

The multiscale organization as a fingerprint of the formation conditions of carbons; a TEM study

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Introduction

The multiscale organization (structure, microtexture, texture) of carbons can be directly imaged by High Resolution Transmission Electron Microscopy (HRTEM) over than 3 orders of magnitude (μm - nm). Two examples of divided and disordered carbons are given on the Figures 1 and 2 : diesel soots, responsible for air pollution, and carbon aerogels, which are possible materials for hydrogen storage. Their multiscale organizations result on two different precursors and two different ways of carbonisation : pyrolysis under pressure of gaseous hydrocarbons for the soots, pyrolysis at atmospheric pressure of an organic oxygen-rich organic obtained by sol-gel chemistry for the carbon aerogels. Details on their multiscale organizations are given in two companion papers presented in this carbon 2004 conference [1,2].

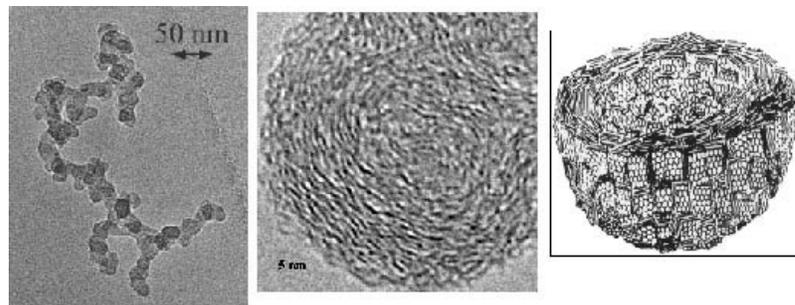


Figure 1. Multiscale organization of soots
(the sketch was proposed for carbon blacks by Heidenreich et al, 1968, [3])

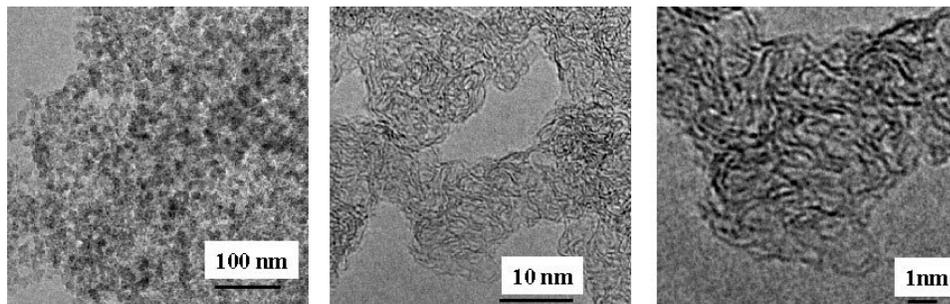


Figure 2. Multiscale organization of carbon aerogels
(micrographs : A. Théry, from [4])

At the textural scale (0.1-1 μm scale), the both carbon forms are made of aggregates of spherules or of more or less coalesced nodules, but the packing is much more compact for the aerogels. At the structural scale (0.1-1 nm), they are made of similar basic structural units (BSU) corresponding to polyaromatic structures, less than 1 nm in size, and frequently stacked by 2 or 3 [5,6]. By contrast, the microtexture, i.e. the the spatial arrangement of the BSUs in the nm- μm range, are completely different. It is concentric in the case of the soots, due to the homogeneous process of growth, whereas the carbon aerogels exhibit a 'crumpled-sheet microtexture'. Such microtexture was previously described for numerous cokes resulting of the carbonization in a quasi solid state of oxygen-rich precursors [6] and involves an high cross-linking of the BSU. Whereas the structural improvement is mainly due to the temperature of treatment, the microtexture is the witness of the chemical nature of the precursor and of the formation conditions. Various microtextures can be obtained from different precursors : for instance : lamellar carbon films formed by condensation of a carbon vapour, lamellar cokes from oxygen-free precursors passing through a well-developed plastic stage before the semi-coke stage (about 500°C), fibrous microtexture after spinning of plastic polymers or pitches, nanotubes in an electrical arc or from a catalytic decomposition of hydrocarbons [6,7].

