Formation of hydrous stishovite from coesite in high-pressure hydrothermal environments

KRISTINA SPEKTOR1†, JOHANNA NYLEN1, RENNY MATHEW1, MATTIAS EDÉN1, EMIL STOYANOV2, ALEXANDRA NAVROTSKY2, KURT LEINENWEBER3, and ULRICH HÄUSERMANN1,*

1Department of Materials and Environmental Chemistry, Stockholm University, SE-10691 Stockholm, Sweden
2NEAT ORU, University of California at Davis, One Shields Avenue, Davis, California 95616, U.S.A.
3Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604, U.S.A.

ABSTRACT

In low-temperature, high-pressure hydrothermal environments coesite transforms into hydrous forms of stishovite. We studied hydrous stishovite produced from hydrothermal treatment of silica glass as initial SiO2 source at temperatures of 350–550 °C and pressures around 10 GPa. The P-T quenched samples were analyzed by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), thermal analysis, and IR and magic-angle spinning (MAS) NMR spectroscopy. The presence of significant amounts of H2O (ranging from 0.5 to 3 wt%) is shown from thermogravimetric measurements. PXRD reveals that at temperatures below 400 °C, hydrous stishovite is obtained as two distinct phases that may relate to the solid ice-VII environment present at prevailing P-T conditions. Initially formed hydrous stishovite is metastable and dehydrates over time in the low-temperature, high-pressure hydrothermal environment. The primary mechanism of H incorporation in stishovite is a direct substitution of 4H+ for Si4+ yielding unique octahedral hydrogarnet defects. In IR spectra this defect manifests itself by two broad but distinct bands at 2650 and 2900 cm⁻¹, indicating strong hydrogen bonding. These bands are shifted in the deuteride to 2029 and 2163 cm⁻¹, respectively. Protons of the octahedral hydrogarnet defect produce 1H MAS NMR signals in the 9–12 ppm region. The presence of multiple resonances suggests that the octahedral defect is associated with various proton arrangements. At elevated temperatures, the NMR signals narrow considerably because of proton dynamics.

Keywords: Coesite-stishovite transition, hydrous minerals, octahedral defects, high-pressure hydrothermal environments

INTRODUCTION

Stishovite is an abundant mineral in the silica-rich sedimentary and basaltic parts of subducted oceanic slabs and crustal fragments at a wide range of depths in the Earth, spanning from the bottom of the upper mantle throughout the transition zone into the lower mantle (Ono et al. 2001; Hirose et al. 2005). At prevailing P-T conditions stishovite may contain up to 5% Al2O3 (Pawley et al. 1993; Smyth et al. 1995; Litasov et al. 2007). The substitution of Al3+ for Si4+ is partially charge balanced by protons, which creates OH groups, or structural water, in crystalline stishovite (Smyth et al. 1995; Gibbs et al. 2004; Bromiley et al. 2006). Al-bearing stishovite is considered an important carrier of water into the deep mantle (Litasov et al. 2007). Litasov et al. (2007) provided a detailed study of Al2O3 solubility and the associated incorporation of protons in stishovite. Although there is a clear correlation between water and Al content in stishovite, it was found that H+ (OH groups) can only compensate for up to 40% of introduced Al3+; the majority of the Al3+ for Si4+ substitution is charge balanced by the formation of O vacancies. The maximum water content of Al-bearing stishovite is 3010 wt. ppm (0.3 wt%) (Litasov et al. 2007).

In the absence of a trivalent cation, stishovite accepts only up to 50 wt.ppm of H2O, and is classified as a nominally anhydrous mineral (NAM) (Pawley et al. 1993; Litasov et al. 2007). It has been speculated that H2O incorporation in nominally Al-free stishovite is associated with a very low concentration of Si4+ vacancies (Bromiley et al. 2006). However, it is not clear whether nominally Al-free stishovite actually contains minor amounts of trivalent cations (Al, Fe) that are charge balanced by H. It came then as a surprise when low-temperature, high-pressure hydrothermal environments afforded hydrous stishovite with water contents exceeding 1 wt%, that is three orders of magnitude higher than known previously for unsubstituted stishovite and one order of magnitude higher than for the Al-substituted variant (Spektor et al. 2011). Without the presence of other metals substituting for Si, the mechanism of hydrogen incorporation in hydrous stishovite is the hydrogarnet-like substitution 4H+ ↔ Si4+. And the presence of previously unknown octahedral hydrogarnet defects in large concentrations has been conclusively proven by NMR spectroscopy (Spektor et al. 2011).

It is uncertain whether octahedral hydrogarnet defects have wider implications as water storage mechanism in NAMs for Earth and planetary interiors. In any case, hydrous stishovite represents an interesting material with a unique bonding situation where four H+ distribute over six O atoms, in contrast with conventional tetrahedral hydrogarnet defects as in grossular garnets where the four O