

## **Protonation in germanium equivalents of ringwoodite, anhydrous phase B, and superhydrous phase B**

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### **ABSTRACT**

To gain insight into hydroxyl solubilities and possible hydration mechanisms of mantle silicates, as well as to test the utility of germanium analog models in studies of water-related defects, our present work is focused on the protonation of germanium analogs of silicates.

For this purpose Ge-analogs of ringwoodite, anhydrous phase B (anhB), and for the first time, superhydrous phase B (shyB), were synthesized in a piston cylinder device at 2 GPa and 950–1000 °C under water-excess conditions. Electron probe microanalysis (EPMA), transmission electron microscopy (TEM), and X-ray diffraction as well as Raman and infrared (IR) spectroscopy were used to characterize the experimental products.

Ge-ringwoodite incorporates from 900 to 2200 ppm H<sub>2</sub>O by weight, which is much less than Smyth et al. (2003) observed for the Si-equivalent synthesized at 22 GPa and 1500 °C, but 200× more than published for  $\gamma$ -Mg<sub>2</sub>GeO<sub>4</sub> by Hertweck and Ingrin (2005). In addition to this discrepancy, the incorporation mechanism of H in Ge-ringwoodite also differs from that of Si-ringwoodite.

Ge-anhB, which is currently believed to be anhydrous in the Si-system, contains from 2400 to 5300 ppm water by weight. A hydration model for germanate anhB was constructed based on single-crystal X-ray diffraction analysis and IR spectroscopy, in which OH is incorporated via the hydrogarnet substitution  $[V_{\text{Ge}} \cdot 4(\text{OH})_0]^x$  and via vacant Mg sites  $[V_{\text{Mg}} \cdot 2(\text{OH})_0]^x$ .

For Ge-shyB the water concentration and incorporation mechanism obtained in this study are identical to results reported for the silicate phase synthesized at 22 GPa and 1200 °C (Koch-Müller et al. 2005). Thus, germanates are good low-pressure analogs for hydrous mantle silicates in which protonation is controlled by stoichiometry. However, for nominally anhydrous minerals we cannot recommend the use of germanates as high-pressure models in water-related studies. In these Ge-analogs, which are usually synthesized at much lower pressures, i.e., lower water fugacities, OH incorporation seems to differ from the high-pressure silicate equivalents qualitatively and quantitatively, as hydroxyl solubility is governed by other factors such as water fugacity and intrinsic defects.

**Keywords:** Germanates, ringwoodite, nominally anhydrous minerals, FTIR, anhydrous phase B, superhydrous phase B