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 (Ca3Al2Si3O12), andradite (Ca3Al2Si3O12), and their solid solutions [Ca3(Al3–xFex+2)xSi2O12], 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 Ca3Al2(SiO4)3–Ca3Al2(H2O)x–CaFe3+(SiO4)3–CaFe3+(H2O)y 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 Ca3Al2H2O12– and CaFe3+(H2O)12-like clusters. The basic substitution mechanism is the hydrogarnet one, where (H2O)x+ ↔ (SiO4)x−, and various local configurations containing different numbers of (H2O)x+ 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, H2O, hydrogarnet clusters, nanoscale, IR spectroscopy; Water in Nominally Hydrous and Anhydrous Minerals

INTRODUCTION

Garnet is a remarkable phase for several reasons (Geiger 2013). One of them is its ability to adapt its crystal structure to accommodate radically different compositions. Indeed, garnet, as both a synthetic phase and as a mineral, exhibits vast chemical variability. One interesting system is the loosely termed “hydrogarnets” or “water-bearing” garnets. The general crystal-chemical formula of anhydrous or “water-free” garnet is {X}[Z][Y]3O12, where dodecahedral {X}, octahedral {Y}, and tetrahedral (Z) represent the three special crystallographic cation sites and their polyhedral coordination in space group Ilh5d. In most rock-forming garnets, Z = Si4+. In true “hydrogarnet,” however, the crystallographically single Z cation is absent and, instead, it is replaced and charge balanced locally by four protons. The resulting general crystal-chemical formula can be written as {X}×{Y}3[OH][H2O] or {X}×{Y}3[OH]x. The former expression is more suitable for describing the vibrational behavior of hydrogarnet and the latter the static crystal chemistry (see discussion below).

Cornu (1905, 1906) was the first to discover hydrogarnet, which he termed hibschite. Other reports of hydrogarnet followed (e.g., Foshag 1920; Belyankin and Petrov 1939; Belyankin and Petrov 1941a) and Foshag introduced the name plazolite for his specimen. Belyankin and Petrov (1941a, 1941b), in their studies, offered the first simplified and correct formula for hibschite as 3CaO·Al2O3·2SiO2·H2O. Passaglia and Rinaldi (1984) analyzed the situation and proposed that the term katoite should be reserved for Ca3Al2(SiO4)3–Ca3Al2(H2O)3 garnets with more than 50 mol% of the latter component and hibschite for those with less than 50%. These two workers, as well as Ferro et al. (2003), described new katoite localities and investigated the garnet crystal structures. It may well have been that Thorvaldson and Grace (1929) and Thorvaldson et al. (1929) were the first to synthesize and characterize Ca3Al2(H2O)3. It can be easily synthesized by reacting Ca3Al2O6 with water at 1 atm. The reaction is highly exothermic, and it is important in the crystallization sequence of some cements including portlandite. Flint et al. (1941) showed that there can be complete solid solution between Ca3Al2(OH)4 and Ca3Al2(SiO4)3.

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