Meaningful relationships can be thus obtained between multiscale organization and conditions of formation, and between organization and numerous properties (graphitizability, reactivity, ...). Consequently, the multiscale organization appears to be a fingerprint of the formation of these carbons. From decades, such approach was successfully applied to various 'classical' industrial carbon materials, including graphitizable carbons or non-graphitizable ones, then, more recently, to 'new' carbon materials (for instance anodes for lithium batteries, adsorbent carbons including aerogels for energy and hydrogen storages). The organization of these new carbons can be tailored until the nanometer scale. However, beyond the material field, the carbon multiscale organization, as seen and quantified by HRTEM, yield new and original clues on the universe science field, and especially on the origin and the history of natural terrestrial and extra-terrestrial carbons. In this key-note, some examples will be given, first on in the classical carbon materials obtained by usual heat-treatment (graphitizable and non-graphitizable carbons), then on more original tailored carbons (carbon cloth covered by pyrocarbon as anodes for lithium batteries application). At last, some recent applications of unusual ways of carbonisation and graphitisation processes in Nature field will be then presented : formation of natural graphite and of interstellar carbon dust.

Classical carbon materials

Their study allows a better understanding of the key-role of the microtexture on the structural improvement, i.e. on the char graphitizability. Two categories of carbon materials were classically distinguished, representing the two extreme behaviours regarding the graphitizability : the graphitizable carbons (soft carbons) which are entirely transformed into polycrystalline graphite at about 3000°C, and the non-graphitizable ones which remains turbostratic, even at 3000°C [6,8]. The first ones come from oxygen-free precursors (for instance, anthracene-based cokes or carbon films),

responsible for a lamellar microtexture resulting on the long-range parallel orientation of the BSU (see Figure 3a). In contrast, the second ones come from oxygen-rich precursors (for instance, saccharose-based chars), the carbonization of which leading to finely porous chars, the parallel orientation of the BSU being limited to small volumes, a few nanometers in size (see Figure 3e). The HRTEM images of the figure 3a-d show the 'movie' of the strong structural improvement (occurrence of big stacks of large planar layers, see figure 3d) corresponding to the progressive and complete graphitisation [8]; such improvement is allowed by the pre-orientation of the BSU, i.e. by the lamellar microtexture. By contrast, in the case of non-graphitizable carbons, the formation of stacks of planar layers from the BSU (one is circled in green in Figure 3e) is strongly limited to the very small volumes (one is circled in red in e); as shown in the Figure 3f, a mesoporous carbon (pore wall about 5-10 nm in size) is obtained at 3000°C; a such carbon remains entirely turbostratic, as attested by the electron diffraction patterns [6,8].

