Sub-micron and full-field XRF analyses of mantle fluids and melts trapped in cloudy diamonds of ultra-deep sources

S. Schmitz[1], F.E. Brenker[1] , J. Garrevoet[2], B. Vekemans[2], M. Krebs[1], J. Rudloff[1]
G. Falkenberg[3], U. Frühling[3], G. Wellenreuther[3]. B. De Samber[2], L. Vincze[2]

[1]Geoscience Institute - Mineralogy, Goethe University, Altenhoeferallee 1, 60438 Frankfurt am Main, Germany
[2]Dept. of Analytical Chemistry, Ghent University, Krijgslaan 281, B-9000 Gent, Belgium
[3]Hamburger Synchrotronstrahlungslabor at DESY, Notkestr. 85, D-22607 Hamburg, Germany

Introduction

Until recently, only indirect methods based on high-pressure techniques and seismological data were applied to study the composition and conditions of the deep Earth [1,2]. During the last decade, inclusions in ultra-deep natural diamond crystals provided a unique possibility to study the Earth´s mantle to depths reaching even the lower mantle (> 670km) [3]. During the growth of a natural diamond, high density fluids, high pressure minerals and even small rock fragments (mineral assemblages) can be trapped within. These inclusions are then shielded from the environment during the transport and exhumation of the diamond host towards the Earth´s surface, preserving their original capture composition and, in some cases, even their high pressure structure [3]. These inclusions provide a uniquely direct way to derive information on the composition and structure of the deep Earth [3].
During an ongoing project at P06 we were able to successfully measure several slices of different cloudy diamonds (Rio Soriso, Machado River, Sao Luiz; Brazil) applying sub-micron and full-field XRF techniques. We were able to demonstrate that even in a single diamond the chemical composition can vary from inclusion to inclusion indicating a complex fluid or melt from which they were separated during the growth of the diamond.
Full-field XRF measurements were performed on larger (single) crystals (few 100µm) containing so-called inclusion clouds (large number of small inclusions (≥100nm)).

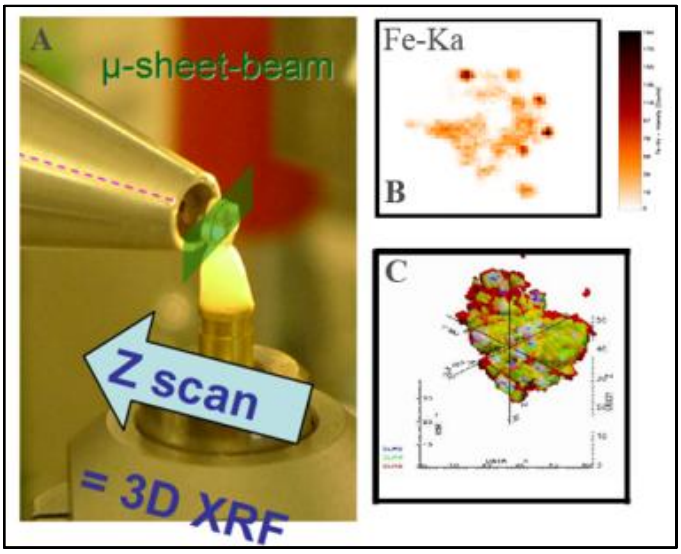

Figure 1: Schematic overview of the working principle using a sheet µ-beam. B) Full-field XRF image (Fe-Ka) of one representative slice through the diamond showing detailed 2D view of the inclusion. C) Calculated 3D view of the P11 inclusion cloud.

Full-field micro-XRF measurements

A novel full-field micro-XRF technique was tested on diamonds containing inclusion clouds and larger (few 100µm) inclusions. For this purpose, the unique SLCam, an energy-dispersive CCD-detector was used. A µ-sheet-beam of 5µm (H) x 1.37mm (V) size with an energy of 18.2keV was used. By scanning through the diamond in the z-direction (towards the detector) (see Fig.1**A**) and recording 2D images at each position, a 3D micro-XRF data-set of the entire diamond is obtained, including the diamond inclusion(s). Diamond P11 (Machado River). was analyzed using 41 vertical slices with 5µm steps and counting time of 30min per slice, leading to a full 3D elemental imaging measurement time of 21h per scanned volume. The long counting time per slice was necessary in order to achieve adequate intensities.

