Intermediate report #2
ESRF LT project EC-70
In situ (sub)micro-fluorescence and-diffraction of mantle fluids
and deep-Earth high pressure phases trapped in diamond

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A. Introduction

Based on the low density of the continental crustal and the resulting buoyant forces during subduction it was assumed that it should be impossible to bring this kind of material very deep into the mantle. Microdiamonds, 10-80 µm in size, discovered during the 1980's within metomorphic rocks related to continental collisions, clearly refute this assumption, suggestion that material from the continental crust has been subducted to at least 150 km deep and later incorporated into mountain chains via tectonic exhumation. However, any evidence for deeper crustal recycling of this material into the Earth´s mantle is still very limited.

Natural diamonds provide <u>the only chemically inert container</u> to bring samples from different depth regions of our Earth up to the surface. In very rare cases these diamonds carry recycled fluids or even ultra deep mantle material (>670km depth). The inclusions provide direct information on the physical and chemical conditions in the deep Earth down to the lower mantle.

In the long-term project we exploit a combination of 3D microbeam XRF and of microbeam XRD to obtain so-far inaccessible *in situ* information on the <u>composition of the fluids and the structure and composition of mineral phases</u> present in these extraordinary inclusions in diamonds of various origin. The captured fluids provide us with unique information on global recycling processes of various elements along wet subduction zones. Sample locations for deep diamonds are rare, but enclose most of the largest subduction zone systems.

The use of advanced micro- and nanoanalytical methods allow to examine these diamonds in detail and to identify the type and nature of the multiphase inclusions that are present inside small and large diamonds, thereby yielding information about the pathway in which carbon and water can be subducted to mantle depths and eventually returned back to earth's surface.

Diamonds from Finsch and Koffiefontein mines, South Africa which originated in the shallow Upper Mantle (<200 km depth) have been investigated in the first year. Both relatively large inclusions (10-100 µm) to quite small ones (a few micrometers in diameter) were examined. In the second project year, a number of diamonds having deep sources down to the lower mantle (>670km) from the Juina mine in Mato Grosso, Brazil showing fairly large inclusions (up to 20 µm in diameter) were examined with exciting results (see below).

Both types of diamond samples containing fluids or deep mantle material are extremely rare. Due to our successful previous work, we have access to unique sample material provided by deBeers (Dr. Jeff Harris) and by a private mining company (Dr. F. Kaminsky).

In the table below an overview is given of the measurement periods about which results are reported.

Scheduling period	Beamline(s)	Shifts	Results expected (cf. Milestones, §2)
2008 /I	ID18F	15	**Milestone 5** : 2D/3D elemental analysis by confocal XRF imaging and scanning μ-XRD studies for structural and **chemical analysis on small single fluid inclusion from clouds** in diamonds from Finsch and Koffiefontein (South Africa), previously examined using the ID22NI nanoprobe by elemental XRF mapping only. **Experimentalists**: B. Vekemans, T. Schoonjans, J. Jaroszewicz, K. Janssens, F. Brenker
2008 /II	ID18F	21	**Milestone 6** : 2D/3D elemental analysis by confocal XRF imaging and scanning μ-XRD studies for structural and **chemical analysis on single fluid inclusion from clouds** in **Juina diamonds originating from the lower mantle** (depth > 670 km) from the alluvial deposit in Mato Grosso, Brazil**. -** emphasis on 2D XRD to identify/confirm water/carbon bearing minerals **Experimentalists**: B. Vekemans, T. Schoonjans, J. Jaroszewicz, K. Janssens, T. Eichner

B. Instrumentation and methods employed.

B.1 Confocal XRF and XRD (ID18F)

In the figure below the mode of operation during diamond inclusion analysis at ID18F is illustrated. A high energy X-ray microbeam is generated by monochromating the primary beam produced in the ID18 undulator to 28 keV. Beam focussing is realized by means of Al and SU8-CRL lenses. The microbeam will excite a tunnel of radiation inside the (large) diamond samples in which also elastic and inelastic scattering occurs.
XRD images are recorded in transmission by means of a Mar CCD detector on a moveable stage; on this stage also a X-ray camera (SensiCam) in mounted for recording of absorption images. Finally, an energy-dispersive detector, mounted at 90^o to the incoming radiation, collected XRF signals emitted by the irradiated material.
Scanning of the samples through the microbeam while simultaneous XRD and XRF datacollection takes place allows to record correlated elemental and crystal phase distributions. Software developed by the LTP proposers is used to reduce the resulting data sets into phase and element maps.

A paper on the operation of the setup is due to appear in 2009:

W. De Nolf, J. Jaroszewicz, R. Terzano, O. Lind, B. Salbu, B. Vekemans, K. Janssens, G. Falkenberg, "X-ray microscopy using synchrotron X-ray powder diffraction with double multilayer and single crystal monochromators", Spectrochimica Acta B (2009), accepted for publication. [Proceedings ICXOM-19 delayed due to journal backlog re. special issues].

In order to reduce the amount of scattered radiation collected by the XRF detector and limit the depth in the sample from which fluorescent signals are recorded, a polycapillary lens is placed between sample and detector. After proper alignment, this allows for a depth selective mapping of trace element distributions at and below the surface of the diamond.

