Dense hydrous magnesium silicates, phase D, and superhydrous B: New structural constraints from one- and two-dimensional $^{29}$Si and $^1$H NMR

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ABSTRACT

To gain new structural insights into phase D and superhydrous B, two phases of potential mantle water reservoir, we have applied a range of one- (1D) and two-dimensional (2D) $^1$H and $^{29}$Si NMR techniques, as well as Raman spectroscopy, to samples synthesized at 24 GPa and 900–1100 °C. These data have revealed that phase D is characterized by disordered and varying local structures around both Si and H. The $^{29}$Si NMR spectra of phase D contain a nearly symmetric, broad peak near –177.7 ppm, attributable to octahedral Si with local structural disorder. The high-resolution $^1$H CRAMPS spectra of phase D contain a main broad peak near 12.6 ppm with shoulders near 10 and 7 ppm, suggesting a distribution of hydrogen bonding distances. For superhydrous B, our comprehensive 2D $^1$H and $^{29}$Si NMR results have clearly revealed that it contains dissimilar hydrogen (H1-H2) pairs and one tetrahedral Si site, consistent with space group Pnn2.

Keywords: Phase D, superhydrous B, NMR, Raman, order/disorder, space group

INTRODUCTION

The potential storage of water in the Earth’s deep interior is an issue of continued pursuit because the presence of water may significantly affect the phase relations and various physical properties such as viscosity, density, and electrical conductivity (Prewitt and Parise 2000). In the MgO-SiO$_2$-H$_2$O system, which represents a simplified model system for mantle minerals, several high-pressure hydrous phases (so-called dense hydrous magnesium silicates, DHMS) have been discovered experimentally, including phase A, B, superhydrous B (=C), E, and D (=F, G) (cf. Angel et al. 2001). These phases may potentially serve as water carriers along cold subduction slabs.

Among the DHMS phases, phase D (=F, G) (with an ideal chemical formula of MgSi$_2$O$_6$H$_2$) has the highest-pressure stability (at least up to 50 GPa), and thus may play a key role in transporting water to the lower mantle (Liu 1987; Ohtani et al. 1997, 2000; Frost and Fei 1998; Kuroda and Irifune 1998; Shieh et al. 1998). The crystal structure of phase D has been solved independently by Kudoh et al. (1997) and Yang et al. (1997), both in space group P$^{3}$_1m, using single-crystal X-ray diffraction (XRD). It is the only DHMS phase in which all Si (and Mg) are in octahedral coordination (Fig. 1). Phase D has been reported to show varying Mg/Si ratios (0.56–0.71, generally greater than the value of 0.5 for the ideal composition), and varying water contents (10–18 wt% H$_2$O; 2.0–3.4 H per formula unit) (Ohtani et al. 1997; Frost and Fei 1998). In the crystal structure refinements, the high Mg/Si ratios were assumed to result from excess Mg substituting for Si, with the deficit charge compensated by H (Si$^{4+}$ = Mg$^{2+}$ + 2H$^+$) (Kudoh et al. 1997; Yang et al. 1997). However, there were also suggestions from compositional variations that Si$^{4+}$ = 4H$^+$ may be another important substitution mechanism (Frost and Fei 1998). As XRD is intrinsically insensitive to the distribution of Mg and Si, because of similar scattering factors, additional information is necessary. The H sites in phase D have been located by difference Fourier map and bond valence analysis (Kudoh et al. 1997; Yang et al. 1997). They are only partially occupied, as revealed by Rietveld refinement of powder neutron diffraction data and also expected from the chemical composition (Suzuki et al. 2001). There is, however, no direct information concerning the H distribution and its relation to the Mg-Si distribution, although these factors would affect the stability and physical properties of phase D.

Solid-state nuclear magnetic resonance (NMR) and vibrational (Raman and infrared) spectroscopy are ideal tools to address the above issues. $^{29}$Si magic-angle spinning (MAS) NMR has been known to be particularly useful in revealing and quantifying cation disorder involving Si, because Si atoms with different nearest neighbors often yield distinct peaks with intensities proportional to site abundances (cf. Kirkpatrick 1988). Both $^1$H MAS NMR and vibrational spectroscopy are sensitive probes of hydrogen bonding (cf. Nakamoto et al. 1955; Novak 1974; Eckert et al. 1988; Libowitzky 1999; Xue and Kanzaki 2004; Xue et al. 2006). Recently, we have applied these techniques to high-pressure minerals in the Al$_2$O$_3$-SiO$_2$-H$_2$O system (Xue et al. 2006; Xue and Kanzaki 2007b). These studies have revealed partial Al-Si disorder in phase egg (AlSiO$_3$OH), and also provided additional constraints on the H distributions and their hydrogen bonding distances in phase egg, δ-AlOOH, δ-Al(OH)$_3$, and topaz- OH [Al$_2$SiO$_4$(OH)$_4$] (Xue et al. 2006; Xue and Kanzaki 2007b).

A unique aspect of NMR is its capacity to directly probe the spatial proximities of nuclei of the same or different types through...