EXPERIMENTAL GRAPHITIZATION AND OXIDATION KINETIC OF NANODIAMOND: IMPLICATION FOR NEBULAR THERMAL PROCESSING.

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Introduction: Nanodiamonds are present in several primitives chondrites [1], from petrologic type 1 to 3.8, together with presolar SiC. They originate from several sources and mechanisms, as shocks in supernovae or condensation in different environments. It is generally believed that they are homogeneously distributed in the nebular gas. Nevertheless, in ordinary chondrites, [2] found a correlation between increasing asteroidal metamorphism and progressive disparition of these presolar grains. Later, [3] also suggested that nanodiamonds from carbonaceous chondrites could have been submitted to a nebular thermal event, as their initial distribution in various unmetamorphosed classes was correlated with bulk meteorite fractionation. In both cases, (asteroidal and nebular), the reaction mechanism of nanodiamond disparition with metamorphism remains unknown, as well as the length and temperature of the episod.

In this work, we have studied experimentally the 'graphitization' (formation of polyaromatic structures) and oxidation kinetics of synthetic nanodiamonds to determine which of those two suspected reactions was relevant to asteroïdal and nebular conditions. Those data are then compared to SiC volatilization rate determined by [4] and a time-temperature couple can be proposed.

Experimental: Experimental 'graphitization' was achieved by pyrolysis of synthetic detonation nanodiamonds (ND) (~5 nm) and treated in $HOCLO_4$ at 190°C to clean potential graphitic impurities. Runs temperatures between 600°C and 1500°C, and duration between 90 s and 15 hours were performed. For each run, the transformed mass fraction of nanodiamonds (sp^3 carbons) into onion-like carbon (sp^2 carbons) was then quantitavely determined by X ray diffraction analysis.

Experimental oxidation was achieved through Thermo Gravimetric Analysis. The temperature ranged from 300°C to 800°C with a rate of 10°C/min in an atmosphere of dry air ($fO_2 = 0.2$). The reaction rate of ND was determined through mass evolution with temperature and activation energy could be extracted.

Results: Graphitization of nanodiamonds, i.e. apparition of the first aromatic units, starts at ~ 1000°C. Above this temperature, a first aromatic layer forms at the diamond surface and concentric layers (onion-like carbon) then progress forward to the heart of the initial crystal [5]. Fig.1 illustrates the transformed volume fraction versus time at 1400°C.
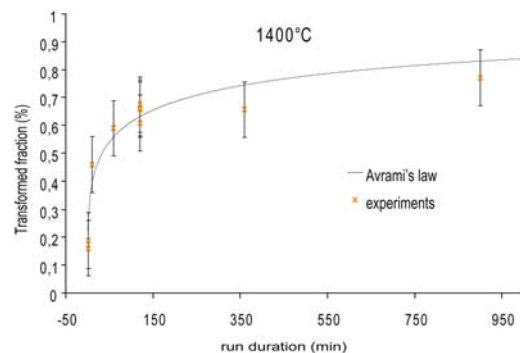

Fig 1. : transformed fraction of nanodiamonds versus run duration for experiments at 1400°C.

It appears that the reaction starts quickly, but then slow down as the transformation progresses. To understand this behaviour, we performed Scherrer analysis of the 111 diffraction line of diamond to evaluate the evolution of the ND size with. Fig 2 shows that the diamond crystals size remains constant while the transformation progress.
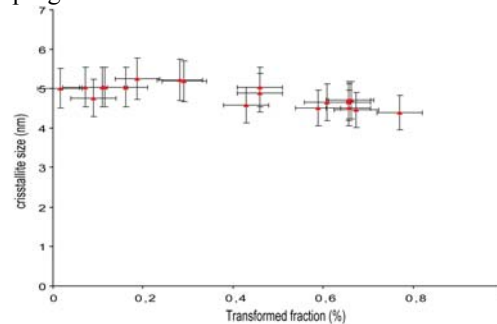

Fig. 2 : Diamond cristallites size remains constant during the progressive transformation of the powder into graphitic onions.