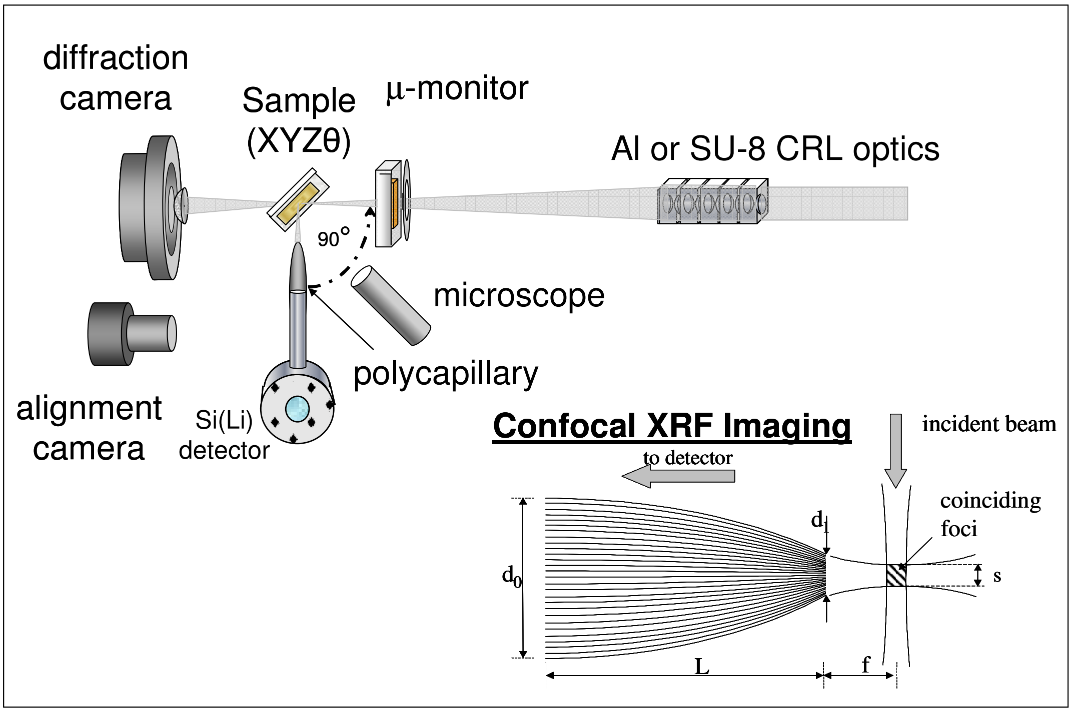


Fig. 1. Experimental setup at ID18F during confocal μ-XRF/μ-XRD experiments

B. Raman spectroscopy

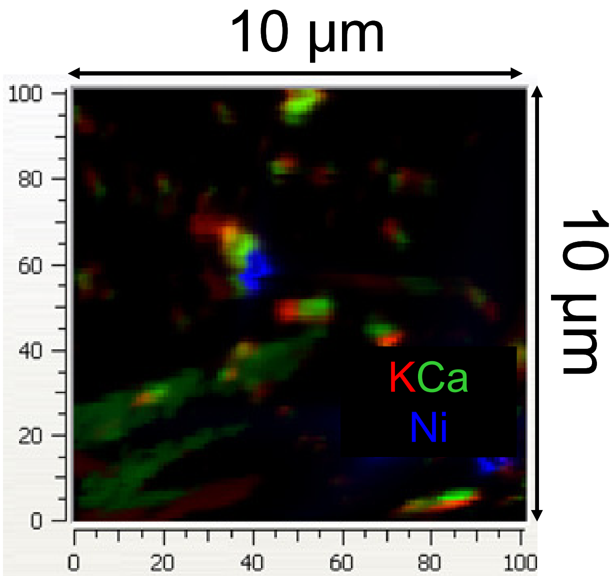
Raman analysis were carried out most of the inclusions prior to XRF/XRD analysis. Raman analyses were carried out by means of a Jobin Yvon LabRam HR system (focal length 800 mm) equipped with Olympus BX41 optical microscope and a Renishaw RM-1000 μ-Raman spectrometer. Both instruments operate with a grating of 1800 grooves/mm in the optical path, and Si-based charge-coupled device detectors. Spectra were excited with a red He–Ne (633 nm) and a green YAG (532 nm) Laser. The wavenumber accuracy was about 0.5 cm−1 and the spectral resolution 0.8 cm−1. The lateral and depth resolution was on the order of several to a few tens of μm depending on the actual sampling depth.

C. Results obtained during ESRF0408 and ESRF1008

During these two measurement sessions, a series of deep earth diamonds from Juina, Matto Grosso, Brazil, were examined. Prior to analysis at ESRF, Raman spectroscopy was used to pre-characterize and pre-select a number of inclusions. On the basis of the Raman data, hypothesis were formulated regarding the presence of minerals and these were verified/nuanceted/expanded upon by means of XRF/XRD point measurements and maps. Also some additional measurements were performed to complete the data set obtaind during ESRF1107 on Koffiefontein diamonds at ID22NI.

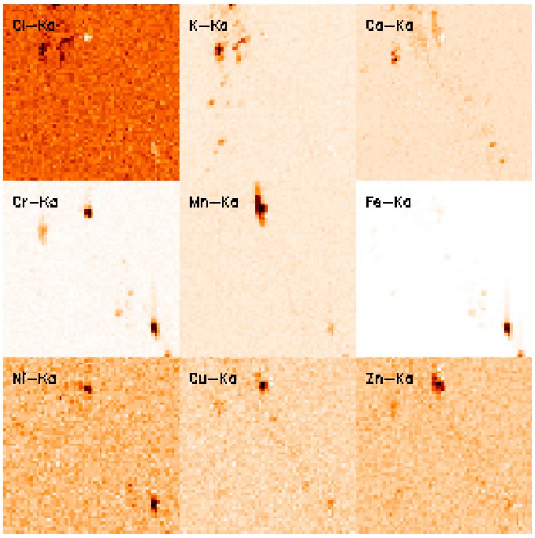
The most noteworthy observations are described below.

C.1 XRD microcharacterization of inclusions previously analysed by n-XRF (Koffiefontein)



As already mentioned in the previous report (spring 2008), at the end of the first project year, we employed the ID22NI nano-probe to record the submicroscopic distribution of trace elements in/near a series of very small fluid inclusions in *Koffiefontein* diamonds in a number of areas of 10x10 µm^2 wide. The fact that a nanometric X-ray beam is available at ID22NI allow to record detailed maps of the distribution of key elements, such as K, Ca and Ni, corresponding to the three categories of "inclusions" previously established at a coarser resolution level (ID18F – see Milestone 3, previous report). Some of the results obtained are shown in the adjacent figure.

