

# Rare earth element partitioning between silicate melt and aqueous fluid at high temperatures and high pressures

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Geological processes involving silicate melts and aqueous fluids play important roles in the evolution of the Earth's crust and mantle. Melt and fluid generation in the crust and in subduction zones and their subsequent ascent towards shallower levels result in large-scale mass and energy transfer in Earth's interior and in abundant volcanic activities on the surface. Detailed knowledge of the physical and chemical properties of these systems is essential for a better understanding and modelling of these processes. The pattern of trace elements, particularly of the REE (rare earth elements, La-Lu), LILE (large ion lithophile elements, e.g., Sr, Rb, Cs, Ba), and HFSE (high field strength elements, e.g., U, Pb, Th, Zr, Ti) of igneous rocks is one of the most important tools in geochemistry to unravel their petrogenesis.

Here, we aimed to determine concentrations of Ba, La, and Y of the fluid in-situ in equilibrium with silicate melts at elevated PT conditions using  $\mu$ XRF analyses of K lines. Experiments were performed at the hard X-ray microprobe beamline P06 using in-house designed hydrothermal diamond anvil cells (HDAC). In order to enable in-situ measurements of even low REE contents, following experimental conditions were required: i) an excitation energy of  $\sim 65$  keV, ii) a high photon flux ( $>10^{10}$  ph/s), iii) a spot size  $<5$   $\mu$ m, and iv) a long focal distance ( $>50$  mm). Therefore, experiments were carried out using the multilayer (ML) monochromator, CRLs, and using a solid state Ge detector with a 2 mm pinhole collimator. The detector was placed in the plane of polarisation and in  $90^\circ$  geometry to the incident X-ray beam to optimize the signal to background ratio. Approximately one and a half days were spent for beamline setup because i) this was the first user application of the newly installed ML monochromator, ii) CRLs were not used before at such high excitation energies in combination with the ML monochromator, and iii) HDAC installation at beamline P06. The spot of the X-ray beam was  $6 \times 20$   $\mu$ m FWHM (hor.  $\times$  vert.) at an excitation energy of 63.4 keV and with a photon flux of  $1.5 \times 10^{10}$  ph/s at the sample position.

Lower limits of detection were calculated from standard solutions loaded in three HDACs and are 15 ppm for Y, 7 ppm for La, and 11 ppm for Ba (Fig.1). In the experiments, the rather large X-ray beam made it difficult to perform measurements of the fluid without signal from the melt droplets or additional crystalline phases present at temperatures up to 750  $^\circ$ C. Nevertheless, a few experiments were realized successfully but in almost all cases concentrations of elements are below lower limits of detection.

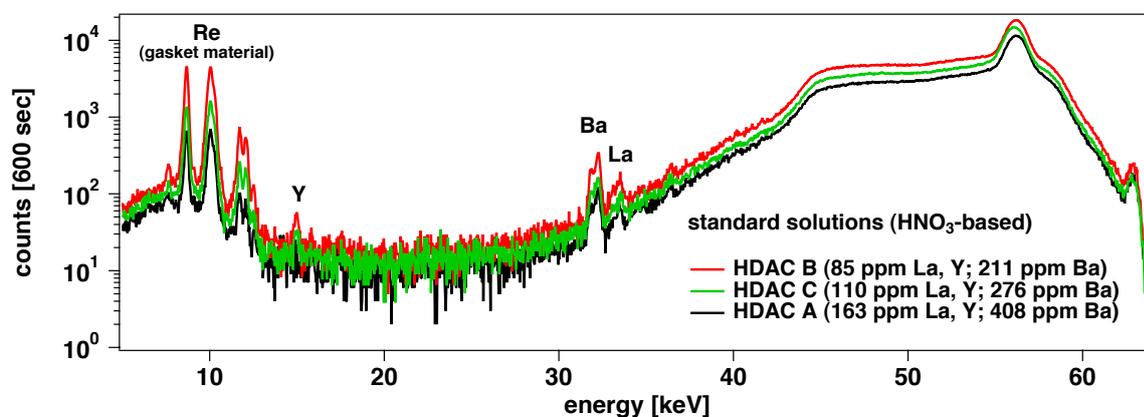


Figure 1: X-ray fluorescence spectra of standard solutions containing Y, Ba, and La loaded in three hydrothermal diamond anvil cells. Spectra of HDAC B and HDAC C are vertically offset for clarity.