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Crystal-chemical complexity in natural garnets: structural constraints on chemical variability

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Abstract: A crystal-chemical database for natural garnets has been developed at the CSCC, Pavia. It presently consists of 281 garnets representative of common chemical compositions and petrogenetic conditions. For most samples, X-ray single-crystal structure-refinement and SEM-WDS analysis were done on the same crystal. Ion-microprobe analysis for detection and evaluation of H, Li, Be, B was also done in some cases; spectroscopic techniques were used to confirm the presence of unusual substitutions. This combined approach allowed detection and characterization of substitutions occurring in natural garnets.

Plots of atomic coordinates and geometrical parameters as a function of the unit-cell edge show that garnet crystal-chemistry is characterized by the presence of strong inductive effects and non-linear behaviour, the quantitative aspects of which are discussed in the companion paper. There are stringent structural constraints on chemical variability due to the extensive edge-sharing between adjacent polyhedra. These phenomena, which make the correct determination of site populations a non-trivial task, have now been analyzed in detail and fully understood. We present here an automatic procedure which allows the determination of reliable site-populations starting from the results of the structure refinement. It is based on multiple regression equations for the independent estimates of each cation content and on their subsequent normalisation according to crystal-chemical constraints.

Key-words: garnet, crystal-structure refinement, crystal chemistry, site population.

1. Introduction

The garnets are an important group of minerals that are stable over a wide range of pressure, temperature and chemical compositions. Their chemical variability is due to the compliance of the garnet structure in all the most abundant divalent, trivalent and tetravalent cations in the Earth's crust. Their remarkable physical properties and use as petrogenetic indicators have made garnets the subject of many studies during the last forty years. However, there has been no comprehensive study of the garnet structure as a function of chemical composition. Our experience with pyroxenes, amphiboles and staurolites (Rossi & Ungaretti, 1989; Hawthorne *et al.*, 1993) suggested that structure refinement and chemical analyses on a large number of garnets of wide-ranging compositions would enable us to unravel average crystal-chemical effects exerted by each chemical substitution at the long-range scale. The goal is to provide an atomic-scale model of the structural effects of cation substitutions, which can be used in interpreting the complex (ideal or non-ideal) behaviour observed in thermodynamic work on garnet solid-solutions

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