

NANODIAMONDS GRAPHITIZATION UNDER TEMPERATURE : IMPLICATIONS ON THEIR EVOLUTION DURING CHONDRITES PARENT BODY METAMORPHISM. C. Le Guillou¹ and J. N. Rouzaud¹, ¹Laboratoire de Géologie de l'ENS, 24 rue Lhomond, 75231-PARIS. cleguill@clipper.ens.fr

Introduction: The discovery of nanodiamonds carrying anomalous trapped noble gases in carbonaceous, ordinary and enstatite chondrites has raised the question on their presolar origin. Because of their noble gases signatures [1], of their twin microstructures [2], and also because of infra red spectra measured in molecular dense clouds and showing possible nanodiamond C-H surface bonds [3], most researchers believe that they are condensates from the atmosphere of carbon rich stars. In that hypothesis, they would predate our solar system, be later incorporated in the solar nebula and accreted within chondrites. Nevertheless, some authors have also proposed an asteroidal origin, by combination of aqueous alteration and heating of metastable carbon compounds within the meteorites parent body [4].

Recently, Huss et al. enlightened a correlation between nanodiamond abundance and thermal metamorphism. For the same meteorite class, the amount of nanodiamond (as well as their P3-component concentration) decreases with increasing metamorphism. This suggests that the same initial amount of nanodiamond was incorporated into meteorites of a given class and that they were further transformed during asteroidal metamorphism. Here, we take this correlation as a starting point to study nanodiamonds behaviour during thermal metamorphism and to specify in which carbon phases it could be transformed.

In meteorites, carbon is mostly present as metastable disordered macromolecular carbon. Actually, this carbon becomes more and more organized during thermal metamorphism (larger and better stacked graphene layers), and this structural organization evolution can be used as a tool to estimate the metamorphism peak encountered by the rock [5, 6]. This has been investigated by [6] using Raman micro spectroscopy on CV and ordinary chondrites. Dire 330°C pour Allende ? Nanodiamonds (mean size ~ 4 nm) are also metastable under temperature. Because of their very high surface/volume ratio, hour-long laboratory experiments show that, under temperature, they turn into onion-like, partially graphitized carbon nanoparticles, fig 1.

In chondrites, the peak temperature is much lower (100-500°C), but the timescale of the thermal event is much longer (assuming ^{26}Al to be the heat source, half-life ~ $7 \cdot 10^5$ years), and nanodiamond could be thus at least partially graphitized.

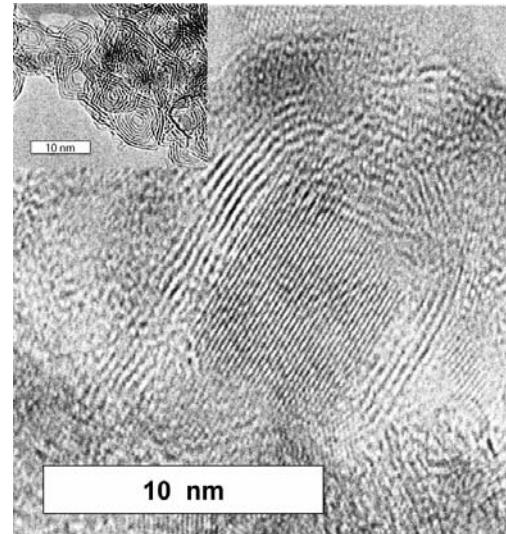


Figure 1 : HRTEM image of synthetic nanodiamond heated at 1100°C. The tight fringes ($d_{111} = 0.206$ nm) correspond to diamond planes. The ring with larger interfringes ($d_{002} > 0.35$ nm) is the forming onion-like nanoparticles. The transformation starts from the surface and finally forms spherical onions with a void centre (upper left side)

Carbon onions have already been reported by several authors in TEM observations of etched residue [7], and their size is in good agreement with graphitised nanodiamonds. This hypothesis is strengthen by the fact that synthetic nanodiamonds usually produced by electric arc for example are always blended with by-products as nanotubes, which have not been found in meteorites. To better constrain our hypothesis, we need the mechanisms and kinetic parameters of the graphitization reaction for the oxygen fugacity range of parent bodies metamorphism.

Experimental:

We focused on the nanodiamond graphitization mechanisms for various temperature by multi-wavelength raman spectroscopy (514 and 785 nm excitation wavelength) and HRTEM (High resolution Transmission electron Microscopy).

The use of several wavelength is complementary as sp^3 and sp^2 bonds have various sensitivities to the excitation wavelength λ_i .

We used synthetic detonation nanodiamonds (amorphous and nanostructured materials.inc) which have about the same size as meteoritic nanodiamonds. They were heated at ambient pressure in an inert atmosphere

furnace between 600°C and 1500°C between 15 min and 17 hours.

