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

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The nominally anhydrous, calcium-silicate garnets, grossular - Ca₃Al₂Si₃O₁₂, andradite - Ca₃Fe³⁺₂Si₃O₁₂ and their solid solutions Ca₃(AlₓFe³⁺₁₋ₓ)₂Si₃O₁₂, can incorporate various amounts of structural 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 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 cm⁻¹. Five synthetic hydrogarnets in the system grossular-andradite-hydrogarnet (Ca₃(AlₓFe³⁺₁₋ₓ)H₁₂O₁₂) were also measured via IR ATR powder methods. The various spectra are rich in complexity and show a number of different wavenumber OH⁻ stretching modes 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 Ca₃Al₂H₁₂O₁₂- and Ca₃Fe³⁺₂H₁₂O₁₂-like clusters with sizes between about 3 and 15 Å. The basic substitution mechanism is the hydrogarnet one, where (H₄O₄)⁴⁻ ⇔ (SiO₄)⁴⁺, and various local configurations containing different numbers of (H₄O₄)⁴⁻ groups define the cluster type. Published proposals invoking purely hypothetical “defect” (e.g., Al³⁺ ⇔ 3H⁺, Ca²⁺ ⇔ 2H⁺) and coupled-substitution mechanisms (e.g., H⁺ + Al³⁺ ⇔ Si⁴⁺, H⁺ + Na⁺ ⇔ Ca²⁺) to account for OH⁻ in garnet are not needed to interpret the IR spectra for OH⁻ modes above about 3560 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 H₂O-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.