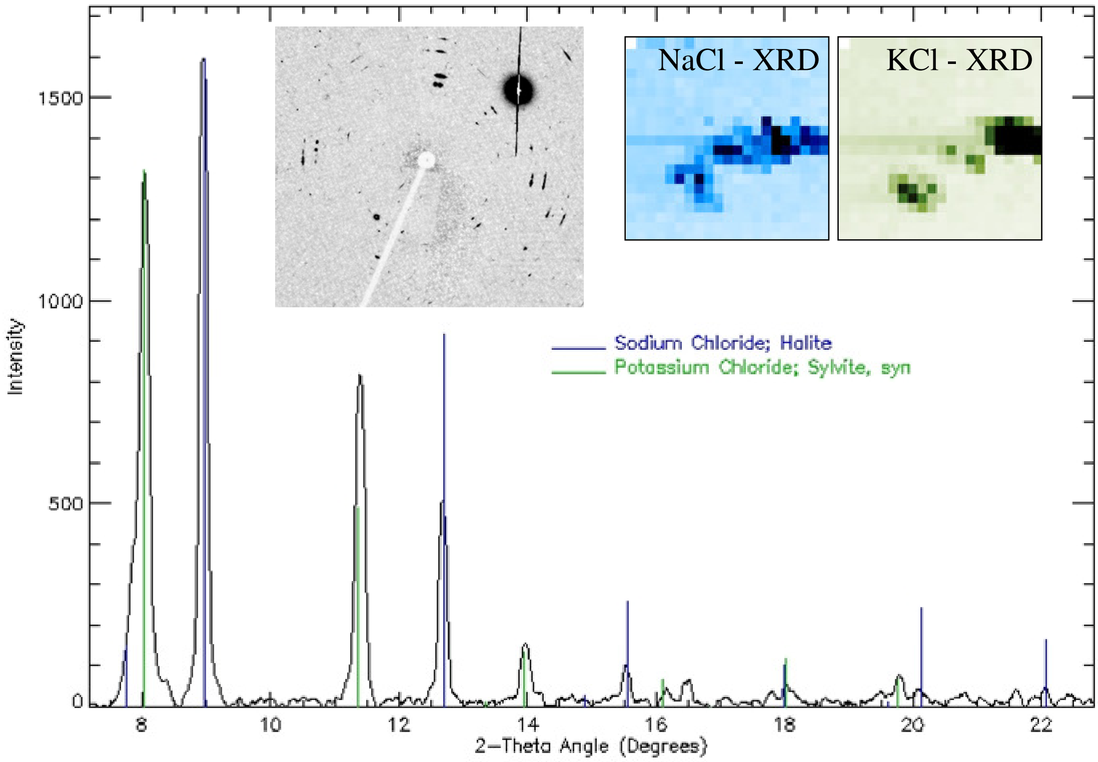
Since only elemental information was obtained from the ID22NI measurements, the same diamond 'needle' of ca 100 µm diameter in which the mapped inclusions were present, was examined using µ-XRD at a coarser resolution at ID18F. For this purpose, a 1x2 µm X-ray microbeam (E=28 keV) was generated by means of SU8-CRL lenses. Since the submicroscopic maps obtained at ID22NI were collected at a position within a large cloud of inclusions that could not be optimally recorded at the nano-probe station, a large effort had to be spent to relocalise the inclusions at the ID18F facility.



Nevertheless these efforts were not without result, as in the resulting XRF and XRD data indications for the presence of a number of Cl-containing salts/minerals could be found.

In the adjacent series of maps, covering an area of 50x50 µm^2, clearly the occurrence of a series of 1-5 µm diameter inclusions with quite a different chemical make-up can be discerned, similar, albeit at a reduced resolution, as is the case in the ID22NI data. Since the cloud of inclusions imaged here was

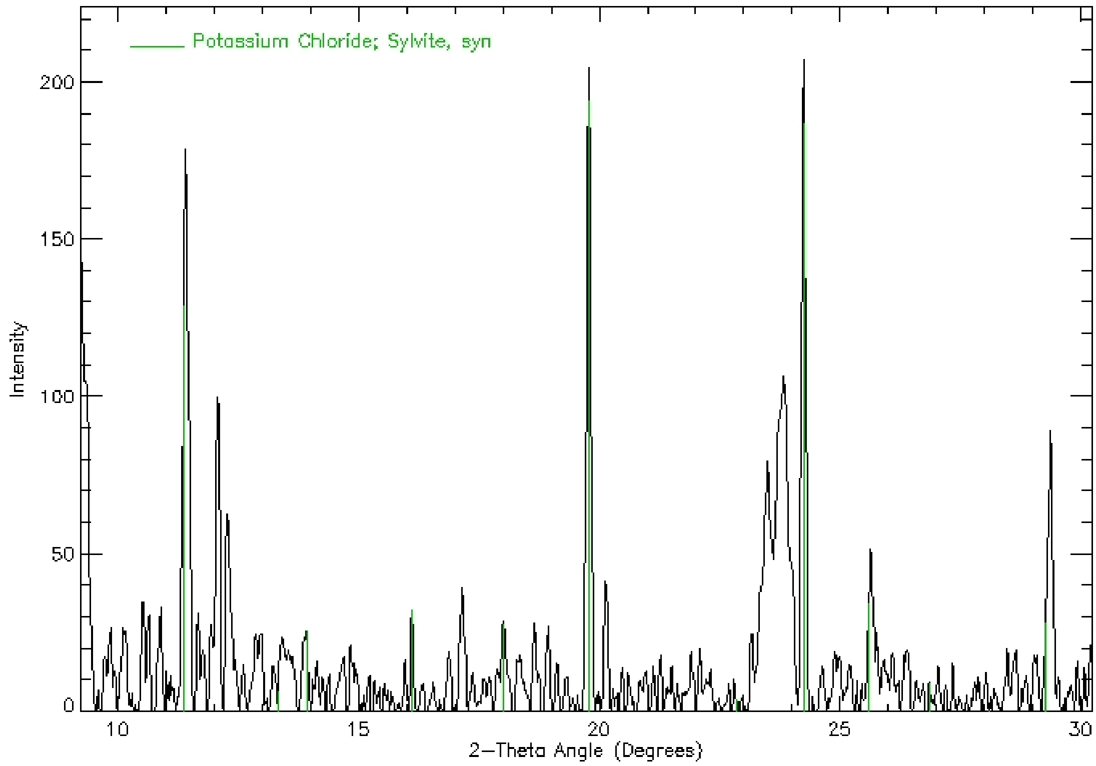
situated very close to the diamond surface, also signals from low-Z elements such as Cl could be collected with reasonable efficiency.
Some of the XRD results are summarized in the following figures. While collecting an scanning XRF/XRD map over a longitunal series of inclusions, partial arcs of diffraction patterns overlapping with the PDF-data of NaCl (rock salt) and KCl (sylvite) were observed. The resulting maps are also shown in the figure below and reveal (even though the resolution in them is insufficient) that adjacent small inclusions contain either small series of NaCl or KCl microcrystals with slightly variable orientation relative to the primary beam. This suggests that inside these inclusions, these salts have crystallised parallel to parts of the curved wall of the inclusions.

