

**CHARACTERIZATION OF THE CARBON TO DIAMOND TRANSITION BY X-RAY DIFFRACTION, RAMAN MICROSCOPY, AND HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (HRTEM) : A WAY TO BETTER CONSTRAIN THE FORMATION OF DIAMOND IN SPACE.** C. Le Guillou<sup>1</sup>, J. N. Rouzaud<sup>1</sup>, F. Brunet<sup>1</sup>. <sup>1</sup>Laboratoire de Geologie de l'ENS, 24 rue Lhomond, 75005 PARIS. cleguill@clipper.ens.fr

**Introduction:** Nanodiamonds with exceptional amount of trapped noble gases were described within disordered carbon of poorly metamorphosed carbonaceous meteorites (1500 ppm in the raw organic part of Orgueil [1]). These nanodiamonds were assumed to be presolar components [2]. Their origin: supernovae shock wave, CVD-like growth in molecular clouds or UV irradiation of graphite grains is still debated [2,3]. Studying these nanocrystals and their relations with the disordered carbon phase at the atomic scale could bring informations on their possible origin. For instance, the fig. 1 shows the relations between a diamond nanocrystal and a carbon disordered nanoparticle in a synthetic product.

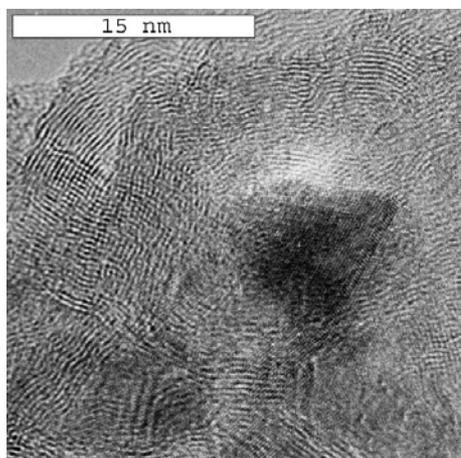


fig. 1: HRTEM image of the carbon black P25 heated at 1500°C, 15 GPa, 15 min (lattice fringe mode) : a nanodiamond ( $d_{111} = 0.206$  nm) is embedded within onion-like graphitic carbon ( $d_{002} \approx 0.35$  nm).

Even if the conditions of formation of these nanodiamonds (heat-treatment at 1500°C, under 15 GPa) are far from those where the meteoritic nanodiamonds are formed, the size of the diamond nanocrystals and the kind of onion like carbon used for these experiments are close to those observed by Daulton et al., and Vis et al. on Orgueil and Allende [4,5]. Such terrestrial analogues could be very useful to study the properties of extra-terrestrial nanodiamonds. Besides these phases relations, following [4], the study of the twins commonly found in natural and synthetic nanodiamonds could be information-rich if they can be linked to the formation conditions.

These extra-terrestrial nanodiamonds have trapped noble gas and their isotopic anomalies is responsible for the presolar origin hypothesis [2]. Three different noble gases volumes are released by pyrolysis at different temperatures, and the accurate characterization of their respective carrier (surface adsorption, internal trapping, ...) might bring constraints on the formation media. While they are very small ( $\sim 3$ nm), their surface/volume ratio is high and the influence of their surface bonds is predominant for chemical and optical characterization. Additional work of characterization of the nanodiamonds is required; it is the aim of this work.

In the present work, we study synthetic nanodiamonds. They are characterized by coupling X Ray Diffraction (XRD), Raman Microspectrometry (RM) and High Resolution Transmission Electron Microscopy (HRTEM).

**Experimental:** The carbon to diamond transition mechanisms and their kinetics depend on many parameters, especially on P/T synthetic conditions and nature of the carbon precursors. Here, we have synthesised diamond at high pressure/high temperature from carbon precursors with various crystallinity (PolyCrystalline Graphite, Carbon Blacks and Quasi-Amorphous Soot) to understand its influence on the transition mechanisms. The experiments were run between 15 and 60 min at 15 GPa in the 1500-1900°C range in a multi-anvil apparatus at the Geodynamic Research Center, Matsuyama, Japan. The study of partially transformed products allows to investigate relations between residual carbon and diamond. The products are analysed by XRD to estimate the transformed volume fraction, by RM to evaluate the carbon organization state evolution, and by HRTEM to understand the near atomic scale crystallographic mechanisms (a special effort was paid for imaging carbon-diamond phase relations and twins).

A well crystallised PolyCrystalline Graphite (PCG) precursor, a disordered Carbon Black (CB) with concentric microtexture and a Quasi Amorphous Soot (QAS) were used as precursors. A convenient technique to evaluate their structural order degree is visible Raman microspectroscopy ( $\lambda_i = 514.5$  nm), where a so-

called “defect band” ( $1350\text{ cm}^{-1}$ ) appears for non-crystalline materials, corresponding to the presence of heteroatoms or defects (as  $sp^3$  bonds) within the structure. The ratio between the defect band and the main graphite  $sp^2$  mode ( $1580\text{ cm}^{-1}$ ) enable to quantify the organization of the carbonaceous material [6] (see fig. 2).

