

## **Micro- and nano-size hydrogarnet clusters in calcium silicate garnet: Part II. Mineralogical, petrological, and geochemical aspects**

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### **ABSTRACT**

The nominally anhydrous, calcium-silicate garnets, grossular ( $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), andradite ( $\text{Ca}_3\text{Fe}_3^{2+}\text{Si}_3\text{O}_{12}$ ), schorlomite ( $\text{Ca}_3\text{Ti}_3^{4+}[\text{Si}_3\text{Fe}_3^{2+}\text{O}_{12}]$ ), and their solid solutions can incorporate structural  $\text{OH}^-$ , often termed “water.” The IR single-crystal spectra of several calcium silicate garnets were recorded between 3000 and 4000  $\text{cm}^{-1}$ . Spectroscopic results are also taken from the literature. All spectra show various  $\text{OH}^-$  stretching modes between 3500 and 3700  $\text{cm}^{-1}$  and they are analyzed. Following the conclusions of Part I of this study, the garnets appear to contain local microscopic- and nano-size  $\text{Ca}_3\text{Al}_2\text{H}_{12}\text{O}_{12}$ - and  $\text{Ca}_3\text{Fe}_3^{2+}\text{H}_{12}\text{O}_{12}$ -like domains and/or clusters dispersed throughout an anhydrous “matrix.” The substitution mechanism is the hydrogarnet one, where  $(\text{H}_4\text{O}_4)^+ \leftrightarrow (\text{SiO}_4)^+$ , and various local configurations containing different numbers of  $(\text{H}_4\text{O}_4)^+$  groups define the cluster type. A single  $(\text{H}_4\text{O}_4)$  group is roughly 3 Å across and most  $(\text{H}_4\text{O}_4)$ -clusters are between this and 15 Å in size. This model can explain the IR spectra and also other experimental results. Various hypothetical “defect” and cation substitutional mechanisms are not needed to account for  $\text{OH}^-$  incorporation and behavior in garnet. New understanding at the atomic level into published dehydration and H-species diffusion results, as well as  $\text{H}_2\text{O}$ -concentration and IR absorption-coefficient determinations, is now possible for the first time. End-member synthetic and natural grossular crystals can show similar  $\text{OH}^-$  “band patterns,” as can different natural garnets, indicating that chemical equilibrium could have operated during their crystallization. Under this assumption, the hydrogarnet-cluster types and their concentrations can potentially be used to decipher petrologic (i.e.,  $P$ - $T$ - $X$ ) conditions under which a garnet crystal, and the rock in which it occurs, formed. Schorlomitites from phonolites contain no or very minor amounts of  $\text{H}_2\text{O}$  (0.0 to 0.02 wt%), whereas Ti-bearing andradites from chlorite schists can contain more  $\text{H}_2\text{O}$  (~0.3 wt%). Different hydrogarnet clusters and concentrations can occur in metamorphic grossulars from Asbestos, Quebec, Canada. IR absorption coefficients for  $\text{H}_2\text{O}$  held in hydrogrossular- and hydroandradite-like clusters should be different in magnitude and this work lays out how they can be best determined. Hydrogen diffusion behavior in garnet crystals at high temperatures is primarily governed by the thermal stability of the different local hydrogarnet clusters at 1 atm.

**Keywords:** Andradite, grossular, schorlomite, nominally anhydrous minerals, hydrogarnet clusters, IR spectroscopy,  $\text{H}_2\text{O}$ , metamorphism; Water in Nominally Anhydrous and Anhydrous Minerals