



	Experiment title: Site location of trace level Dy in natural garnets by K-edge X-ray Absorption Spectroscopy	Experiment number: 08-01-601
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Report:

The site location and geometry of trace amounts of dysprosium (299 ppm) in a natural melanite garnet (A204) from carbonatitic rocks have been studied by high energy fluorescence-detected X-ray Absorption Fine-Structure Spectroscopy. XAFS measurements at the commonly used REE L_{III} edge are impossible in this sample because of the presence of the Fe K_α interfering fluorescence line originating from the matrix, which cannot be resolved by a solid-state fluorescence detector. These problems have been overcome with the use of the Dy K-edge because at these energies (53789 eV) there are no problems of overlapping absorption edges and fluorescence lines. A high photon brilliance at these energies can be obtained at the "GILDA" beamline. The Dy K-edge XAFS spectra were collected in the transmission mode for the standard compound Dy₂O₃ and in the fluorescence mode for the garnet. The monochromator was operated in the dynamically sagittally-focussing mode. The measurements were performed at 77 K in order to reduce the thermal damping of the signal. A 13-element hyper-pure Ge detector with fast digital electronics was used. The data were recorded with a spacing of 0.2 eV in the XANES region and 2 eV in the extended part of the spectrum. The analysis of the raw, background subtracted, spectrum was limited to the first coordination shell of the REE. The FEFFIT (Newville et al., 1995) routine was used, using

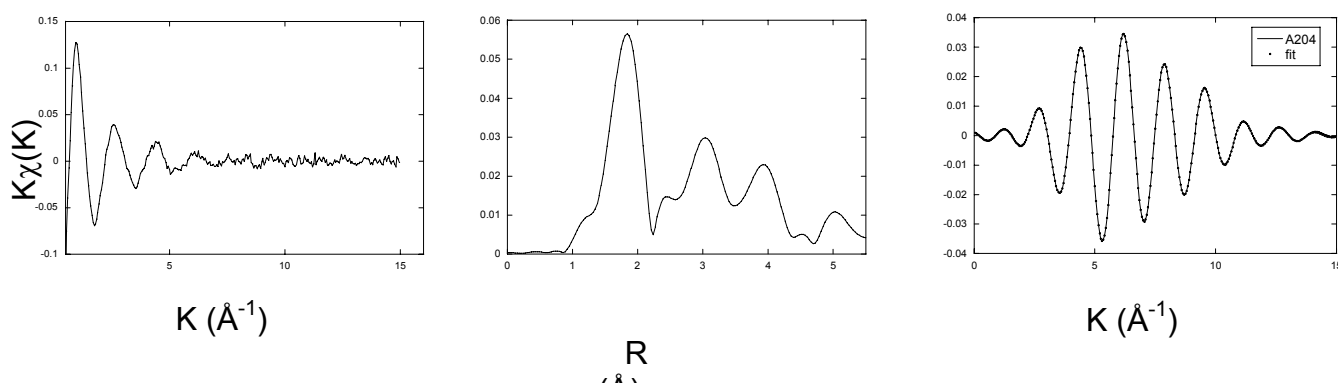
theoretical phase functions and amplitudes generated by FEFF8 (Ankudinov et al. 1998). Data analysis was performed in the ranges $k_{\min} = 1.6$ to $k_{\max} = 14.4 \text{ \AA}^{-1}$ and $R_{\min} = 1.5$ to $R_{\max} = 2.3 \text{ \AA}$, using a k -weight equal to 1. The fitting parameters, based on a structural model with Dy in dodecahedral site, were the Debye-Waller factor σ^2 and the coordination distances of the first two oxygen shells. The coordination numbers of the oxygen shells were kept fixed ($N_1 = N_2 = 4$) as requested by the garnet structure.

The measurements demonstrate that the trace element is located in the dodecahedral X site with the following bond distances: X1-O = 2.32, X2-O = 2.53 \AA . These bond distances are consistent with the ionic radius of the trace element, confirming the strong crystal-chemical control on the partitioning of these elements among the magma and the coexisting mineralogical phases. Moreover, the comparative study of the local site geometry of Dy with those of different major and trace elements incorporated in the dodecahedral site of this and other garnets (Quartieri et al. 1995, 1997, 1999a,b, 2002) indicates that the shorter X1-O bond distance seems to be more sensitive to the variations of the host cation ionic radii, mainly reflecting the local site deformation induced by the trace element incorporation. This work confirms the capability of fluorescence XAFS at high energy of providing direct structural information on the site geometry of heavy trace-elements in minerals and, hence, its great relevance for the Earth Sciences.

Fig. 1 - Background subtracted EXAFS signals of Dy in A204 sample at 77 K.

Fig. 2 - Fourier Transform (FT) of $k \chi(k)$ Dy signal in A204 sample.

Fig. 3 - Fit (dotted line) to the back Fourier Transform (full line) of Dy K-edge data shown in Fig. 1 performed in the range 1.5 – 2.3 \AA .



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