ESRF	**Experiment title:** *Non-destructive compositional and structural investigations of inclusions in sub-lithospheric diamonds*	**Experiment number**: CH 1780
Beamline:	**Date of experiment**: (long term) from: July 2004 to: August 2005	**Date of report**: 31 August 2005
Shifts: 42 (until now)	**Local contact(s)**: Dr Rémi Tucoulou Dr Sylvain Bohic Dr Gema Martinez-Criado	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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1. Long term project, general aspects of experimental sessions

The period of the long term project extends from July 2004 to July 2006. Until now 42 shifts are used during two experimental sessions described below.

Inclusions of diamonds from two different origins, Juina and Kankan, were measured using the confocal XRF imaging technique (single volume element measurement, line scan, slice or full 3D) and scanning XRD (single point or 2D). The investigation of the series of inclusions within different diamonds was complemented with micro-Raman studies (not mentioned in this report) and with an experimental session at HASYLAB beamline L for REEs determination (see indication "*" in the sample list of experimental session 1).

Wout De Nolf, a PhD student of Prof. K. Janssens, started the development of a program to automate the evaluation of single and series of diffraction images. Anja Szymanski joined the group of Dr. F. Brenker with the specific task to interprete the XRD images.

The evaluation and interpretation of the XRF/XRD data of both experimental sessions is still in progress.

2. Experimental sessions

2.a. Experimental session 1 (28 January – 5 February 2005, 21 shifts)

Participants : Rémi Tucoulou, K. Janssens, L. Vincze, F. Brenker, B. Vekemans
Topic : identification of inclusions in diamonds
Experimental set-up : confocal XRF imaging base of polycapillary lenses, complementary micro-XRD where necessary; 28 keV, beamsize typically 2 μm (V) × 10 μm (H), polycapillary acceptance 22 μm (Au-L).
Overview :

RS68-diamond			
	RS68-C	multiphase + walstromite	**3D-XRF + 2D diffractionmap** *
	RS68-E	walstromite	P (XRF + XRD) *
	RS68-G	calcite	P (XRF + XRD)
	RS68-F	calcite ?	P (no XRF response, XRD)
RS35-diamond			
	RS35-B	calcite	**3D-XRF**, P (XRF + XRD) *
	RS35-A2	walstromite	line-scans
	RS35-C	calcite ?	P (XRF)
	RS35-A	walstromite	P (XRF, XRD)
RS37 diamond			
	RS37-A	walstromite	**3D-XRF + 2D diffractionmap** *
	RS37-small	?	P (XRF, XRD)
	RS37-crack	Fe-rich	P (XRF)
RS63 diamond			
	RS63-B	calcite polished to the surface	slice through inclusion (XRF)
RS53 diamond			
	RS53-C	Al2O3 or (Mg)O ?	no XRF, XRD line scans
	RS53-B	not well defined by Raman	no XRD signal
RS56 diamond			
	RS56-B	?	no XRF signal
	RS56 Fe-Ni	magnetite from Raman	slice through inclusion (XRF)
			P (XRF, XRD)
			XRD map on subarea 5
	RS56-E	magnetite	P (XRF, XRD)
	RS56-C2	strong Fe signal	P (XRF, XRD)
	RS56-F	?	P (XRF, XRD)
	RS56-G	low Z material	no XRF signal
RS69 diamond (RS69C: trapped multiphase melts or fluids)			
	RS69-C1	magnetite	P (XRF)
	RS69-C2	?	line scans (XRF, XRD)
	RS69-C3-4	-	no XRF signal
	RS69-C5	?	slice through inclusion (XRF)
			P (XRF)
	RS69-C9	black inclusion	P (XRF)
	RS69-C10	?	**3D-XRF**
	RS69-C13	Zn-rich + Ca	P (XRF)
	RS69-C14	?	P (XRF)
	RS69-C[15-18]	fluid inclusions ?	P (XRF)

"P" indicates single point measurements
"*" indicates additional measurements for REE determination (capillary optics, 30 micron polychromatic X-ray beam) performed in June 2004 at HASYLAB beamline L.