Results and discussion:

Reaction mechanisms:

X-Ray-Diffraction is commonly used to identify the beginning of the reaction and to quantify the transformed volume fraction. Authors usually propose 1000-1100°C as the nanodiamond graphitization starting temperature [8]. Here, we show that the diamond band at 1331 cm⁻¹ ($\lambda = 514$ nm) is no more visible since 800°C, whereas no graphitic fringes can be seen in our HRTEM images. It suggests that a local surface reconstruction mechanism could “hide” the sp³ signal since 800°C. We also observed modifications in IR spectra. All this is coherent with a surface starting reaction as proposed by [8].

Raman of graphitic carbon present two principal modes: at 1580 cm⁻¹ for the E_{2g} graphite mode and 1350 cm⁻¹ and 1300 cm⁻¹ for 514 nm and 785 nm, respectively. The latter is usually called defect band and is wavelength dispersive.

From 1000°C, with both 514 nm and 785 nm Raman excitation wavelengths, the sp³ carbon is no longer detected and only sp² signal contributes to the spectra (D and G bands), whereas HRTEM only show sporadic graphitic fringes around nanodiamonds. It is thus possible to quantify the organisation degree of the transformed sp² material at the very beginning of the reaction (Fig. 2). The complementarity of the two wavelengths is shown in Fig. 2. While the evolution of the D band Full Width at Half Maximum (FWHM) with temperature is similar, the surface percentage (R=D/(D+G)) of the defect band evolves in two different manners. As shown by previous authors, it decreases with 514 nm with temperature, but we show here that it tends to increase with 785 nm excitation wavelength.

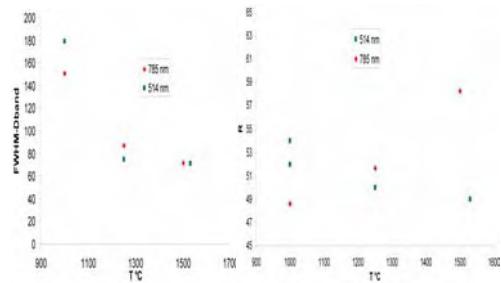


Figure 2 : raman parameters versus temperature measured with 514 nm and 785 nm excitation wavelength.

Two experiments (4 and 17 h) show that longer run duration leads to an optically darker powder, indicating a more advanced transformation and thus a kinetic control of the reaction.

At 1250°C, nanodiamonds are almost completely transformed (Fig 1); but the onions are slightly less structured than at 1500°C for the same run duration. The organization degree increases with temperature.

Kinetics:

If nanodiamonds graphitize during metamorphism, it should be interesting to determine the activation energy of the reaction to link the diamond amount with the metamorphic temperature peak on parent body, assuming an effective heating duration corresponding to the ²⁶Al half-life (7.10⁵ years). Data from the literature propose activation energy value of ca. 188 +/- 17 kJ/mol for nanodiamond graphitization reaction under vacuum and 365 kJ/mol for micro diamond graphitization [8]. The nanodiamonds are then much easier to graphitize than the microdiamonds, probably thanks to their larger reactive surface. The latter were found on Earth to be graphitized during slow exhumation of metamorphic rock for temperature under 800°C, showing the true possibility for nanodiamonds to graphitize at “low” parent body temperature [9].

We calculated the activation energy corresponding to the ²⁶Al decreasing timescale, for temperature of about 330°C (proposed by [6] from a calibrated raman thermometer, [10]), and following the Arrhenius equation : K = Aexp(-Ea/RT). We found a value of 171 kJ/mol, which is in the uncertainty range proposed by [8].

Finally, both mechanisms and kinetics are coherent with a graphitization process occurring on the parent body. With better constraints on activation energy, it may then be possible to link nanodiamond amount and metamorphic temperature for different meteorite classes. This would explain the occurrence of at least a part of the onion-like carbon particles present in chondrites. It would also help to better classify them and to go further in asteroidal processes understanding.

References:

- [1] Huss G. R., Lewis R. S. (1994) *Meteoritics*, 29, 791-810. [2] Daulton et al. (1996), *GCA*, 60, 4853-4872. [3] Allamandola L. J., Sandford S. A. et al., (1992) *The astrophys J*, 399, 134-146. [4] Kouchi A. et al., (2005) *The Astrophysical Journal* 626:129–132 [5] Quirico E., Rouzaud JN et al., (2005) LPSC #1657. [6] Bonal, (2005) *GCA*, 70, 1849-63. [7] Vis et al. (2002) *Meteoritics and Planetary Science*, 37, 1391-1399. [8] Qian J. (2004) *Carbon* 42 2691-97 [9] Bostick C., (2003) *American Mineralogist* 88, 1709-17. [10] Beyssac (2002) *J of Metamorphic Geology*, 20, 859.