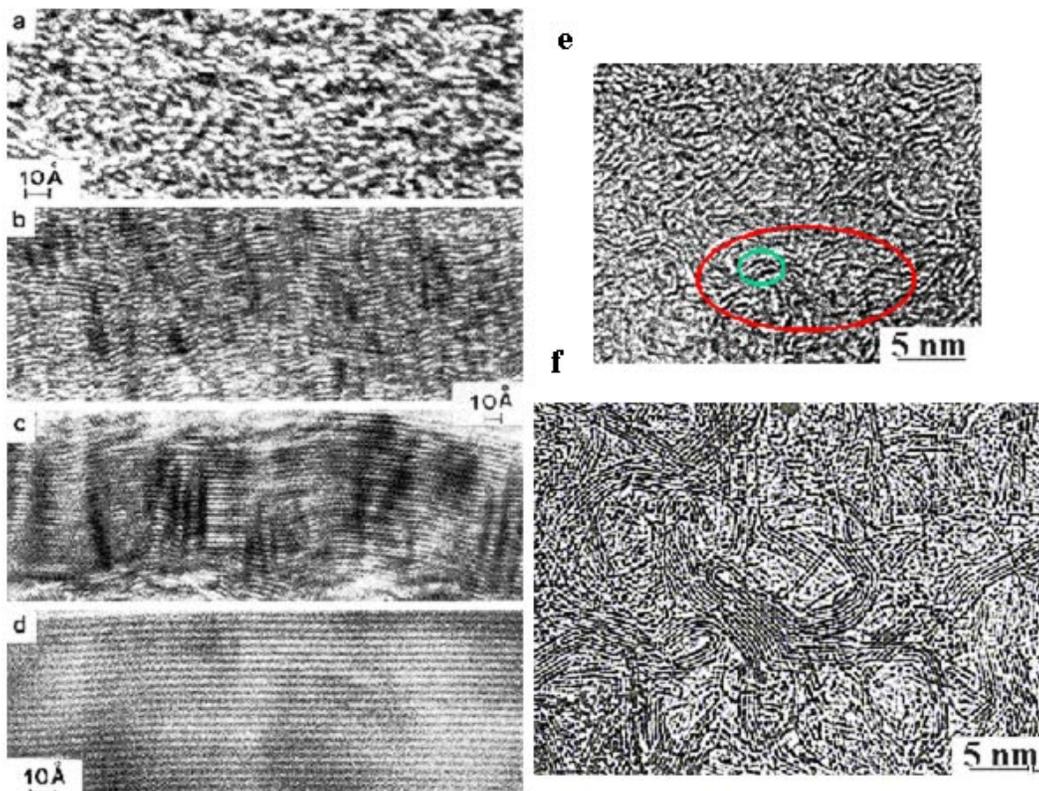


Figure 3. Graphitizable carbon heated at : a : 500°C; b : 1500°C; c : 1800°C; d : 2100°C. Saccharose-based chars heated at 1000 (e) and 3000°C (f).

Between these two extreme behaviours, Oberlin and co-workers demonstrated the existence of a continuous series between these two poles : the lower the oxygen/hydrogen ratio of the precursor, the larger the volumes of preferential orientation in the chars obtained above 500°C, the higher the graphitisation degree reached at 3000°C, under the atmospheric pressure ([6] and references within) These results indicate that the microtexture, and especially the extent of the volume within the BSU were previously oriented in parallel, appears to be a key parameter governing the graphitizability.

Similar relationships between the microtexture and the graphitizability were found in other carbon forms : black carbons [6] and carbon aerogel [2] : the larger the radius of curvature of the carbon spherules, the higher the graphitizability above 2500°C.

This key-role of the microtexture was strengthened by the experiments of graphitisation under pressure. When heat-treatment is performed under high pressure (at least 0.5 GPa), thermally non-graphitizable carbons such as glassy carbons become graphitizable at temperatures below 1700°C [6,9]. Such structural improvements are allowed by microtextural changes : the microporous glassy carbon is suddenly changed in a partially graphitised shelly carbon, then in graphite lamellae. Recent experiments of graphitisation performed at 1000°C under increasing pressures (until 4 Gpa), detailed this mode of graphitisation occurring at 'low' temperature from thermally non-graphitizable carbons (see Figure 4 from [10]).