2.b. Experimental session 2 (16-24 June 2005, 21 shifts)

Participants : Sylvain Bohic, Gema Martinez-Criado, K. Janssens, L. Vincze, F. Brenker, Anja Szymanski, B. Vekemans

Topic : identification of inclusions in diamonds

Experimental set-up : confocal XRF imaging base of polycapillary lenses, complementary micro-XRD where necessary; 28 keV, beamsize typically 2 μm (V) × 10 μm (H), polycapillary acceptance 22 μm (Au-L).

Overview :

"P" indicates single point measurements

KK106 diamond			
	KK106-f	?	line scan (XRF, XRD)
	KK106-g	red inclusion	line scan (XRF, XRD)
	KK106-h	?	no XRF signal, XRD line scan
	KK106-c	garnet	no XRF signal, XRD line scan
	KK106-d	single crystal ?	slice through inclusion (XRF)
RS36 diamond			
	RS36-a	?	slice through inclusion (XRF)
	RS36-b	?	no XRF signal, P (XRD)
RS43 diamond			
	RS43-a	Fe-rich phase	P (XRF, XRD) Slice through inclusion (XRF) + XRD map
	RS43-B	not possible to find	
	RS43-D	no XRF signal	
RS66 diamond			
	RS66-D	Fe-rich	P (XRF, XRD)
	RS66-E	Fe-rich	P (XRF, no XRD)
	RS66-A	40 micron	slice through inclusion (XRF) + XRD line scan
	RS66-A2	?	P (XRF)
RS65 diamond			
	RS65-B	?	slice through inclusion (XRF) + XRD map
RS58 diamond			
	RS58-a	?	no XRF/XRD signals
KK200 diamond			
	KK200-3	multiphase	**3D-XRF** + XRD map
	KK200-8	Pb	XRD line scan
	KK200-4	REEs !	**3D-XRF**

3. Planned experimental sessions

High resolution local X-ray fluorescence tomography are planned to study reaction volumes within composite diamond inclusions. These high-resolution studies will require the installation of the new generation of polymer CRLs with sub-micron capabilities. These lenses were manufactured by the Forschungszentrum Karlsruhe and acquired by the MiTAC group.