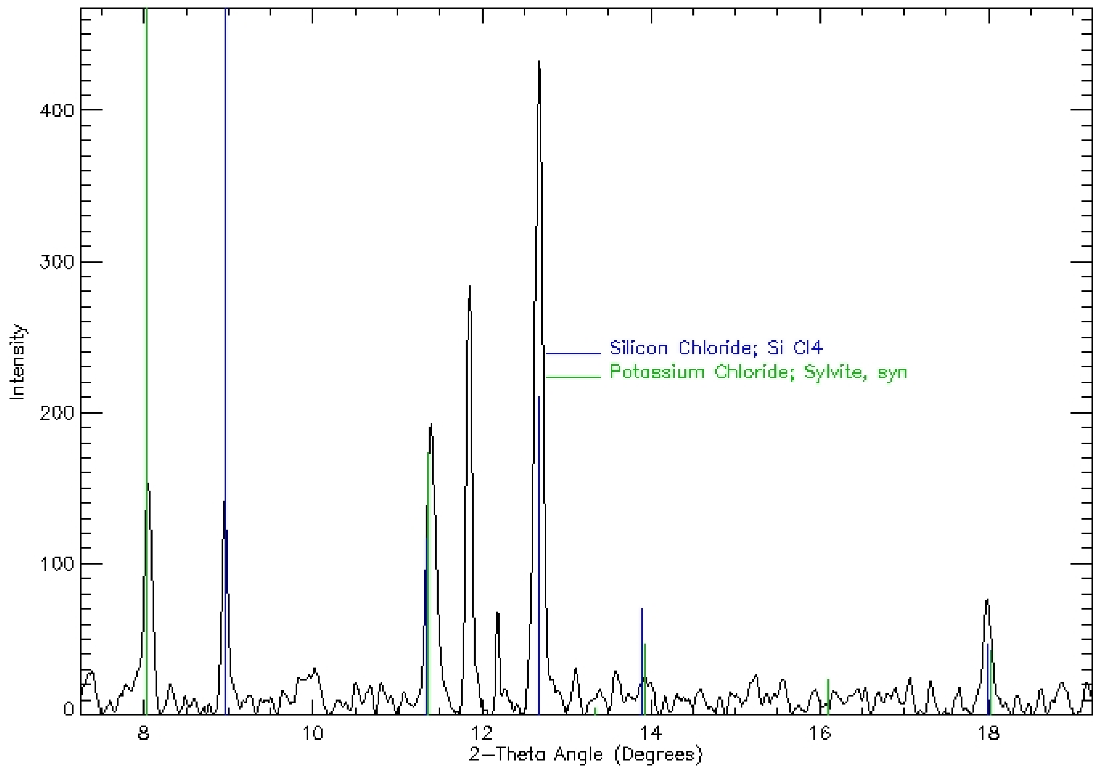


In other inclusions, the presence of sylvite (KCl) by itself, sometimes in the presence of silicon-tetrachloride ($SiCl_4$) was observed. This is suggestive of a prevalence of Cl^- among the anions in the fluids present in these small inclusions.

Alkali brines are well known as fluid inclusions in diamonds having a shallow origin (<150 km). Thus our findings in cloudy Koffiefontein diamonds reproduces the expected record. Beside details of the diamond forming fluids which can be extracted from the phases present and the chemical distribution, this observation clearly demonstrate that the analysis method employed here is capabable to detect even the smallest brine inclusions.

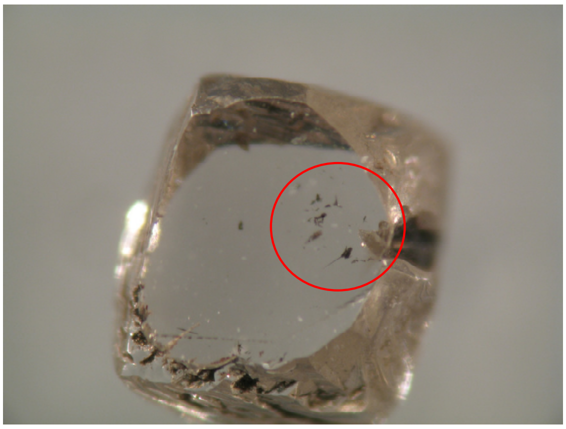
Confrontation of the results obtained in year 1 and 2 of the LTP (as detailed below) **now allows us to compare lower mantle fluids with those of the shallow mantle directly**. Our data clearly shows that deeper mantle fluids (Juina, Kankan) differ significantly from fluids of the shallow mantle (Koffiefontein, Finsch). Fluids in the shallower diamonds contain Cl-rich phases while F- and REE-rich phases appaer to dominate the inclusion paragenesis of deep Earth materials (see below).





C.2 Inclusions in Diamond MR#6 (Juina).

In Diamond MR#6, a cloud of inclusions, surrounded by dark-coloured concoidally shaped areas is present, somewhat similar to the inclusions studied in the previous project year. We previously could detect a concentration of trace elements in these areas from which the hypothesis could be formulated that nanocrystals have formed here in crack-like openings in the diamond lattice that surrounds each inclusion.



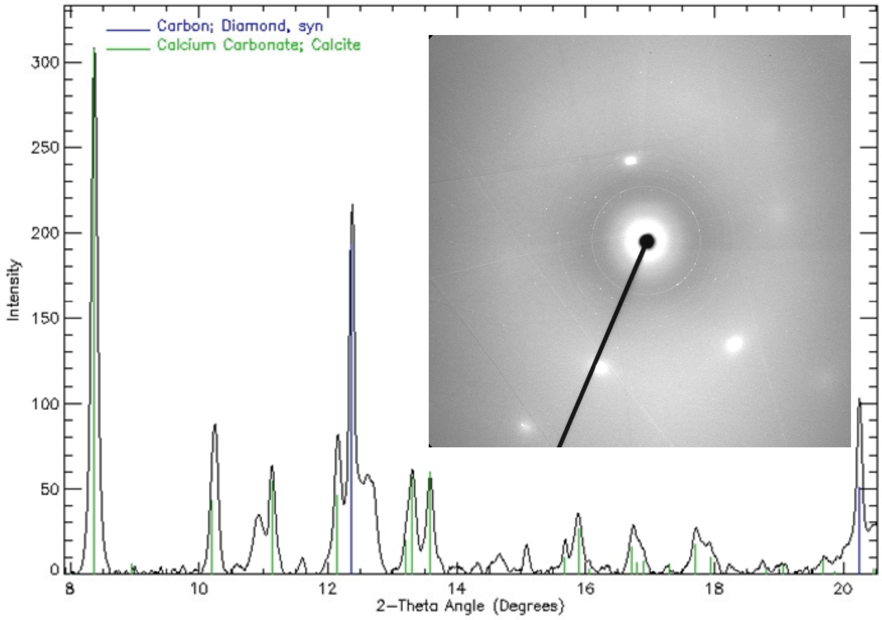
Especially inclusions #6.3 and #6.4 revealed interesting information. A more detailed photograph of inclusion #6.3 also shown, indicating the size of the central, transparent part of the inclusion and of the dark 'wings'.