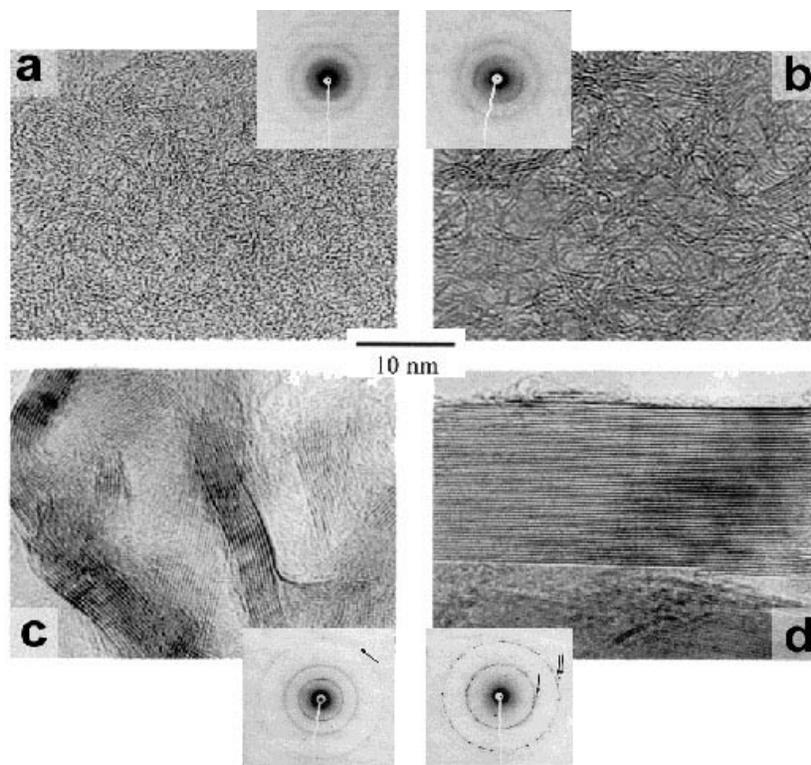


Figure 4. Saccharose-based chars heated at 1000°C during 95 hours at increasing pressures ; a : 0.1 Mpa; b : 0.1 Gpa; c : 1 Gpa; d : 2 Gpa

An example of tailored carbon : carbon cloths as anodes for lithium-ion battery

Most of the commercially available lithium-ion batteries are based on a graphite negative electrode, the reversible capacity of graphite being limited to 372 mAh/g. Higher reversible capacities were demonstrated by disordered carbons (hard carbons) giving up to twice the reversible capacity of graphite. However, these carbons are characterised by an important irreversible capacity due to the electrolyte decomposition on the carbon surface. For our experiments, a carbon fiber cloth was prepared by carbonisation of a

viscose tissue under nitrogen for 15 minutes, at 1000°C. The carbon cloth was then coated with pyrolytic carbon, using chemical vapor decomposition of propylene during 10 minutes at 900°C. The as tailored composite carbon material exhibits a very low irreversible capacity and 1.5 times the reversible capacity of graphite [11]. The viscose-based carbon, as the pyrocarbon, are made of short and poorly stacked polyaromatic layers with a large distribution of layer length and interlayer spacings; consequently, various sites are available for lithium or ions trapping. Neither de-averaged structural data, nor microtextural information can generally be obtained by X-ray diffraction. By contrast, HRTEM allows the organization to be imaged directly. However, up to now, the information from such complex images was mainly qualitative, whereas quantitative structural and microtextural data are required to precisely describe the organization. Consequently, image analysis techniques are required to obtain more quantitative data [12,13]. We developed an in-house HRTEM image analysis procedure allowing useful structural data to be extracted [12]. After skeletonization of images obtained at 310,000 x, our software allows to analyze each fringe individually and in relation with its neighbours and to specify the boundaries of coherent domains and the proportion of non-stacked layers. De-averaged structural data can then be extracted, giving the distributions of : L the fringe length (i.e. the polyaromatic layer extent), d_{002} the interlayer spacings, L_c and L_a the height and the diameter of the coherent domains respectively, and N the number of stacked layers forming a coherent domain. The errors on the measurements can be estimated here to be lower than ± 0.05 nm. Based on these HRTEM data, a sketch of the composite multiscale organisation is proposed in Figure 6.

