

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

CHARLES A. GEIGER^{1,*,\dagger} AND GEORGE R. ROSSMAN²

¹Department of Chemistry and Physics of Materials, Section Materials Science and Mineralogy, Salzburg University, Jakob Haringer Strasse 2a, A-5020 Salzburg, Austria

²Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125-2500, U.S.A.

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 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 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 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 OH^- stretching modes at wavenumbers between 3500 and 3700 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 OH^- dipole and the structural incorporation mechanism of OH^- , respectively. It is argued that 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 OH^- modes above about 3670 cm^{-1} . They were not recognized in earlier studies. Published proposals invoking different hypothetical “defects” and coupled-substitution mechanisms involving H^+ are not needed to interpret the IR spectra, at least for OH^- modes above about 3560 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, H_2O , hydrogarnet clusters, nano-scale, IR spectroscopy; Water in Nominally Hydrous and Anhydrous Minerals