The plots shown below summarize the information revealed by XRD:
- in inclusion #6.3 the presence of $K(Mg,Al)_{2.04}(Si_{3.34}Al_{0.66})O_{10}(OH)_2$ (JCPDS 40-0020) was observed while
- in inclusion #6.4, the occurrence of $CaCO_3$ (calcite, JCPDS 83-0577) was revealed.

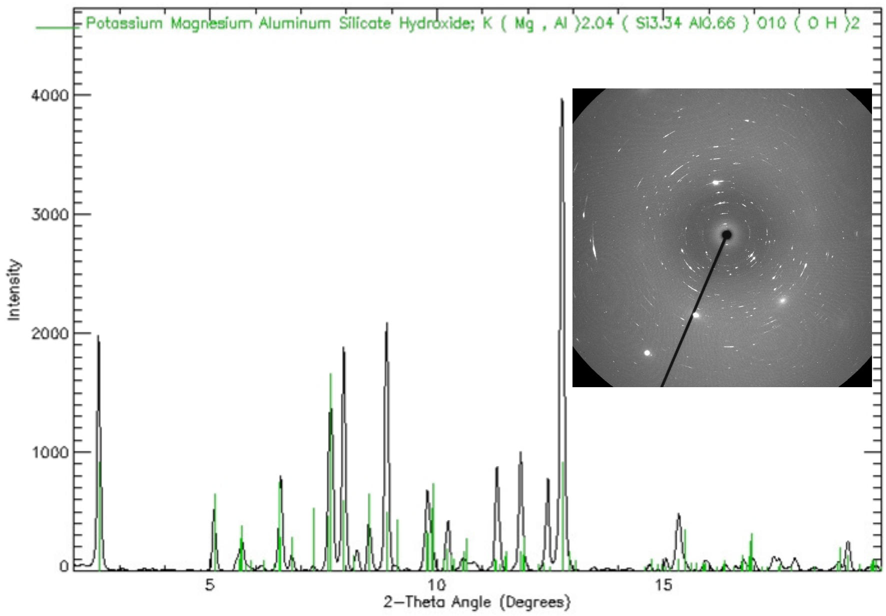
The potassium magnesium aluminium silicate hydroxide phase in inclusion #6.3 is a material that is formed at high pressure and temperature. This observation is also consist with the Raman data available for this inclusion, showing a prominent peak at 1614 cm^{-1} (hydroxides).

The presence of the calcite mineral in inclusion #6.4 is in good agreement with our previous findings in Juina diamonds of the presence of associations of olivine+walstromite-structured $CaSiO_3$+calcite and the supposition that the origin of deep mantle carbonates is due to the subduction of carbonate-rich crustal or lithospheric materials.

Example of a diffractogram collected from inclusion #6.3



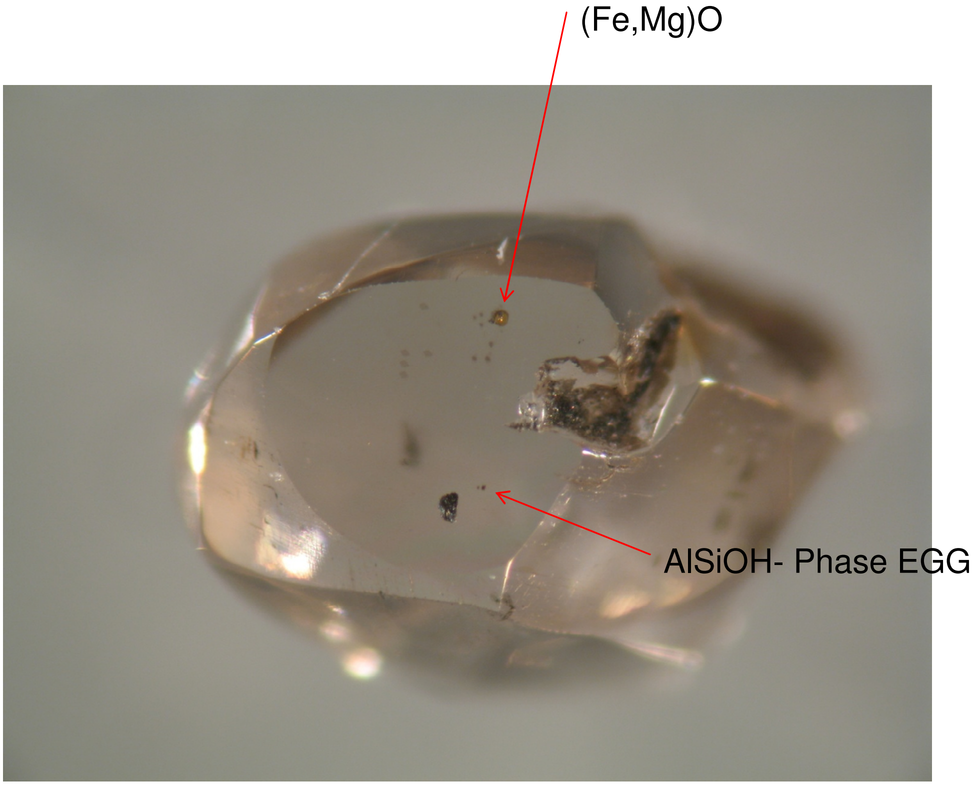
Example of a diffractogram collected from inclusion #6.4



Carbonates are typical constituents of fluid inclusions found in diamonds having a shallow origin. Together with a high pressure K Mg Al Silicate hydroxide it is a further indication of deep fluid recycling within the Earth.

C.3 Inclusions in Diamond MR#12 (Juina).

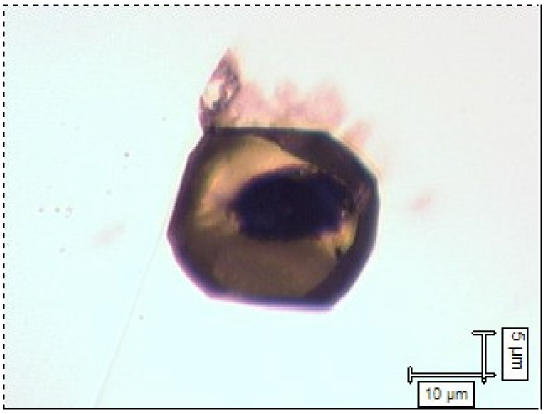
This diamond proved to be very interesting, as two well-defined and fairly large inclusions were present. A window was polished in such a way that both inclusions were as closes a possible to the surface (within 10-15 µm) so that also XRF signals from lower-Z constituents could be detected with reasonable sensitivity. The photograph below shows an overview picture of the polished area.

