Micro- and nano-size hydrogarnet clusters in calcium silicate garnet: Part II. Mineralogical, petrological, and geochemical aspects

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ABSTRACT

The nominally anhydrous, calcium-silicate garnets, grossular (Ca3Al2Si3O12), andradite (Ca3Fe3+2Si3O12), schorlomite (Ca3Ti5+[Si,Fe3+]O12), and their solid solutions can incorporate structural OH−, often termed “water.” The IR single-crystal spectra of several calcium silicate garnets were recorded between 3000 and 4000 cm−1. Spectroscopic results are also taken from the literature. All spectra show various OH− stretching modes between 3500 and 3700 cm−1 and they are analyzed. Following the conclusions of Part I of this study, the garnets appear to contain local microscopic- and nano-size Ca3Al2H2O12− and Ca3Fe3+H2O12−-like domains and/or clusters dispersed throughout an anhydrous “matrix.” The substitution mechanism is the hydrogarnet one, where (H2O)n+ ↔ (SiO4)2−, and various local configurations containing different numbers of (H2O)n+ groups define the cluster type. A single (H2O)4 group is roughly 3 Å across and most (H2O)4-clusters are between this and 15 Å in size. This model can explain the IR spectra and also other experimental results. Various hypothetical “defect” and cation substitutional mechanisms are not needed to account for OH− incorporation and behavior in garnet. New understanding at the atomic level into published dehydration and H-species diffusion results, as well as H2O-concentration and IR absorption-coefficient determinations, is now possible for the first time. End-member synthetic and natural grossular crystals can show similar OH− “band patterns,” as can different natural garnets, indicating that chemical equilibrium could have operated during their crystallization. Under this assumption, the hydrogarnet-cluster types and their concentrations can 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. Schorlomites from phonolites contain no or very minor amounts of H2O (0.0 to 0.02 wt%), whereas Ti-bearing andradites from chlorite schists can contain more H2O (~0.3 wt%). Different hydrogarnet clusters and concentrations can occur in metasomatic grossulars from Asbestos, Quebec, Canada. IR absorption coefficients for H2O held in hydrogrossular- and hydroandradite-like clusters should be different in magnitude and this work lays out how they can be best determined. Hydrogen diffusion behavior in garnet crystals at high temperatures is primarily governed by the thermal stability of the different local hydrogarnet clusters at 1 atm.

Keywords: Andradite, grossular, schorlomite, nominally anhydrous minerals, hydrogarnet clusters, IR spectroscopy, H2O, metamorphism; Water in Nominally Hydrous and Anhydrous Minerals

INTRODUCTION

In Part I (Geiger and Rossman 2020a) of this work it was argued that micro- to nano-size hydrogrossular- and hydroandradite-like clusters can be found in the nominally anhydrous garnets grossular, andradite, and their solid solutions. The discussion, therein, concentrated largely on analyzing the vibrational behavior of the OH− dipole and its spectroscopic nature, assigning various OH− stretching modes observed in IR spectra and constructing a local crystal-chemical cluster model for garnets within the compositional system Ca3Al2Si3O12-Ca3Fe3+[Si,Fe3+]O12-Ca3Al2H2O12−-Ca3Fe3+H12O12. In this Part II, the focus of our research is more applied and we concentrate our efforts on different mineralogical, petrological, and geochemical aspects of the new findings and proposals. Original scientific understanding is obtained because the cluster model explains IR spectra and, furthermore, it permits an atomistic interpretation of many varied experimental results obtained on the nature of “water” in various calcium silicate garnets over many years. The amount of data and results that are available is wide ranging. Considerable and diverse research has been undertaken on OH−-bearing garnets over the last approximate four decades. And, here, it should be noted that of the many grossular samples that have been studied by IR spectroscopy, that we are not aware of any “water”-free crystals. Much has been learned, but much is still not understood. What has been done?

In short, there have been: (1) several analytical compositional, diffraction, and spectroscopic studies undertaken that describe the structural and crystal-chemical properties of many various calcium silicate garnets (see references in Part I and in this work), (2) Experimental studies made to determine hydrogen or