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Coupled hydrogen and fluorine incorporation in garnet: New constraints from FTIR, ERDA, SIMS, and EPMA

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Abstract

It is well known that some garnet compositions can incorporate hydrogen and/or fluorine at levels up to several wt%. However, accurate measurement of these elements can be difficult at trace to minor concentration levels, so they are frequently ignored in routine chemical analysis. Furthermore, the mechanisms of H incorporation are still under debate, and only one mechanism for F substitution is commonly considered. We employed infrared spectroscopy (FTIR), elastic recoil detection analysis (ERDA), secondary ion mass spectrometry (SIMS), and electron probe microanalysis (EPMA) to measure H and F concentrations and constrain incorporation mechanisms in ten grossular garnets. We also present SIMS data for 11 spessartine and two andradite garnets. Three grossular garnets were measured with ERDA to obtain an infrared integral molar absorption coefficient (ε_i) for H_2O of 13 470 L/(mol·cm^2). Grossular H_2O and F concentrations range from 0.017 to 0.133 wt% and 0.012 to 0.248 wt%, respectively. Correlations between ^{16}OH and ^{19}F and interpretation of FTIR spectra prompt us to consider various coupled substitutions of H and F for Si, which can explain some high-frequency IR absorption bands that have been attributed previously to "hydrogrossular clusters" (variably sized clusters in which 4H substitute for Si) or to inclusions of hydrous minerals. A strong correlation between ^{16}OH and ^{19}F in spessartine and similar high-frequency IR bands implies a similar role for H-F substitution. Coupled H-F substitution is also probably relevant to some andradite-rich garnets, rare pyrope from the Dora Maira massif, and some synthetic garnets. Improvements in analytical methods for trace to minor H and F open up more possibilities for using these elements to calculate the activities of H_2O and F-species in fluids that were in equilibrium with garnet-bearing phase assemblages, as well as constraining the recycling of these elements into the mantle via study of xenoliths.

Keywords: Fluids and aqueous geochemistry, geochemistry, mineralogy, infrared spectroscopy, Mössbauer spectroscopy