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

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We have applied one-dimensional (1D) $^1$H and $^{29}$Si MAS NMR and $^1$H-$^{29}$Si cross-polarization (CP) MAS NMR, and 2D $^1$H NOESY, high-resolution $^1$H CRAMPS (FSLG)–MAS NMR, $^1$H double-quantum filtered (DQF) single-quantum (1Q) -1Q correlation MAS NMR and $^1$H-$^{29}$Si heteronuclear correlation (HETCOR) NMR techniques to gain new insights into the structure of two phases of potential mantle water reservoir, phase D and superhydrous B.

Two samples have been synthesized from a starting material of reagent-grade SiO$_2$ and Mg(OH)$_2$ in a molar ratio of 1.8 : 1, one (#1) at 24 GPa and 900°C for a duration of 3 hr., another (#2) at 24 GPa and 1100°C for 1 hr. The high-pressure experiments were performed using a 5000-ton Kawai-type double-stage uniaxial split-sphere multi-anvil apparatus (USSA-5000). Electron microprobe (chemical analysis and mapping) and micro-Raman spectroscopy have been employed for phase identifications. Sample #1 was found to consist dominantly of phase D, with some superhydrous B, stishovite and ringwoodite. Sample #2 consists dominantly of perovskite, phase D and stishovite with some superhydrous B. The Mg/Si ratio of phase D is 0.58(0.03) for sample #1 and 0.61(0.04) for #2.

For phase D in both samples, the NMR data have revealed that it has a disordered and varying local structure around both H and Si. The $^{29}$Si NMR spectra contain a nearly symmetric, broad peak near -177.7 ppm, attributable to octahedral Si. The peak shape is consistent with a disordered local structure arising from combined Mg-Si substitution and Si site vacancy. High-resolution $^1$H CRAMPS spectra contain a main peak near 12.6 ppm with two shoulders near 10 and 7 ppm, suggesting a disordered distribution of protons, mostly with shorter hydrogen bonds than suggested from previous single-crystal X-ray diffraction.

For superhydrous B in both samples, our comprehensive 2D NMR data have clearly revealed that it contains dissimilar proton (H1-H2) pairs and one tetrahedral Si site. These results are consistent with the space group Pnn2, but not with Pnmm (containing only a single unique H site) or P2$_1$mn (containing two types of similar proton (H1-H1 and H2-H2) pairs, and two tetrahedral Si sites).

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