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

SYLVIA-MONIQUE THOMAS,1,* MONIKA KOCH-MÜLLER,1 VOLKER KAHLENBERG,2 RAINER THOMAS,1 DIETER RHEDÉ,1 RICHARD WIRTH,1 AND BERND WUNDER1

1GeoForschungsZentrum Potsdam (GFZ), Section 4.1, Telegrafenberg, 14473 Potsdam, Germany
2Institute for Mineralogy/Petrography, University Innsbruck, Innrain 52, A-6020 Innsbruck, Austria

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 H2O 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 γ-Mg3GeO5 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 [Vw4(OH)x] and via vacant Mg sites [Vms2(OH)y] for Ge-anhB.

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

INTRODUCTION

A significant number of high-pressure and high-temperature experiments have been carried out in the past to characterize phase relations in the system MgO-SiO2-H2O (MSH). Numerous investigations have established that major mantle constituents, e.g., olivine and its two dense polymorphs, are able to dissolve several wt% water, although their formulae indicate that they are nominally anhydrous minerals (NAMs) (e.g., Kohlstedt et al. 1996; Smyth 1987; Smyth et al. 1997; Kudoh et al. 2000; Bolfan-Casanova et al. 2000; Kleppe et al. 2002; Kohn et al. 2002). Cubic ringwoodite [γ-(Mg,Fe)2SiO4] with the space group Fd3m is thought to be one of the most abundant minerals in the Earth’s transition zone, from about 525 to 660 km depth. Therefore, the ability to store hydroxyl in its structure is of particular interest. Likewise, many dense hydrous magnesium silicates, first discovered by Ringwood and Major (1967), have been recognized that are stable at very high pressures and temperatures and cover a wide range of water and silica contents (e.g., phase D and phase E; e.g., Yamamoto and Akimoto 1974; Akaogi and Akimoto 1986; Kato and Kumazawa 1985; Kanzaki 1991; Gasparik 1993; Luth 1993; Cynn et al. 1996; Frost 1999; Ohtani et al. 2001, Ganguly and Frost 2006). One of these phases is anhB (Mg18Si17O44(OH)x) with an atomic Mg/Si ratio of 2.8. It was first synthesized at 2380 °C and 16.5 GPa by Herzberg and Gasparik (1989). Another phase in the MSH system is shyB [Mgs4Si3O12(OH)y], a nominally hydrous phase with an atomic Mg/Si ratio of 3.3 and 5.8 wt% of stoichiometrically incorpo-