This implies that the reaction proceeds by successive nucleation of individual grains, and that the rate limiting factor is nucleation and not simultaneous progressive graphitic layer migration from the ND periphery towards the center of the crystal, as suggested by [5]. The analysis of this mechanism enable to determine an activation energy from an Arrhenius law for the graphitization mechanism (Ea = 144 +- 12 kJ.mol^{-1} and A = 4.9 +-1.5 s^{-1}).

$$\frac{dN}{dt} = -k.N \qquad \text{were N is the number of nanocrystals,}$$

$$k = \frac{Ln(\frac{mi}{mf})}{\Delta t} = A.\exp(-\frac{Ea}{R.T}) \qquad \text{were m is the initial and final diamond}$$

mass

We were also able to determine activation energy for nanodiamonds oxidation from DTG experiments. The procedure used to extract activation energies is similar to [6] methods. Different activation energies are found for different temperature range indicating the existence of several mechanisms at the atomic scale ($200 +-15$ kJ.mol^{-1} with $A=10^{10}$ s^{-1} for $T<480°C$ and 373 kJ.mol^{-1} with $A=10^{22}$ s^{-1} at $T>480°C$). The Ea found here are close to [6,7] values determined at lower fO_2.

Extrapolation to "chondritic" conditions : The main factor governing the relative rate of oxidation over graphitization is the oxygen fugacity. To investigate nebular and asteroïdal conditions, we need to extrapolate the oxidation rate to lower fO_2.

[7] and [8] showed that the oxidation mechanism does not depend on fO_2, which means that we can use the same activation energies. The oxidation rate will then be simply proportional to fO_2 itself. Extrapolation in terms of temperature and duration are possible thanks to the activation energy of the reaction.

Graphitization ratio depends on duration and temperature, and corrections are not necessary.

Concerning the asteroidal thermal event, the oxygen fugacity estimated from oxide equilibrium [9] (10^{-26} at $T = 450°C$) is much lower than that of our experiment for similar temperature ($300°C-600°C$). Graphitization appears to be the dominant mechanism for diamond disparition. The time-temperature extrapolation of the graphitization rate indicate that classical timescale of asteroidal thermal event ($\sim$ Myears) requires less than $300°C$ to transform the nanodiamonds. This value is clearly in the lower range of metamorphism temperature proposed in the litterature [10] and seems unlikely. It may imply that the graphitization mechanism and activation energy relevant to low temperature are different.

Fig. 3 illustrates the time-temperature couple necessary to destroy 50% of a given diamond population through oxidation or graphitization for the canonical total pressure (10^{-3} bar) and an upper estimation for the fO_2 (IW -2) of the solar nebula [9]. Our choice of fO_2 value is in the high range of those proposed in the literature but graphitization still occurs faster than oxidation below $1500°C$ and 1h.
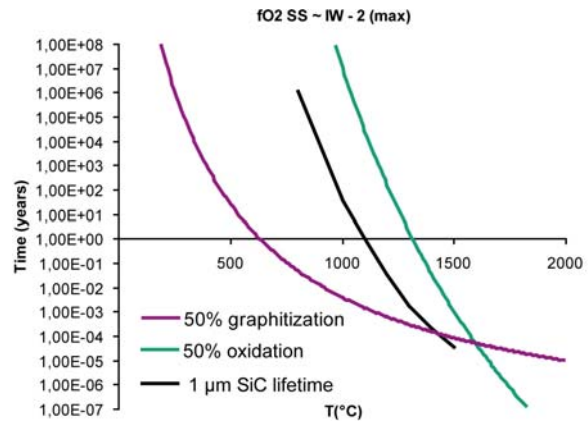

Fig 3. Time-temperature couple for the studied kinetic reaction.

When comparing the graphitization curve to the one determined for SiC volatilization by [4], it comes out that conditions relevant to the simultaneous disparition of nanodiamonds and SiC are high temperature ($\sim1400°C$) and short time ($\sim$ hours) events. Interrestingly, those conditions are close to the chondrules forming event conditions.

The interest of this experimental work is also to explain the presence of onion-like carbon of nanometer size present for exemple in Allende [11] that we were also able to observe in an HF/HCl residu of Kainsaz by TEM imaging.
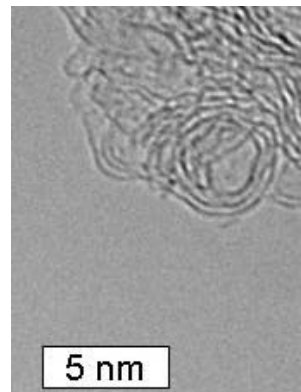
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