



	Experiment title: SITE PREFERENCE AND PARTITIONING OF SCANDIUM IN SILICATIC GARNETS: FIRST DIRECT STRUCTURAL STUDY.	Experiment number: CH1545
Beamline: ID26	Date of experiment: from: 08-10-2003 to: 13-10-2003	Date of report: 17 Feb 2004
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Report:

Among the rock forming minerals, garnets are intensively studied because of the complexity of their crystal chemistry and solid solution properties and of their stability over a wide range of physico-chemical conditions. Moreover, understanding of trace-element behaviour in garnets is crucial for geochemical modelling of petrogenetic processes in the upper-mantle region; the available trace-element data indicate that their behaviour is not linear in the pyrope-grossular solid-solution, but no sound model has been yet provided to explain this evidence.

For most of the many minor and trace elements which can enter the garnet structure there is no sound information on the site preference. Scandium is generally present in trace amounts in natural garnets. In principle, its ionic radii may allow incorporation in the garnet structure both in octahedral (i.r. = 0.745 Å) and in dodecahedral (i.r. = 0.870 Å) coordination, i.e. both at the Y and the X sites. As a matter of fact, Sc is usually considered as an octahedral constituent in geochemical modelling of garnets. Therefore, Sc is an ideal element to check whether changes in the garnet major-element composition provoke a different partitioning or even a different site preference. Data obtained on synthetic Sc end-members (or on garnets where Sc is a major-element component) cannot be used to this purpose, because the geometry of the garnet matrix would be significantly different from that of the pyrope-grossular join.

Our experiments were thus designed to determine the site location of Sc as a very minor or trace element level in the pyrope-grossular solid-solution. Four garnet compositions were synthesised (Pyr, Pyr60Gr40, Pyr20Gr80 and Gr), after adding to the starting powders 5% of Sc₂O₃. For the characterisation of the run products, we adopted a multi-disciplinary experimental–theoretical approach, which combines electron microprobe analysis, single-crystal and powder X-ray diffraction, Sc K-edge XAFS, and full-multiple scattering calculations of Sc XANES spectra. In particular, EMP analysis confirms that Sc is completely incorporated in the synthetic garnet.

The XAFS experiments were successfully performed at ID26 on the four synthetic samples described above. The normalised XANES spectra reported in Fig. 1 clearly show significant differences in the spectral features of grossular and pyrope, suggesting that the local environment of Sc in the grossular-type matrix is different from that in a pyrope-type matrix.

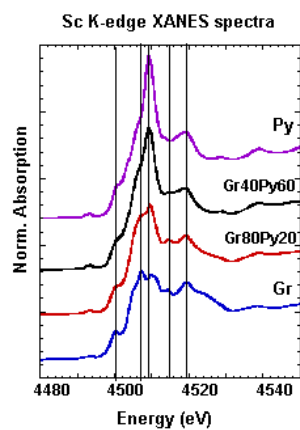


Fig. 1 – Experimental Sc K-edge XANES spectra of the Sc-bearing end-members grossular and pyrope and of two solid solutions of intermediate composition.

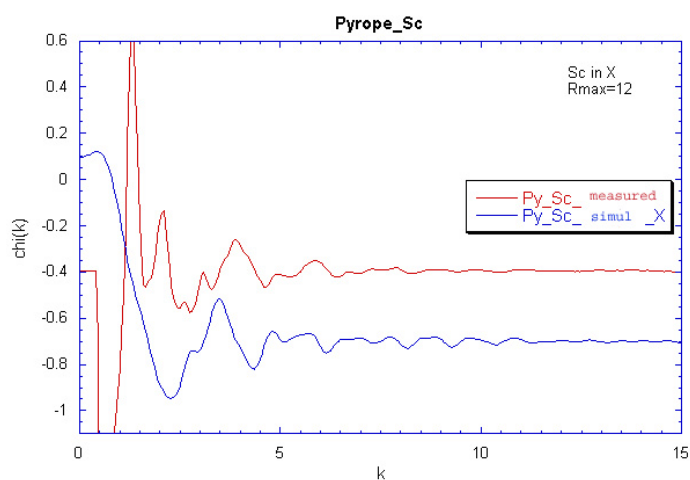


Fig. 2 – Comparison between the EXAFS signal measured at Sc K-edge and that simulated for Sc occurring at the X site in the pyrope matrix.

This finding is supported by the results of the preliminary analysis of the EXAFS signals. Fig. 2 reports the comparison between the EXAFS signal measured at the Sc K-edge on Sc-doped pyrope and that simulated with Sc occurring at the X site in a pyrope matrix. The strong similarity of the two signals, supports the conclusion that, contrary to the common geochemical assumptions, Sc is incorporated into the dodecahedral site in the pyrope structure. On the contrary, preliminary results obtained for the EXAFS signal of Sc-doped grossular suggest that the octahedral Y site is also (but not solely) involved in Sc incorporation in grossular. The geometrical parameters of the Sc environments in the different garnet matrices will be quantitatively defined by the detailed EXAFS analysis, which is presently in progress.

The proposed model is supported by subtle details of the structure refinement results (e.g., differential changes of the shared and unshared polyhedral edges and components of the atomic displacement parameters).