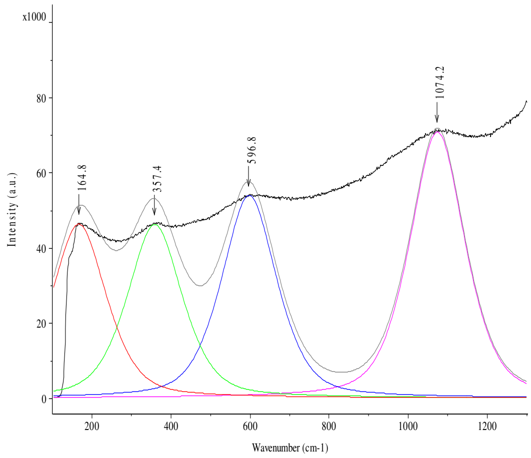


C.3.1 XRF/XRD local analysis and mapping of the Ferropericlase inclusion in Juina diamond MR#12

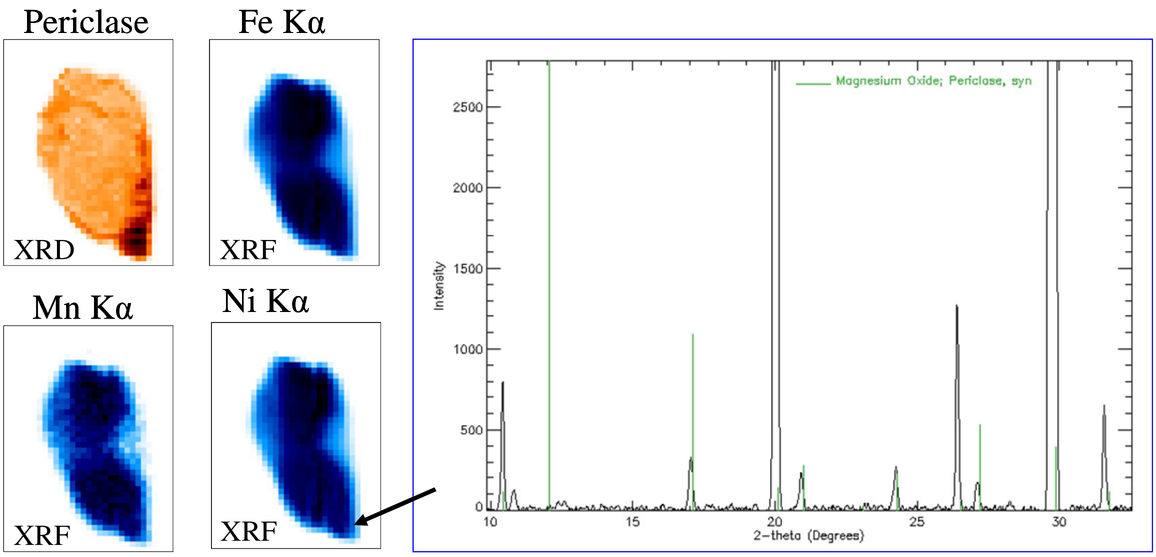
In the figure below, a micrograph of the syngenic inclusion is shown, indicating the presence of a fluid phase in contact with a microcrystal. Micro-Raman spectroscopy yielded a spectrum featuring peaks at 596.8 and 1074.2 cm^{-1} that fit reasonably well with literature values for bulk MgO of 595.719, and 1096 cm^{-1} and of nano crystals of MgO (592 and 1088 cm^{-1}). This is suggestive of the presence of a (ferro-)periclase phase.

The MgO-FeO system as attracted the interest of scientists for many decades. Periclase (MgO), Wuestite (FeO) and their solid solutions are of fundamental importance in geoscience because (Mg,Fe)O is believed to be one the main components of the Earth's lower mantle. It is the second most abudant phase after $(Mg,Fe)SiO_3$ perovskite. MgO is stable in the NaCl-like structure up to pressures of at least 227 GPa and its elastic properties at high pressures are well known; this MgO is often used to calibrate internal pressure at SR high-pressure experments. The structure can also be calculated from first principles with high accuracy.





In the figures below, high-resolution (1 µm step) XRF and XRD maps of inclusion#12 (ca 35 µm in height) showing the distribution of periclase (similar to MgO, JCPDS 45-0946, cubic, a = 4.211 Å) and the minor constituents Mn, Fe and Ni are shown, indicative of the substitution of Mg by these divalent elements in the MgO lattice. The observed diffractogram (from the lower right corner of image) is also shown below. The observed shift (corresponding to a lattice parameter a of 4.230 Å) is consistent with the presence of a $MgO_{0.25}$:$FeO_{0.75}$ solid solution (a_{FeO} = 4.296 Å).



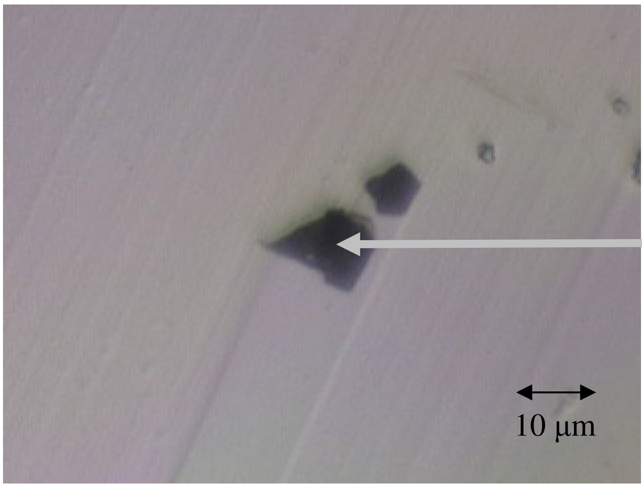
Coinciding with periclase phase, in some locations also the diffraction patterns of chamosite: [$(Fe,Al,Mg)_6(Si,Al)_4O_{10}(OH)_8$ (JCPDS 21-1227)] and phlogopite [$KMg(Si_3Al)O_{10}F_2$ (JCPDS 16-0344)] were observed (see below).

