LETTER

Si-rich Mg-sursassite Mg₄Al₂Si₂O₇(OH)₅ with octahedrally coordinated Si: A new ultrahigh-pressure hydrous phase

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ABSTRACT

The crystal structure of a new high-pressure hydrous phase, Si-rich Mg-sursassite, of ideal composition Mg₄Al₂Si₂O₇(OH)₅, that was produced by sub-solidus reaction at 24 GPa and 1400 °C in an experiment using a model sedimentary bulk composition, has been determined by single-crystal X-ray diffraction. The phase was found to be topologically identical to Mg-sursassite, Mg₅Al₂Si₂O₇(OH)₅, and has space group P2₁/m and lattice parameters a = 8.4222(7), b = 5.5812(3), c = 9.4055(9) Å, β = 106.793(8)°, V = 423.26(6) Å³, and Z = 1. The empirical formula determined by electron microprobe analysis of the same crystal as used in the X-ray experiment is [Mg₂.93Fe₀.01]²⁺[Al₂.99Si₀.04]³⁺[Cr₀.04]⁶⁺[Si₂.02]⁵⁺[O₂.05](OH)₅, with hydroxyl content implied by the crystal-structure analysis. The most significant aspect of the structure of Si-rich Mg-sursassite is the presence of octahedrally coordinated Si. Its structural formula is M₅V⁴⁺Mg²⁺Mg⁵⁺Al⁶⁺Al⁷⁺Si⁴⁺Si⁵⁺Si⁶⁺[O²–][O₂²–]₂⁺[OH]⁻. Si-rich Mg-sursassite joins the group of hydrous ultrahigh-pressure phases with octahedrally coordinated Si that have been discovered by experiment, and that may play a significant role in the distribution and hosting of water in the deep mantle at subduction zones. The reactions defining the stability of Si-rich Mg-sursassite are unknown, but are likely to be fundamentally different from those of Mg-sursassite, and involve other ultrahigh-pressure dense structures such as phase D, rather than phase A.

Keywords: Mg-sursassite, hydrous dense magnesium silicate, synthesis, microprobe analysis, X-ray diffraction, crystal structure

INTRODUCTION

Sursassite, ideally Mn₃Al₂Si₂O₇(OH)₆, occurs in Mn ore deposits (Nagashima et al. 2009) and is characteristically a low-pressure mineral. It is a sorosilicate with Si₇O₂₆ and SiO₄ groups that is related structurally to pumpellyite and ardennite. However, a fully Mg-substituted analog of composition Mg₄Al₂Si₂O₇(OH)₅ was first reported by Schreyer (1988) in experiments in the MgO-Al₂O₃-SiO₂-H₂O (MASH) system up to 5 GPa, 900 °C; he referred to this phase as “MgMgAl-pumpellyite.” Fockenberg (1998) determined the maximum stability of this phase to 10 GPa and found that it had a thermal limit of 800 °C defined by the reactions Mg₄Mg₃Si₃Si₇S₆O₂₅(OH)₅ ↔ pyrope + topaz-OH + coesite/stishovite + H₂O. Using a model with ultrabasic bulk composition, Bromiley and Pawley (2002) determined the phase relations of Mg-sursassite to 10 GPa and showed that Mg-sursassite replaces chlorite as a major host of H₂O above 6 GPa via the reaction chlorite + enstatite = Mg-sursassite + forsterite + H₂O. The high-temperature limit of Mg-sursassite at 7–10 GPa (700–750 °C) for ultrabasic bulk compositions is defined by the reaction Mg₄Mg₃Si₃Si₇S₆O₂₅(OH)₅ ↔ pyrope + H₂O + enstatite = pyrope + H₂O + enstatite. The general structural formula of sursassite-group minerals is M₅V⁴⁺Mg²⁺Mg⁵⁺(Mg⁶⁺Al₃⁷⁺)⁶⁺[Si⁴⁺Si⁵⁺Si⁶⁺O²–][O₂²–]₂⁺[OH]⁻. The possible significance of this new type of sursassite is considered.

EXPERIMENTAL METHODS

A high-pressure experiment was performed at 24 GPa and 1400 °C using a 2000-ton Kawai-type multi-anvil apparatus at the Geodynamics Research Center, Ehime University, Matsuyama, Japan. A sintered mixture of 83% MgO + 17% CoO form a sorosilicate Si₂O₂₆ unit. Occupancies of H sites vary from 0.5 to 1. Compositional variation in sursassite-type phases involves (1) homovalent substitution at (1,2) sites, e.g., Mg, Mn³⁺, Fe³⁺; (2) heterovalent substitution at the M₁,IV site, e.g., Mg for Al; and (3) charge balancing by O²⁻ ↔ OH⁻. Two distinct stoichiometries have been reported: Mg₄Mg₃Si₃Si₇S₆O₂₅(OH)₅ and Mg₅Al₂Si₂O₇(OH)₅, being related by the substitution Al¹⁺ + O²⁻ ↔ M²⁺ + OH⁻. In this paper we add a new stoichiometry, Mg₅Al₂Si₂O₇(OH)₅, which we refer to as Si-rich Mg-sursassite.

In sursassite sensu stricto, the M₃ site is fully occupied by Al, and there are five non-equivalent H sites bonded to three non-equivalent oxygen atoms; four of the H sites are half-occupied (Nagashima et al. 2009). The M₃ site in Mg-sursassite has an average composition Mg₉₀₃Al₃0₄ and there are four non-equivalent H sites, one of which is half-occupied. The structural formula of end-member Mg-sursassite is M₄V⁴⁺Mg₃⁺Mg⁵⁺(Mg⁶⁺Al₃⁷⁺)⁶⁺[Si⁴⁺Si⁵⁺Si⁶⁺O²–][O₂²–]₂⁺[OH]⁻. As described above, the new phase Si-rich Mg-sursassite has the structural formula M₅V⁴⁺Mg²⁺Mg⁵⁺(Mg⁶⁺Al₃⁷⁺)⁶⁺[Si⁴⁺Si⁵⁺Si⁶⁺O²–][O₂²–]₂⁺[OH]⁻. The possible significance of this new type of sursassite is considered.