

## **Micro- and nano-size hydrogarnet clusters and proton ordering in calcium silicate garnet: Part I. The quest to understand the nature of “water” in garnet continues**

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### **ABSTRACT**

The calcium-silicate garnets, grossular ( $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), andradite ( $\text{Ca}_3\text{Fe}_2^{3+}\text{Si}_3\text{O}_{12}$ ), and their solid solutions [ $\text{Ca}_3(\text{Al}_x\text{Fe}_{1-x}^{3+})_2\text{Si}_3\text{O}_{12}$ ], can incorporate various amounts of structural  $\text{OH}^-$ . This has important mineralogical, petrological, rheological, and geochemical consequences and extensive experimental investigations have focused on the nature of “water” in these phases. However, it was not fully understood how  $\text{OH}^-$  was incorporated and this has seriously hampered the interpretation of different research results. IR single-crystal spectra of several nominally anhydrous 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  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3\text{-Ca}_3\text{Al}_2(\text{H}_4\text{O}_4)_3\text{-Ca}_3\text{Fe}_2^{3+}(\text{SiO}_4)_3\text{-Ca}_3\text{Fe}_2^{3+}(\text{H}_4\text{O}_4)_3$  were also measured via IR ATR powder methods. The various spectra are rich in complexity and show several  $\text{OH}^-$  stretching modes at wavenumbers 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  $\text{Ca}_3\text{Fe}_2^{3+}\text{H}_{12}\text{O}_{12}^-$ -like clusters. The basic substitution mechanism is the hydrogarnet one, where  $(\text{H}_4\text{O}_4)^{4-} \leftrightarrow (\text{SiO}_4)^{4-}$ , and various local configurations containing different numbers of  $(\text{H}_4\text{O}_4)^{4-}$  groups define the cluster type. Some spectra also possibly indicate the presence of tiny hydrous inclusion phases, as revealed by  $\text{OH}^-$  modes above about 3670  $\text{cm}^{-1}$ . They were not recognized in earlier studies. Published proposals invoking different hypothetical “defects” and coupled-substitution mechanisms involving  $\text{H}^+$  are not needed to interpret the IR spectra, at least for  $\text{OH}^-$  modes above about 3560  $\text{cm}^{-1}$ . Significant mineralogical, petrological, and geochemical consequences result from the analysis and are discussed in the accompanying Part II (this issue) of the investigation.

**Keywords:** Grossular, andradite, nominally anhydrous minerals,  $\text{H}_2\text{O}$ , hydrogarnet clusters, nano-scale, IR spectroscopy; Water in Nominally Hydrous and Anhydrous Minerals