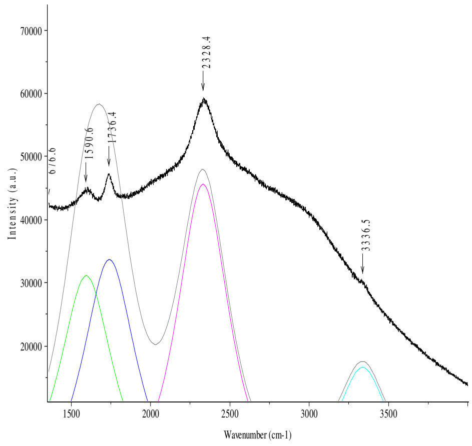
Ferropericlase found as inclusion in diamond is indicative for a lower mantle origin of the diamond host. The occurrence of two F,OH-bearing mantle phases within the same inclusion indicates that these phases or their respective higher pressure equivalents were captured in the lower mantle as well. Although it is not expected that the observed phases themselves are stable in lower mantle of the Earth it is a compelling evidence, that high density fluids can exist in this depth region. **This is the <u>first direct evidence</u> of the existence of high density fluids in deeper parts of the Earth which may indicate that the global fluid recycling process has an extension at least down to the upper part of the lower mantle.**

F.E. Brenker, L. Vincze, B. Vekemans, K. Janssens, G. Bulanova, "Fluid bearing phases as inclusions in super deep diamonds. Record of the Earth´s deep mantle fluid recycling?", in prep.

C.3.2 Phase Egg inclusion in diamond MR#12 (Juina).

µ-Raman spectroscopy revealed a spectrum with peaks at 1590.6, 1736.4, 2328.4 cm^{-1} (OH-stretch region), suggesting the possible presence of Phase Egg ($AlSiO_3OH$) or related minerals such as topaz-OH [$Al_2SiO_4(OH)_2$], δ-AlOOH or related high-pressure minerals in inclusions that are ca 5-10 µm in size.





The presence of phase "Egg" nanocrystals was very recently reported for the first time in ultra deep diamonds from Juina (Mato Grosso State, Brazil). Together with topaz-OH [$Al_2SiO_4(OH)_2$] and δ-AlOOH, phase "Egg" ($AlSiO_3OH$) is a hydrous phase in the Al_2O_3-SiO_2-H_2O system that has been found to be stable at successively higher pressures up to those corresponding to the lower mantle; thus these phases may be important water reservoirs in the deep mantle.

R. Wirth, C. Vollmer, F. Brenker, S. Matsyuk, F. Kaminsky, "Inclusions in nanocrystalline hydrous aluminium silicate "Phase Egg" in superdeep diamonds from Juina", EPSL, 249 (2007) 384-399.

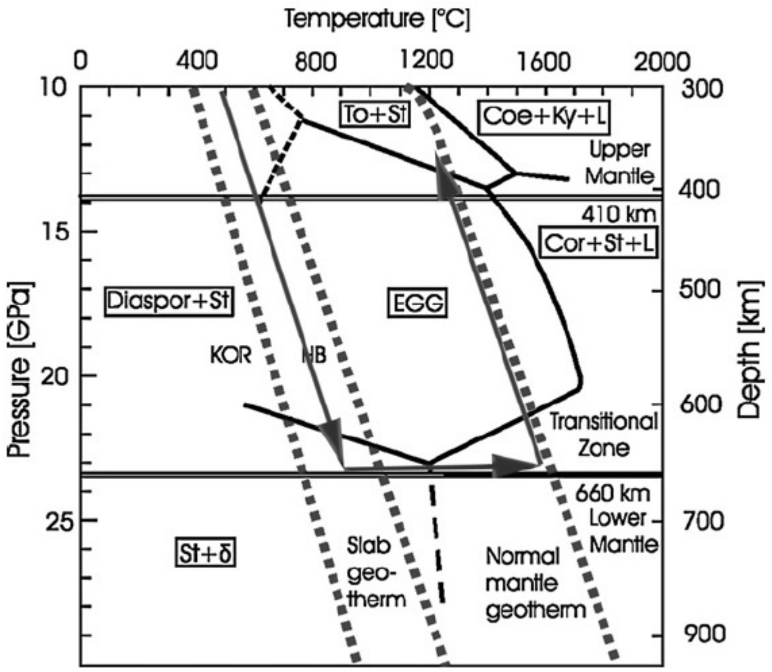
Phase Egg, $AlSiO_3OH$, is an important candidate for water reservoir in the cold slabs descending into the transition zone. It was first described by Eggleton et al. (1978) then synthesized by Schmidt et al. (1998), who report a monoclinic structure with spacegroup P21/n. It is relevant to consider it P,T stability field. Phase "Egg" was found to be stable at least up to 1273 K and 22 GPa. Two decomposition reactions were observed:
- phase Egg decomposes into δ-AlOOH and stishovite at 1273 K and above 22 GPa
- it transforms into corundum + stishovite + fluid at 25 GPa and above 1473 K.

On the basis of the confirmed presence of Phase "Egg" in nano-diamond inclusions, two hypotheses can be formulated regarding the formation of the diamond inclusions during subduction of crustal material into the mantle:
(a) first, a prograde formation can be considered in a subducted slab, following a path bounded by a cold and hot slab geotherm at the central parts of the slab. α-AlOOH (diaspor) as an Al-rich and water carrying phase and and SiO_2 phase (quartz, coesite

or stishovite) are subducted deep into the upper mantle reaching the Transition zone at 410 km (see P,T-diagram below). On its way down, in the stability field of diamond, diamond growth encapsulates diaspor+SiO_2 to form an inclusion. When approaching the 410 km discontinuity, diaspor + SiO_2 (as stishovite) react to form phase "Egg" without release of water.

(b) alternatively, a retrograde formation is also possible. Here again, diaspor+SiO2 are transported downward reaching P,T conditions of P > 23 GPa and T<1200 ^{o}C near the 600 km discontinuity, where phase "Egg" decomposes into δ-AlOOH + stishovite. Upon reaching the discontinuity, the downward movement of the slab comes to a halt and its temperature starts to equilibrate to that of the mantle at that depth. With rising temperature that finally exceeds 1200^{o}C at 23 GPa, δ-AlOOH decomposes to corundum+stishovite+fluid. At that point, it can be assumed that diamond forms and during growth incorporates corundum+SiO_2+fluid. During uplift of the diamond following a normal mantle geotherm, the inclusion composed of corundum+SiO_2+ fluid reacts to form phase "Egg" again.

While scenario (a) does not explain the observed porosity of the phase "Egg", in scenario (b) the porosity of the inclusion can be easily explained by the presence of the fluid.