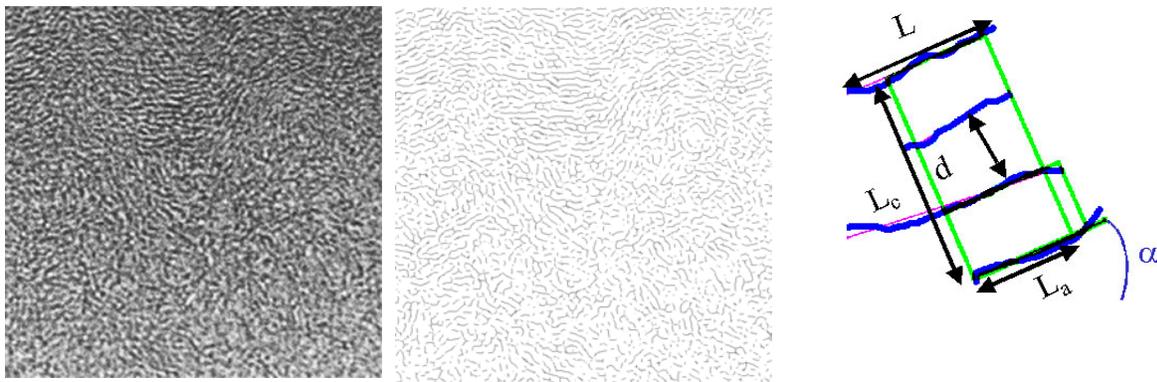


Figure 5. HRTEM image analysis. a : raw HRTEM image; b : corresponding skeletonized image; c : limits of a coherent domain, definition of the structural parameters. In this image, a lamellar pyrocarbon (at the top) coated a microporous fiber (at the bottom).



Figure 6. Sketch of the cross-section of a carbon fiber coated by pyrocarbon,

Coupling HRTEM image analysis, *in situ* ^7Li NMR experiments and galvanostatic cycling of lithium/composite carbon cells, we showed that during reduction, lithium intercalates at first in the smallest intervals between the nanometer size graphitic type layers, then diffuses into the slit-shaped pores, forming the quasi-metallic clusters. The pyrocarbon coating contains much less defects and, due to its lamellar microtexture, forms a barrier preventing the diffusion of the large solvated lithium ions to the active sites of the fibers, that results in a low value of irreversible capacity.

The role of the multiscale organization of carbon aerogels on energy and hydrogen storage is shown in a companion paper of Théry et al (this Carbon 2004 conference [2]).

Applications in universe sciences

Beyond the material field, the utilization of the multiscale organization quantified by HRTEM was recently used to obtain original information in the Earth and Universe Science field. Natural carbons can be considered as precious witness of the conditions of formation of the universe and of the earth. Their multiscale organization should yield new clues about the origin and history of terrestrial and extra-terrestrial carbons. As seen in the images a-d of the figure 3, the carbon structure improvement could be used as paleothermometer, whereas the microtextural changes shown in the figure 4 could reveal events involving pressure effects (see Figure 4). Two recent examples of studies of such natural carbons will be presented in this key-note : a realistic way of graphite formation at low temperature ($< 1000^\circ\text{C}$) in agreement with the metamorphism conditions on earth [14], and a possible mode of carbon interstellar dust formation [15]. For the both cases, our approach involves the coupling of direct or indirect analyses of these carbons with experimental approaches in order to simulate their formation in Nature : an heat-treatment under high pressure for the graphite formation and laser pyrolysis of hydrocarbons for the cosmic carbon dust. The pyrolysis of organic precursors under pressure until 4 Gpa and temperatures until 1200°C allows to reproduce conditions of temperature and pressure met in terrestrial metamorphisms where graphite is frequently formed [14]. The laser pyrolysis device allows to obtain carbon nanoparticles from hydrocarbons in conditions similar to the ones found in the vicinity of an old star and responsible for the formation of interstellar dust [15]. However, in the first case, the experimental carbons can be directly sampled and compared to natural carbons. This is no longer possible for the interstellar cosmic dust which is too far from earth to be sampled. For these extra-terrestrial carbons, we only have optical information (for instance the infra-red light absorbed or emitted from these objects); consequently the infra-red spectra of the soot obtained by laser pyrolysis and the ones analysed from the cosmic dust have to be confronted and discussed, in order to test the astrophysical relevance of these possible earth analogues.

