

## A New Paradigm for “Water” in Garnet: Micro- & Nano-Size Hydrogarnet Clusters

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The nominally anhydrous, calcium-silicate garnets, grossular -  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ , andradite -  $\text{Ca}_3\text{Fe}^{3+}_2\text{Si}_3\text{O}_{12}$  and their solid solutions  $\text{Ca}_3(\text{Al}_x\text{Fe}^{3+}_{1-x})_2\text{Si}_3\text{O}_{12}$ , can incorporate various amounts of structural  $\text{OH}^-$ . This has important mineralogical, petrological, and geochemical consequences and extensive experimental investigations have focused on the nature of “water” in these phases. However, it was not known how  $\text{OH}^-$  was incorporated and this has seriously hampered the interpretation of many different research results.

The IR single-crystal spectra of a number of calcium silicate garnets, both “end-member” and solid-solution compositions, were recorded at room temperature and 80 K between 3000 and 4000  $\text{cm}^{-1}$ . Five synthetic hydrogarnets in the system grossular-andradite-hydrogarnet ( $\text{Ca}_3(\text{Al},\text{Fe}^{3+})\text{H}_{12}\text{O}_{12}$ ) were also measured via IR ATR powder methods. The various spectra are rich in complexity and show a number of different wavenumber  $\text{OH}^-$  stretching modes between 3500 and 3700  $\text{cm}^{-1}$ . The data, together with published results, were analyzed and modes assigned by introducing atomic-vibrational and crystal-chemical models to explain the energy of the  $\text{OH}^-$  dipole and the structural incorporation mechanism of  $\text{OH}^-$ , respectively. It is argued that  $\text{OH}^-$  is located in various 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 clusters with sizes between about 3 and 15 Å. The basic 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. Published proposals invoking purely hypothetical “defect” (e.g.,  $\text{Al}^{3+} \Leftrightarrow 3\text{H}^+$ ,  $\text{Ca}^{2+} \Leftrightarrow 2\text{H}^+$ ) and coupled-substitution mechanisms (e.g.,  $\text{H}^+ + \text{Al}^{3+} \Leftrightarrow \text{Si}^{4+}$ ,  $\text{H}^+ + \text{Na}^+ \Leftrightarrow \text{Ca}^{2+}$ ) to account for  $\text{OH}^-$  in garnet are not needed to interpret the IR spectra for  $\text{OH}^-$  modes above about 3560  $\text{cm}^{-1}$ .

Key, new understanding into published dehydration and H-species diffusion is now possible for the first time at the atomic level. The same is the case for  $\text{H}_2\text{O}$ -concentration and IR absorption-coefficient studies. Similar IR “OH-band patterns” are found among different natural, calcium-silicate garnets possibly indicating that chemical equilibrium operated during their crystallization. Under this assumption, the hydrogarnet-cluster types and their concentrations could 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.