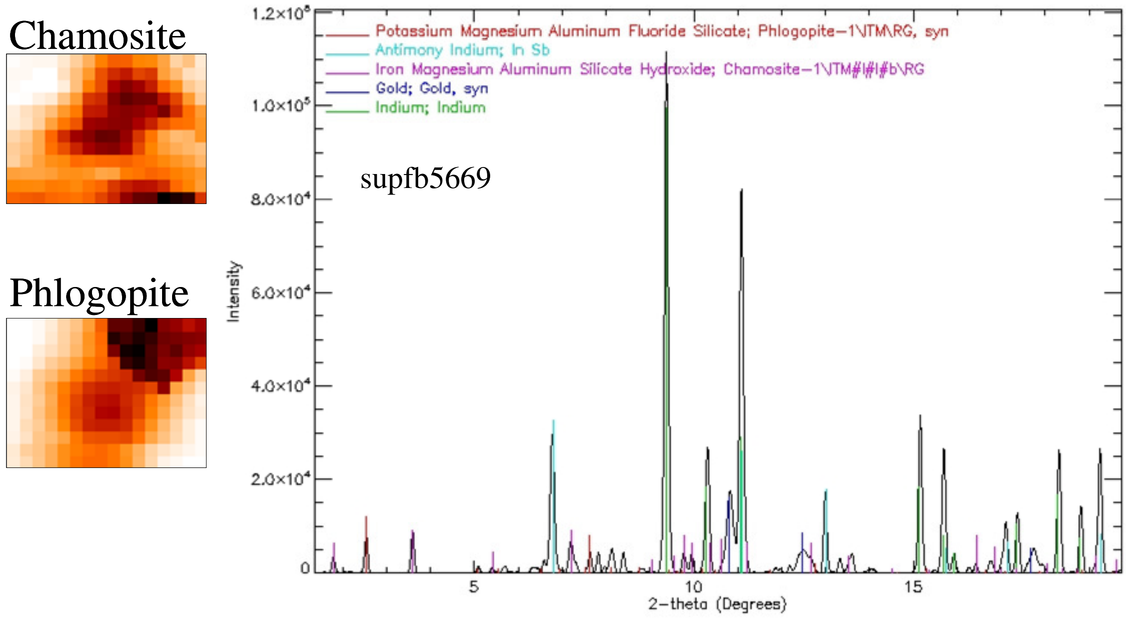


In the figure below, the main results obtained by means of XRD mapping (16x12 μm^2, step size 1 μm2) of this inclusion are summarized. Next to demonstrating the presence of SiO_2 (JCPDS 85-0798) the XRD patterns of two mica-like minerals were observed:

- Chamosite: $(Fe,Al,Mg)_6(Si,Al)_4O_{10}(OH)_8$ (JCPDS 21-1227) and
- Phlogopite: $KMg(Si_3Al)O_{10}(F,OH)_2$ (JCPDS 16-0344)

While the diffraction pattern of SiO_2 was only present in selected spots, indicating the presence of mineral grains smaller than the beam size, chamosite and phlogopite were found throughout the inclusion.

The presence of the (F,OH)-containing mineral phlogopite is consistent with our previous discovery of inclusions in deep-earth diamonds featuring the minerals fluorite and florencite while the combined presence of SiO_2 and the mica-like minerals confirms the above-mentioned hypothesis (b) about the genesis of Phase “Egg”.



Wirth et al. 2007 found Phase “Egg”, an OH-rich phase that is stable only above about 21 GPa in the lower part of the transition zone (> 500km). The sample studied here may represent the second finding of this important dense hydrous mineral. **The presence of chamosite and phlogopite in relation to a possible presence of Phase “Egg” again indicate fluid transport to unexpected depths. Furthermore it documents that the transition zone is not only capable to store enormous amount of fluids, but that at least partly dense hydrous F-bearing fluids indeed exist.**

D. Conclusions/Summary of main points

The XRF/XRD results obtained from the inclusions in diamond MR#12 support hypothesis (b) and place the origin of depth of the Juina diamonds firmly in the transitional zone of the mantle between 400 and 610 km depth. These results, together with recently published observations made on nano-inclusions in micro-diamonds all support the concept of diamond crystallization from a supercritical carbon-oxygen-hydrogen containing fluid at this depth and emphasis the role of a ‘crustal’ source of carbon. This leads to the formation of several water- and carbonate bearing phases in small inclusions in the diamonds.

The discovery of ferro-periclase inside the diamond inclusions we examined is the first direct evidence of the existence of high density fluids in deeper parts of the Earth which may indicate that the global fluid recycling process has an extension at least down to the upper part of the lower mantle.

The presence of chamosite and phlogopite in relation to a possible presence of Phase “Egg” again indicate fluid transport to unexpected depths. Furthermore it documents that the transition zone is not only capable to store enormous amount of fluids, but that at least partly dense hydrous F-bearing fluids exist.

Confrontation of the results obtained in year 1 and 2 of the LTP now allow us to compare lower mantle fluids with those of the shallow mantle directly. Our data clearly shows that deeper mantle fluids (Juina, Kankan) differ significantly from fluids of the shallow mantle (Koffiefontein, Finsch). We can conclude that F- and REE-rich phases dominate the inclusion paragenesis of deep Earth materials whereas shallower fluids contain Cl-rich phases.

E. Outlook

In year 3 of the LTP our intention is to gather more data on the chemical make-up of diamonds originating from the lower regions of the earth mantle. In particular, we will endeavour to collect more direct evidence of the presence of high pressure hydrous minerals of the phase “Egg”, topaz-OH, δ-AlOOH, phlogopite series. We hope that this will allow to support further the currently formulated hypothesis on the genesis of these type of phases.

F. Conference presentations

K. Janssens, “Analysis of materials at different length-scales” (plenary lecture), HASYLAB User’s meeting, Hamburg, Germany, 25 January 2008.

K. Janssens, “Analysis of materials at different length-scales” (plenary lecture) AXAA2008 (Australian X-ray Analysis Association meeting), Melbourne, Australia, 2-5 February 2008.

F.E. Brenker, Vincze, L., Vekemans, B., Szymanski, A., De Nolf, W., Janssens, K., Stachel, T. & Harris, J. “Detection of a REE-rich, F- and P-bearing fluid component in superdeep diamonds from Kankan (Guinea)” – 9IKC, Frankfurt, 2008.

T. Pisternick, Silversmit, G., Schoonjans, T., Brenker, F.E., Vincze, L., Vekemans, B., De Nolf, W., Janssens, K. & Harris, J. “S-XRF and XANES Analysis of Fluid-Inclusions in Cloudy Diamonds from Koffiefontein and Finsch” – 9IKC, Frankfurt, 2008.

K. Janssens, “Obtaining information on surface alteration of archaeological and cultural heritage materials by means of non-destructive X-ray based methods”, (invited lecture), AIC-SIMP Meeting, Sestri Levante, Italy, 110-14 September 2008.

K. Janssens, W. De Nolf, V. Rouchon, B. Vekemans, L .Vincze, F. Brenker, O.C. Lind, B. Salbu, “X-ray micro/nano beam analysis of environmental, geological and cultural heritage materials of strongly heterogeneous nature”, (plenary lecture), SOLEIL User’s meeting, 21-22 Februari 2009