therefore also its thermal expansivity (Ye et al. 2009) and compressibility (e.g., Yusa et al. 2000; Smyth et al. 2004), and significantly reduces its elastic moduli (e.g., Inoue et al. 1998; Wang et al. 2003, 2006; Jacobsen et al. 2004; Jacobsen and Smyth 2006). However, the relationship between H₂O content and its influence on various physical properties important to geophysical research relies on precise determination of H₂O concentrations in the crystal lattice, which have suffered from the absence of an absolute spectroscopic calibration for water content. The increasing amount of SIMS data for Mg-ringwoodite samples justifies an updated

* E-mail: yey@colorado.edu
† Present Address: Department of Geoscience, University of Nevada Las Vegas, Las Vegas, Nevada 89154, U.S.A.