The installation of the new multilayer monochromator at P06 will reduce the acquisition time for a full 3D elemental distribution data-set by a factor of ~50.
One representative 2D full-field micro-XRF slice is shown in **Figure 1B** for the Fe-Kα distribution. The intense Fe hotspots are located in the surrounding of a large inclusion with sizes of a few microns. **Figure 1C** shows the calculated 3D image obtained from the single 2D XRF slices of the largest inclusion of diamond P11. The colors represent Fe with blue having the highest intensity, green medium- and red lowest intensity.
Details of isolated inclusions show that even single micron sized inclusions are composed of a complex assembly of mineral phases, most likely crystallized from a trapped high density melt or fluid.

Sub-micron scanning XRF studies on diamond slices

Slices of diamonds with a thickness of ~1-2 mm were analysed with a sub-micron X-ray beam of 400nm (H) x 500nm (V). Various slices of different diamonds were measured, e.g. RS55, RS51, RS01 (Rio Soriso, Brazil). The focus was on so-called cloudy diamonds with inclusions that may be so numerous that the brilliance of the diamond is impaired. The size of the inclusions can vary reaching small sizes, below the micron size. Due to the small size of the inclusions, a sub-micron sized beam was used. As an example, **Figure 2** shows 2D XRF overview maps for several inclusions with elements Ca, Ni, Fe, Sr-Kα. Here, Fe is mainly associated with Ni, Mn, Ti, Cr, and a distinct Ca /Sr rich hotspot can be observed. Some of the Fe-rich inclusions show a “ring” structure (red square indicated in **Figure 3 (right)**), representing a core (bright colour) and a corresponding rim (darker colour). Concentrations resp. elemental intensities vary between core and rim, indicating elemental diffusion from the inner parts to outer parts. The ring structure can be an indicator for the presence of fluid inclusions, which will be further studied by sub-micron resolution scanning-XRF measurements.

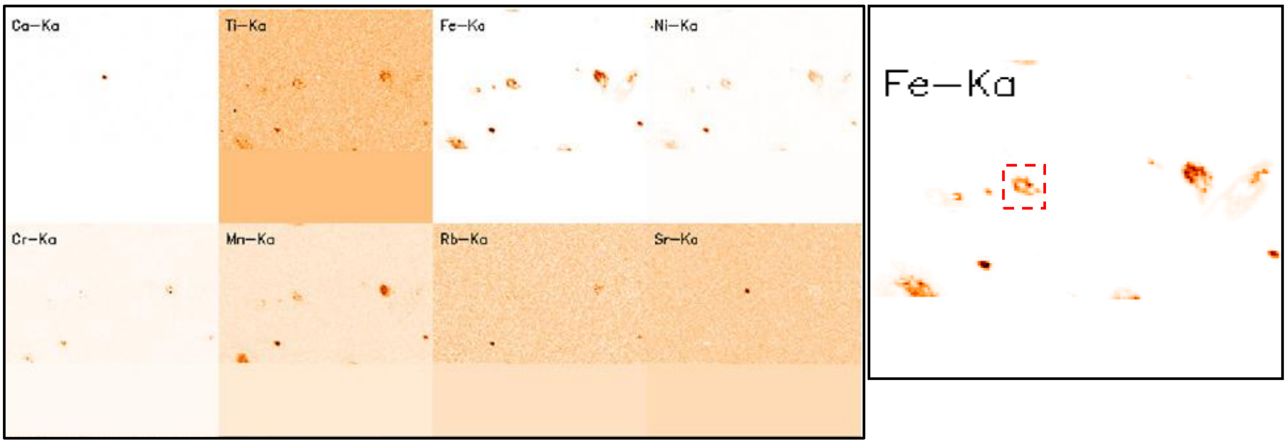

Figure 2. Left: 2D overview XRF map of a cloud of inclusions in diamond RS55_sl1 (Ca, Ti, Fe, Ni, Cr, Mn, Rb, Sr-Kα). The scanned area is 60x60 μm^2. Right: The dashed red square shows a ring structure indicating probably a fluid inclusion, with low Fe concentration in the center and higher intensity in the surrounding area.

References

[1]. B.H. Scott Smith, Danchin, R. V., Harris, J. W. & Stracke, K. J. in “*Kimberlites I: kimberlites and related rocks* “(ed. Kornprobst, J.) 121-142 (Elsevier, Amsterdam, 1984).
[2] R.O. Moore, & Gurney, J. J. *“Pyroxene solid solution in garnets included in diamonds*”. Nature 318 (1985) 553-555.
[3] B. Harte, Harris, J. W., Hutchison, M. T., Watt, G. R. & Wilding, M. C. in *“Mantle Petrology: Field Observations and High Pressure Experimentation: A tribute to Francis R. (Joe) Boyd”* (eds. Fei, Y., Bertka, C. M. & Mysen, B. O.) 125-153 (The Geochemical Society, Houston, 1999).