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) for H2O of 13470 L/(mol·cm²). Grossular H2O and F concentrations range from 0.017 to 0.133 wt% and 0.012 to 0.248 wt%, respectively. Correlations between 16OH and 18F 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 16OH and 18F 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 H2O 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

Introduction

Considerable progress has been made in the last three decades in understanding how trace amounts of hydrogen can be incorporated in nominally anhydrous minerals and how this H (most commonly incorporated as structurally bound OH- groups) affects geophysical and petrologic processes in the Earth and other planetary bodies. Recent work has also highlighted the potential importance of trace fluorine (substituting for O2- ) in nominally anhydrous minerals (Hervig and Bell 2005; Mosenfelder et al. 2011; 2015; Beyer et al. 2012; Bernini et al. 2013; Dalou et al. 2012; Mosenfelder and Rossman 2013a, 2013b; Crépillon et al. 2014; Roberge et al. 2015; Grützner et al. 2017; Klemme and Stalder 2018; Yoshino and Vazhakuttiyakam 2018). In the case of garnets, it has long been recognized that both H and F can be structurally incorporated at levels up to several wt% (see Grew et al. 2013 for review). Researchers have taken advantage of this phenomenon to constrain the activities of H2O and F-species in fluids in equilibrium with garnet-bearing phase assemblages (Manning and Bird 1990; Visser 1993; Arredondo et al. 2001; Chakhmouradian et al. 2008).

Hydrogen and/or F may be almost ubiquitously present in trace to minor amounts in garnets but are commonly ignored during chemical analysis because of difficulties in measuring trace concentrations of light elements with commonly available techniques such as electron probe microanalysis (EPMA). Note that when we specify “H2O” or “H” concentrations in this paper, we are primarily referring to the equivalent in structurally bound OH- groups, because H is not incorporated in the form of structurally bound H2O groups in garnet.

Hydrogen can be detected easily using Fourier transform infrared spectroscopy (FTIR) in transmission mode, which