



	Experiment title: Micro-XRF analyses of trace elements in deep Earth materials using high-energy X-rays	Experiment number: EC387
Beamline: ID22	Date of experiment: from: 22.04.2009 to: 28.04.2009	Date of report: 27.07.2009
Shifts: 18	Local contact(s): Jean Cauzid	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Max Wilke*, Christian Schmidt*, André Stechern* GeoForschungsZentrum Potsdam, D-14473 Potsdam, Manuela Borchert* Universität Potsdam, D-14476 Potsdam, Karen Rickers* HASYLAB at DESY, D-22607 Hamburg, Laszlo Vincze* University of Ghent, B-9000 Ghent, Frank Brenker* Frankfurt University, D-60438 Frankfurt		

Report:

The aim of the experiments was to identify and quantify trace elements, e.g., rare earth elements, in small diamond-confined samples (aqueous solutions, fluid inclusions) using high energy X-rays for μ XRF analyses. The combination of a high energy beam and a spot size in the μ m range requires special optic devices. In these experiments, we tested a new Kirkpatrick-Baez (KB) mirror, which is based on a multilayer structure. It focuses hard X-rays up to 65 keV into a spot of a few μ m. Using this setup, two experiments were performed: a) Determination of trace element concentrations in aqueous solutions equilibrated with aluminosilicate melts are measured directly at elevated PT conditions using hydrothermal diamond-anvil cells (HDAC), and b) determination of trace element composition of inclusions in natural diamonds. A synchrotron beam with a photon energy of 50 keV for excitation and a spot size of $5 \times 2 \mu$ m was used for both experiments.

Figure 1 shows the minimum detection limits (MDL) calculated for two standard glasses (NIST612 and ATHO) and one standard solution measured in the HDAC. The MDL in the standard glasses are ≤ 20 ppm for elements with atomic numbers (Z) between 25 and 47, and ~ 1 ppm for elements with $48 < Z < 60$. The standard solution measured in the HDAC show slightly higher MDL of ~ 30 ppm for Y, ~ 15 ppm for Ba and La, and ≤ 10 ppm for Sm and Eu.

The collected XRF spectra show a very broad inelastic scattering peak between 35 to 50 keV, in the region of many K-lines of interest. This problem can be solved by shifting to a higher excitation energies, but this was not possible because no camera was available that can be used during beam focusing.

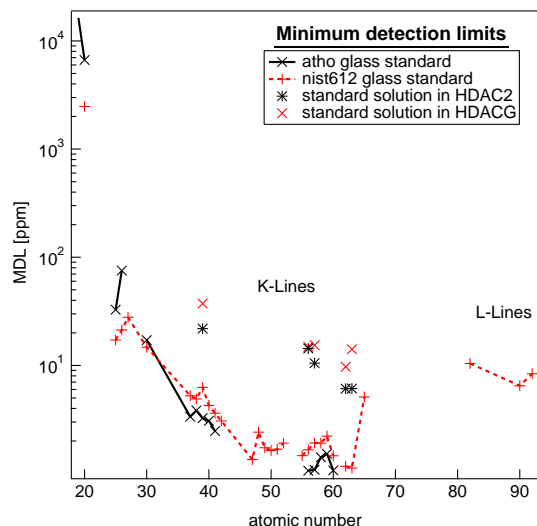


Fig. 1: Minimum detection limits for standard glasses and the standard solution.

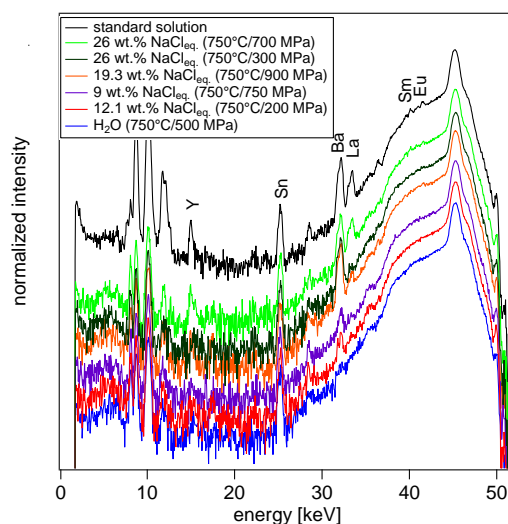


Fig. 2: XRF spectra of a standard solution and samples with varying salinity and pressure.

Hydrothermal diamond-anvil cell (HDAC) experiments:

The goal was to determine partitioning of Ba, La, Y, Sm and Eu between aqueous solutions and aluminosilicate melts at 750°C for various pressures and salinities. Because such magmatic fluids are not quenchable, we determined the trace element concentrations in the fluid in-situ at elevated PT conditions using a HDAC and μXRF analyses. Figure 2 shows that no data for Sm and Eu could be obtained because of the broad inelastic scattering peak. Yttrium and Lanthan are close to or below the detection limit in almost all runs which is probably due the formation of REE silicates during the runs. For Ba, a suite of data was collected that showed that the partitioning is mainly controlled by the salinity of the fluid, and to a lesser extent by the pressure. The Ba concentrations varied between 50 ppm in experiments with H_2O and 400 ppm in experiments with salt solutions.

Inclusions in diamonds:

The goal was to investigate crystalline and non-crystalline inclusions trapped in diamonds from the Earth's interior. During the time remaining after the HDAC experiments several inclusions in various diamonds could be found and mapped. The number of inclusions that could be investigated was additionally limited by problems with the detector electronics. These investigations particularly benefitted from the small focal spot achieved with the KB optic. Due to the excitation energy of 50 keV and the strong Compton scattering by the diamond, the sensitivity for the lanthanides was still quite low. This can probably be improved by excitation at 65 keV.

In conclusion, the tested new Kirkpatrick-Baez mirror is a useful optic device to collect μXRF spectra using high excitation energies. To obtain analyzable spectra, the excitation energy should be 15 to 20 keV above the K-lines of interest due to the broad inelastic scattering peak.