4. Publications

- L. Vincze, B. Vekemans, F. E. Brenker, G. Falkenberg, K. Rickers, A. Somogyi, M Kersten, and F. Adams; "Three-dimensional trace element analysis by confocal X-ray microfluorescence imaging"; Analytical Chemistry 76 (22), 6786-6791, 2004.
  Abstract. A three-dimensional (3D) variant of scanning micro X-ray fluorescence (XRF) is described and evaluated at the ID18F instrument of the European Synchrotron Radiation Facility (ESRF). The method is based on confocal excitation/detection using a polycapillary half-lens in front of the energy dispersive detector. The experimental arrangement represents a significant generalization of regular twodimensional (2D) scanning micro-XRF and employs a detector half-lens whose focus coincides with that of the focused incoming beam. The detection volume defined by the intersection of the exciting beam and the energy dependent acceptance of the polycapillary optics is 100-350 μm^3. Minimum detection limits are sub-ppm and sensitivities are comparable with regular scanning XRF. Next to the reduction of in-sample single/multiple scattering, the set-up provides the possibility of sample depthscans with an energy dependent resolution of 10-35 μm in the energy range of 3-23 keV, and the possibility of performing 3D-XRF analysis by simple XYZ linear scanning. This provides a suitable alternative to X-ray fluorescence tomography. The method is illustrated with results of the analysis of solid inclusions in diamond and fluid inclusions in quartz.
- B. Vekemans, L. Vincze, F. E. Brenker, F. and Adams; "Processing of three-dimensional microscopic X-ray fluorescence data"; J. Anal. At. Spectrom., 19 (10), 1302 – 1308, 2004.
  Abstract. A novel polycapillary based confocal X-ray fluorescence (XRF) technique was applied for the first time at the ID18F beamline of the ESRF to obtain directly 3-dimensional (3D) compositional information of an inclusion inside a natural diamond sample (KK200). Preliminary analysis of the results on the basis of the trace elements Sr, Y/Zr, and Th suggest three phases, two of which were identified by earlier micro-Raman spectroscopy as larnite (β-Ca_2SiO_4) and $CaSiO_3$-walstromite, two minerals with significantly different Ca content. In order to support this multiphase model for the investigated inclusion the data set was analysed combining the conventional multivariate method of PCA and K-means clustering procedure after application of instrument specific routines such as spectral evaluation and normalization. Through the knowledge of the full spatial 3D structure of the different phases, it was possible to correct for absorption of the fluorescent radiation in the different phases of the inclusion and the surrounding diamond.
- F. E. Brenker, L. Vincze, B. Vekemans, L. Nasdala, T. Stachel, M. Kersten, A. Somogyi, C. Vollmer, F. Adams, W. Joswig & J. W. Harris; "Evidence for a Ca-rich lithology in the Earth's deep upper mantle"; Earth and Planetary Science Letters, 2005, in press.
  Abstract. Earth's deep convecting upper mantle is believed to represent a rather homogenous geochemical reservoir of spinel or garnet lherzolite with primitive major element and moderately depleted trace element composition. Only where subduction occurs is this homogeneity disrupted by a suite of rocks ranging from eclogites/garnet pyroxenites (former oceanic crust) to residual harzburgites. In addition to these well documented peridotitic and metabasaltic rocks we have now discovered the presence of a chemically distinct reservoir in the deep upper mantle. In situ structural analyses (micro X-ray diffraction and micro Raman spectroscopy) and three-dimensional trace element mapping (confocal micro X-ray fluorescence imaging) of polyphase inclusions in a diamond from Guinea that formed at about 300-360 km depth reveal the existence of a deep Ca-rich source, in the absence of several common mantle minerals, like olivine, garnet and Ca-poor pyroxene. This reservoir may represent metasomatized oceanic lithosphere (rodingites, ophicarbonates) or metamorphosed carbonaceous sediments.
- R. Terzano, M. Spagnuolo, L. Medici, B. Vekemans, L. Vincze, K.Janssens, P. Ruggiero; "Copper stabilization by zeolite synthesis in polluted soils treated with coal fly ash"; Environmental Science and Technology, 39(16), 6280-6287, 2005.
  Abstract. This study deals with the process of zeolite formation in an agricultural soil artificially polluted by high amounts of Cu (15 mg of Cu/g of soil dry weight) and treated with fused coal fly ash at 30 and 60 °C and how this process affects the mobility and availability of the metal. As a consequence of the treatment, the amount of dissolved Cu, and thus its mobility, was strongly reduced, and the percentage of the metal stabilized in the solid phase increased over time, reaching values of 30% at 30 °C and 40% at 60 °C. The physicochemical phenomena responsible for Cu stabilization in the solid phase have been

evaluated by EDTA sequential extractions and synchrotron radiation based X-ray microanalytical techniques. These techniques were used for the visualization of the spatial distribution and the speciation of Cu in and/or on the neo-formed zeolite particles. In particular, micro XRF (X-ray fluorescence) tomography showed direct evidence that Cu can be entrapped as clusters inside the porous zeolitic structures while *í*-XANES (X-ray absorption near edge structure) spectroscopy determinations revealed Cu to be present mainly as Cu(II) hydroxide and Cu(II) oxide. The reported results could be useful as a basic knowledge for planning new technologies for the on site physicochemical stabilization of heavy metals in heavily polluted soils.

5. Conferences and Meetings

2005 Denver X-ray Conference (DXC2005), Colorado Springs, Colorado, USA (1-5 August 2005)

- *Towards, 3D Trace Element Microscopic XRF Analysis*; B. Vekemans, L. Vincze, K. Janssens. invited Lecture.

ESRF-CNRS Workshop on "Synchrotron Radiation in Art and Archaeology", 9-11 February 2005, Grenoble, France

- *SR Techniques: new and future applications*, K. Janssens, opening lecture.

AIRMON05 - Fifth International Symposium on Modern Principles of Air Monitoring (including biomonitoring), Loen, Norway , June 12-16, 2005

- Speciation of Ni in the Monchegorsk aerosol, K. Janssens, plenary lecture