H and Al incorporation mechanisms in stishovite: New insights from multi-nuclear NMR and first-principles calculation

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Aluminous stishovite has been recognized as an important water carrier in subducted oceanic basalts, and may be responsible for some observed seismic anomalies. In order to constrain how the incorporation of H and Al in stishovite affects its physical properties, it is important to understand how these elements are incorporated in the crystal structure. Previous studies generally reported that the H/Al ratios in stishovite are significantly below unity, requiring both coupled Al+H substitution for Si and excess Al accompanied by oxygen vacancies. However, there have been little direct supporting evidences for the proposed substitution mechanisms. In this study, we performed a comprehensive ^{1}H MAS and static NMR, ^{27}Al MAS and 3QMAS NMR, ^{1}H-^{29}Si and ^{1}H-^{27}Si CPMAS NMR study on a hydrous aluminous stishovite sample, which was first described in Xue et al. (2006) Am Mineral 91, 850-861, and synthesized from a nominal bulk composition of 0.95SiO_2.0.05AlOOH at 18 GPa and 1800˚C. NMR measurements were made using a Bruker Avance NEO 400 spectrometer. We also performed first-principles calculation with the GIPAW method using the Quantum-ESPRESSO package (v.7.0) on various optimized model structures containing coupled Al+H substitution for Si and substitution of 2Al+1O vacancy for 2Si to help interpretation. It was found that the sample consists of a hydrous aluminous stishovite phase containing about 0.3 wt% H2O, coexisting with Al_2O_3 corundum. The stishovite phase yields a ^{1}H MAS NMR peak near 9.4 ppm, a ^{1}H-^{29}Si CPMAS NMR peak near -191 ppm with a weak shoulder toward less negative chemical shift, attributable to octahedral Si, and a ^{1}H-^{27}Al CPMAS NMR peak with a maximum near 1.9 ppm, attributable to octahedral Al. The main features of all the observed NMR spectra are consistent with first-principles calculation results for coupled Al-H substitution for Si. No four- or five- coordinated Si or Al, which should occur if the substitution mechanism of 2Al+O vacancy for 2Si operates, were revealed, although expected to be observable (e.g., calculated C_Q^{Al} around 6.0~9.4 MHz for Al^{V}). This study thus casted doubt on the general validity of views held thus far about H and Al incorporation mechanisms in stishovite. Raman and EPMA analyses are also under planning, and the latest results will be presented at the meeting.

Keywords: water, stishovite, NMR, first-principles calcualtion, aluminum