Distinct Local Environments for Ca in Pyrope-Grossular Garnets: a New Model based on XRD and EXAFS Studies

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A multi-technique approach (based on electron microprobe analysis, X-ray structure refinement, and EXAFS analysis at the Ca K-edge) was used to characterise the local geometry of Ca in synthetic and natural garnet compositions referable to the pyrope-grossular solid-solution. Multi-shell fits of the EXAFS data indicate that Ca assumes the standard [4 + 4]-fold coordination (the polyhedral shape being a triangular dodecahedron) when Ca > 1.50 atoms per formula unit (apfu), but assumes a nearly regular [8]-fold coordination when Mg + Fe > 1.50 apfu. In the latter situation, both Ca-O bonds converge towards the value of the longer Mg-O bond in pyrope.

This anomalous change of coordination may explain the strong non-ideality of many structural features and geochemical and thermodynamic properties observed along the pyrope-grossular solid solution, which is the one most relevant for the use of garnets in petrogenetic studies of igneous and subdaction environments.

This feature must be taken into account when building theoretical models of the garnet solid solutions, which are at the moment the most promising approach to calculate thermodynamic properties and to interpret and predict trace-element behaviour in this crucial mineral phase.

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