American Mineralogist, Volume 91, pages 1230–1239, 2006

Site preference and local geometry of Sc in garnets: Part I. Multifarious mechanisms in the pyrope-grossular join

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ABSTRACT

We applied different independent techniques (electron microprobe analysis, structure refinement, and X-ray absorption spectroscopy) to unravel the possible mechanisms of Sc incorporation in the pyrope-grossular join. Samples were synthesized at elevated pressure and temperature by adding 5 wt% of Sc_2O_3 to selected nominal compositions (pyrope, $pyrope_{60}grossular_{40}$, $pyrope_{20}grossular_{80}$, and grossular). In this way, the site of incorporation was not pre-determined, and only depends on the availability of a mechanism for local charge-balance. The EXAFS spectra of the two end-members could be analyzed by a multi-shell fit procedure, whereas the chemical heterogeneity of the Sc-doped solid-solution terms prevented this approach. However, the available information allows detection of different mechanisms of incorporation, which are active as a function of the bulk composition. In pyrope, Sc mainly enters the dodecahedral X site, and the local charge balance is achieved by incorporation of Mg at the adjacent tetrahedral Z site. Local charge-balance requirements suggest that a Z site occupied by Mg bridges two X sites occupied by Sc. When the entrance of Ca provides relaxation of the averaged structure, Sc may enter all the three available cation sites via the coupled heterovalent exchange ${}^{X}Sc_1{}^{Z}Sc_1{}^{X}Mg_{-1}{}^{Z}Si_{-1}$ and the homovalent exchange ${}^{Y}Sc_1{}^{Y}Al_{-1}$. In the samples of this work, there is an apparent limit in the Sc incorporation at the Y site, which is in contrast to the favored mechanism of incorporation in Sc-doped andradites. This limit can be explained in terms of relative dimensions of the structural sites when Al is the dominant Y cation. These results must be taken into account when evaluating trace-element behavior in garnets for geochemical purposes. In particular, they explain why D_{Sc} can be treated together with D_{REE} in models based on the elastic strain theory in garnets close to the pyrope composition, but deviate from the parabolic fit in grossular-rich garnets.

Keywords: Crystal structure, garnet, trace elements and REE, scandium, XAS, XRD data, crystal synthesis