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OH-redistribution in andradite and grossular studied by FTIR spectroscopy

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Despite the great variability and complexity of OH-stretching bands present in IR spectra of garnets most authors refer to the (4H)Si hydrogarnet substitution as a prominent hydrogen incorporation mechanism in garnet. However, evidence for multiple OH-defects in garnets are confirmed by polarized IR-spectroscopy (Andrut et al., 2002) and NMR-data (Cho & Rossman, 1993). A reasonable assignment of OH bands remains difficult or rather speculative.

In this study, dehydration experiments in air and hydrogen-deuterium exchange experiments were performed between 700 and 950°C on natural near end-member andradite and intermediate grossular-andradite garnets. The infrared spectra of partly dehydrogenated samples show a change in relative intensities of existing OH-stretching bands while new OH-stretching bands appear. Three different kinds of bands can be distinguished: (a) fast decreasing bands, (b) slow decreasing bands, (c) newly created bands. The ratio of the different bands is directly related to the total amount of hydrogen extracted and is independent of the temperature. On the contrary, during O-D exchange the pattern of the OH and OD-stretching bands remains the same regardless of the exchange rate. A possible explanation for these results is that fast decreasing OH bands represent OH defects that are charge compensated by redox mechanisms involving transition elements like Fe or Ti, whereas the more resistant bands may correspond to more stable hydrogarnet defects.

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