



ESRF

**Experiment title:**  
**XAFS CHARACTERIZATION OF MINOR AND TRACE  
RARE EARTH ELEMENTS IN NATURAL AND  
SYNTHETIC GARNETS**

**Experiment  
number:**  
**CH-218**

|                                     |   |   |
|-------------------------------------|---|---|
| <b>Beamline:</b><br><b>D8-GILDA</b> | <b>Date of experiment:</b><br>from: <b>27/9/96</b> to: <b>29/9/96</b> | <b>Date of report:</b><br><b>27/1/97</b>        |
| <b>Shifts:</b><br><b>9</b>          | <b>Local contact(s):</b><br><b>Stefano Colonna</b>                    | <i>Received at ESRF:</i><br><b>24 FEB. 1997</b> |

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**Report:**

The silicate garnets (general formula  $X_3Y_2Z_3O_{12}$ ; space group *Ia3d*) **represent** one of the fundamental mineral groups found in the Earth. The crystal structure of garnets can be described as a tridimensional framework constituted by alternating  $SiO_4$  tetrahedra and  $YO_6$  octahedra (where Y is mainly Al,  $Fe^{3+}$ , Cr) which share corners. In the structure are also present triangular dodecahedra  $XO_8$  consisting of eight oxygens which coordinate bivalent cations (mainly Mg, Fe, Ca, Mn).

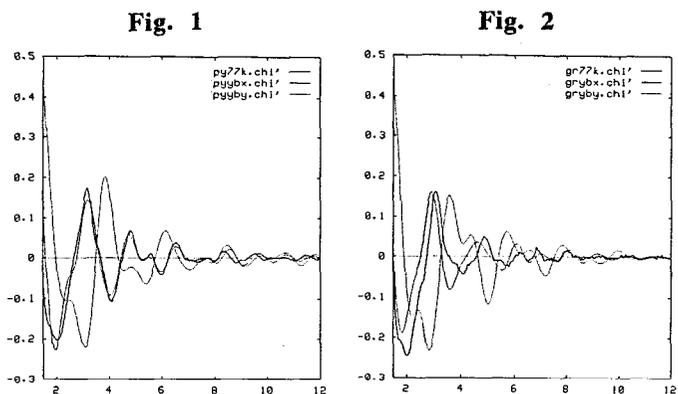
Garnets of low crust mafic and ultramafic rocks usually contain rare earth elements in trace amounts (few tens of ppm). Although REE diffusion coefficients among garnets and coexisting phases are widely used as petrological parameters to interpret the crystallization and the metamorphic history of crustal rocks, there is up to now no direct crystal chemical characterization, due to the difficulty in obtaining structural information on trace and minor species.

In this work we have taken advantage of the unique attributes of EXAFS spectroscopy to determine the local structural environment of minor levels of Yb (about 1.0 wt%) in synthetic pyrope and grossular garnets.

The Yb  $L_I$  and  $L_{III}$ -edges XAFS spectra were collected in fluorescence mode at three different temperatures ranging from 77 to 343K at GILDA-CRG. A dynamically sagittal focussing Si(311) monochromator was used; grazing incidence mirrors eliminated higher harmonics. For detection of the fluorescence HP-Ge and Si-photodiode were used. The experimental data have been analyzed using standard background subtraction and Fourier

Filtering, whereas the determination of the structural parameters has been accomplished through FEFFIT. (UWXAFS package) which uses theoretical phase shifts and amplitudes from FEFF6 software. The reliability of the theoretical phases and amplitudes was assessed by applying them to  $\text{Yb}_2\text{O}_3$ , which was used as a standard compound with known structure.

Figs.1 and 2 report the experimental EXAFS signal of Yb-pyrope and Yb-grossular, respectively, compared with the theoretical signals calculated assuming Yb in X or in Y sites of the garnet structure. It is evident that Yb is located in the X dodecahedral site in both the garnets, even if with a rather different local geometry with respect to the main X cation (Mg and Ca, for pyrope and grossular, respectively). Tab. 1 reports the results of the XAFS analysis for Yb-Pyrope and Yb-Grossular at the two extreme temperatures 77 and 343K.



**Table 1** - Crystallographically independent bond distances of the dodecahedral X site for the two Yb-bearing garnets compared with those determined by single-crystal X-ray diffraction on pure pyrope and grossular and on the synthetic end-member  $\text{Y b}_3\text{Al}_5\text{O}_{12}$

|                                | Pyrope    | Yb-Pyrope | Grossular | Yb-Gross | $\text{Yb}_3\text{Al}_5\text{O}_{12}$ |
|--------------------------------|-----------|-----------|-----------|----------|---------------------------------------|
| $R_{\text{X}(1)}\text{-O}$ (Å) | 2.1959(1) | 2.25(2)   | 2.321(1)  | 2.24(2)  | 2.283(7)                              |
| $R_{\text{X}(2)}\text{-O}$ (Å) | 2.3334(1) | 2.33(2)   | 2.483(1)  | 2.38(2)  | 2.397(7)                              |

### Conclusions

-Yb enters the garnet structure and is located in the X dodecahedral site in both pyrope and grossular samples.

-The local geometry of Yb in pyrope and grossular X site is significantly different from those of Mg and Ca in the two pure end-members, and also from that of Yb in the reference garnet  $\text{Y b}_3\text{Al}_5\text{O}_{12}$ .

-The thermal motion of  $\text{Yb}^{3+}$  in Yb-Py and Yb-Gr is less anisotropic than that of Fe in almandine.

-The results of this work indicate that, at this concentration level, the host garnet matrix exerts a clear structural control on the REE incorporation, which is imputable to lattice sites and not to structural defects.