**Results:** As in primitive carbonaceous meteorites, the diamonds formed are nanometric ( $\sim 10\text{ nm}$ ). It appears that under those conditions, mechanisms depend on the organization degree of the precursors. Before diamond forms, the graphite structural order decreases (Raman R ratio increases from 15% to 35%, while diamond has formed, fig 2b) while CB and QAS, already disordered, do not evolve.

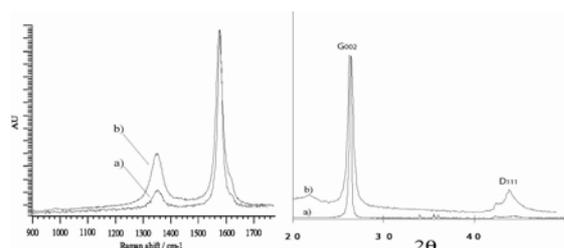


fig 2: Raman spectra (left) and XRD pattern (right) of PCG. a) starting graphite, b) after experiment at 15 GPa, 1500°C and 15 mn.

HRTEM enables to observe the carbon-diamond phase relationship at the nanometer scale. Parallelism between graphitic structure and diamond dense plans (002 and 111, respectively, see figs. 1&3) is always the rule, the atoms displacement being limited by sudden nucleation.

Nevertheless, different features are obtained for each precursor. PCG structure seems to be first delaminated while diamond  $sp^3$  bonds forms. Diamond replaces graphite and no grain boundary phase could be detected (fig 3). With Carbon Black, the concentric microtexture is preserved almost until the end of the transformation; diamond nucleates in the middle of the particle and only after replaces the rim of this onion like carbon (see fig. 1). QAS don't show any graphitization evolution, the 002 fringes of residual carbon are still very short ( $\sim 1\text{nm}$ ) and winkled after almost entire transformation.

Twinned crystals are very frequent in our products, the twins being very similar to those described by Daulton et al. for diamond synthesised under hydrostatic conditions (multiple twins are non linear, i.e with secant grain boundaries).

Lonsdaleite, the hexagonal form of diamond only appears with the PCG precursor (probably by martensitic mechanism) but not with the disordered materials.

While lonsdaleite has been described in meteorites [4] and not within CVD samples, it suggests that it might be formed later from crystalline carbon (from graphite or cubic diamond).

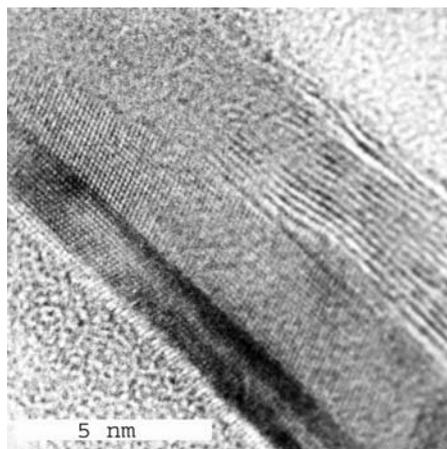


fig 3: HRTEM image of PCG, 1500°C, 15 GPa, 15 min (lattice fringe mode) : a nanodiamond (left) nucleate parallel to graphite (right).

**Conclusion-perspectives :** Nanodiamonds characterization frequently appears difficult due to their very small size and the consequent role of their surfaces. Our preliminary study shows the pertinence of coupling HRTEM, Raman and XRD. The case of the meteoritic nanodiamonds will be a second step of this work. Because of the small amount present in the raw meteorites, detecting possible phase relation by HRTEM requires their previous separation from the bulk rock. The organic part has to be purified first, by classical HCl-HF attack on the whole rock, then the diamond is separated by a heavy procedure of differential oxidation assuming that diamond is more resistant than the other carbon phases and especially the poorly organised ones [2]. This key-point hypothesis has to be carefully studied. We have to check if all the non-diamond carbon phases are really eliminated, if eventual phase relations could be however preserved, and how the nanodiamond structure and surface are perturbed by the treatment.

**References:** [1] Lewis et al. (1987) *Nature*, 325, 160-162. [2] Huss G. R., Lewis R. S. (1994) *Meteoritics*, 29, 791-810. [3] Koscheev et al. (2001) *Nature*, 412, 615-617 [4] Daulton et al. (1996), *GCA*, 60, 4853-4872. [5] Vis et al. (2002) *Meteoritics and Planetary Science*, , 37, 1391-1399. [6] Tuinstra, Koenig (1970), *J. Chem. Phys*, 53, 1123-1130.