Formation of natural graphite in terrestrial metamorphic rocks [14]

The graphitisation of carbonaceous material (CM) in a high-pressure, low-temperature metamorphic gradient was characterized along a cross section in the 'Schistes Lustrés' formation, Western Alps. Along this 25-km cross section, both the CM precursor and the

host-rock lithology are homogeneous, and the evolution of the metamorphic conditions well constrained from the lower blueschist facies (1.3 GPa, 330°C) up to the eclogite-facies (2 GPa, 550°C). The observation of the CM multiscale organization shows the presence of a microporous phase, similar to a saccharose-based char (image of the sample 1 in the figure 7) which is known to be non-graphitizable under the effect of the temperature at ambient pressure. With increasing metamorphic grade, the graphitisation of the CM proceeds up to the triperiodic graphite stage (sample 12). This is due to microtextural changes, from microporous to lamellar carbons, *via* mesoporous (sample 5) and macroporous ones (sample 8), allowing subsequent structural improvement of the starting material. It must be noticed the striking similar evolution between the graphitization of the natural carbonaceous matter under increasing metamorphism (coupled effects of pressure and temperature) and the one observed for the pyrolysis at 1000°C of a saccharose-based char submitted to increasing pressures up to 2 GPa.

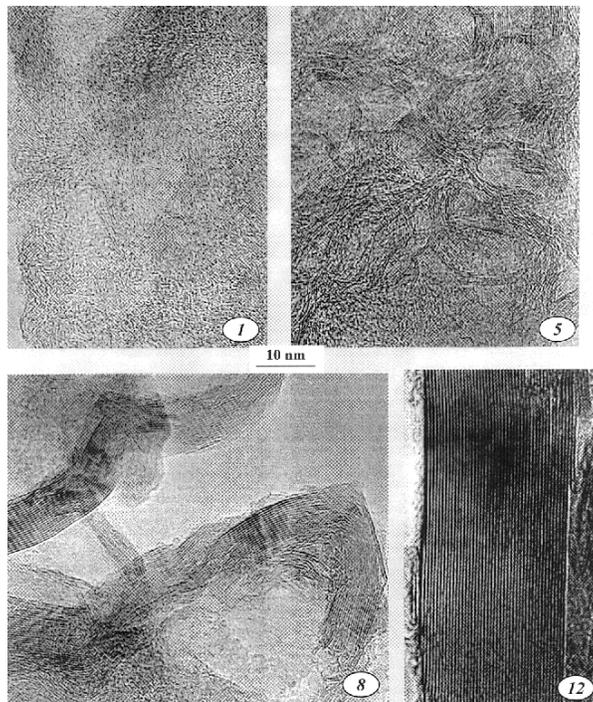


Figure 7. HRTEM images of carbonaceous materials with increasing degrees of metamorphism given by the mineral matrix : sample 1 : 1.3 GPa, 330°C; sample 5 : 1.7 GPa, 350°C; sample 8 : 1.9 GPa, 380°C; sample 12 : 2 GPa, 500°C.

The way of the natural graphitization in terrestrial metamorphic rocks appears thus completely different of the classical industrial graphitisation performed at 3000°C from an oxygen-free precursor. In Nature, thanks to the pressure, the temperature of graphite formation is strongly lowered, until 500°C.

Carbon nanoparticles from laser pyrolysis as analogues of cosmic carbon dust [15]

Carbon nanoparticles synthesised by laser pyrolysis of hydrocarbons in a flow reactor have been investigated as a function of the laser power, i.e. of the flame temperature (from about 950 to 1400°C). Samples were cross-characterized by HRTEM and infrared (IR) spectroscopy. Nanoparticles appear highly aromatic in character in all the experimental conditions explored here. As the flame temperature increases, the nanoparticles evolve drastically from quasi-amorphous, highly hydrogenated samples toward turbostratic concentric particles of carbon. The multiscale organization of the samples and its evolution with the synthesis parameters (especially the flame temperature) were quantitatively determined thanks to our method of HRTEM image analysis presented before. Such quantitative structural data allow the correlation between the structure of these nanoparticles with the IR spectra characteristics. For instance, the increase of the extent of the polyaromatic layers with the flame temperature can be precisely determined (and can be used as a paleothermometer). As far as the IR spectroscopy is concerned, the group of bands between 600 and 1000 cm^{-1} is characteristic of the aromatic C-H out-of-plane bending modes. These modes are very sensitive to the ring substitution and give rise to three main components according to the number of adjacent hydrogen atoms on a ring : the band at 752 cm^{-1} corresponds to 3 and 4 adjacent H, whereas the band at 885 cm^{-1} is attributed to lone H. Consequently the increase of the polyaromatic layers must be accompanied by a decrease of the ratio of IR bands intensity : $I_{752 \text{ cm}^{-1}} / I_{885 \text{ cm}^{-1}}$. This is well observed in the figure 8. Moreover, the existence of a such relationship, which cross-links data obtained by two completely different techniques, can be considered as an *a posteriori* proof of the reliability of our HRTEM image analysis procedure.

From the astrophysical point of view, the IR spectra of these laser nanoparticles were found interesting because the IR bands attributed to aromatic species are observed by the astronomers in an ubiquitous manner. However, the precise attribution of these bands is still controversial. The coupling between HRTEM and IR data obtained here gives quantitative data which could be useful to determine the size of the polyaromatic units of the carbon cosmic dust. The extrapolation of the quasi-linear fit of the data of the figure 8, up to the limit case where the 752 cm^{-1} band disappears (as frequently observed by the astronomers for the cosmic dust), gives a mean polyaromatic layer of 2.2 nm, thus involving at least 60 rings and around 150 carbon atoms. Such structures reveals the presence of solid carbon nanograins, rather than Poly-Aromatic Hydrocarbons (PAH) as frequently proposed.

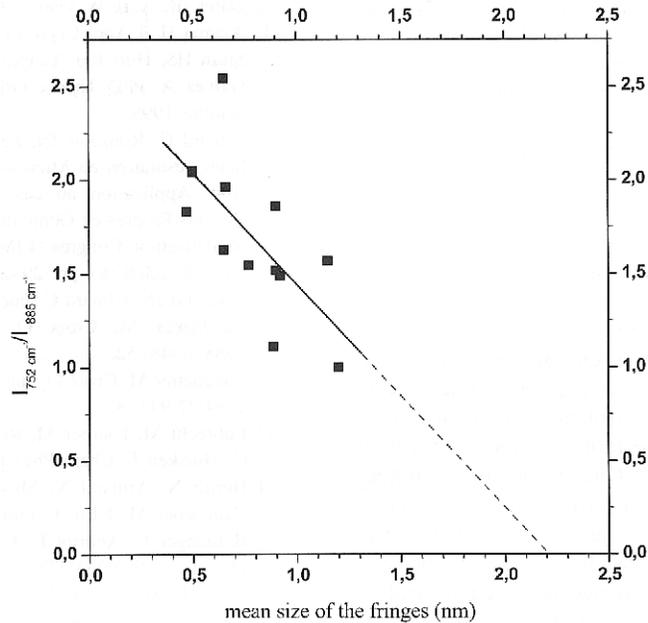


Figure 8. Correlation between the $752/885 \text{ cm}^{-1}$ ratio deduced from FTIR spectra and L, the average size of the fringes determined by HRTEM image analysis

Conclusion

The multiscale organization of carbons can be directly imaged by HRTEM over than 3 orders of magnitude (μm -nm). Previous studies, carried out on the graphitisation of homogenous precursors show that the structural improvement is due to the temperature of treatment, and can be considered as a paleothermometer, whereas the microtexture (spatial arrangement of structural units) appears as a key parameter limiting the structural improvement. In order to access to more quantitative data, an in-house analysis of HRTEM images was developed and has allowed to obtain de-averaged structural parameters. Meaningful relationships can be thus obtained between conditions of formation, multiscale organization and properties. Consequently, the multiscale organization appears to be a fingerprint of carbons. Beyond the 'usual' field of industrial carbon materials, the utilization of the multiscale organization quantified by HRTEM should yield new and original clues about the origin and metamorphic history of terrestrial and extra-terrestrial carbons. This approach is now tested to carbon nanoparticles [1], as diesel engine soots, polluting our Environment.

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pyrolysis and the wonderful consequences of this method on astrophysics and cosmic carbon dust.

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