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# Carbons at the heart of questions on energy and environment: A nanostructural approach

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ABSTRACT

The organization of disordered carbons at the nanometer scale, or nanostructure, reveals very precisely their formation conditions, either in Nature or in the laboratory or in industry. Its study allows a better understanding of the properties of such solids. Only High-Resolution Transmission Electron Microscopy (HRTEM) allows a direct imaging of the nanostructure, whereas Raman microspectrometry provides quantitative but averaged structural data. Applications of the original coupling of Raman with HRTEM, especially in the fields of Energy and Environment, are numerous and promising. Two examples are given concerning the decontamination of irradiated nuclear graphite waste and detection of hydrocarbons trapped in oil and gas shales. Moreover, the study of wood carbonization led our team to propose a novel Raman-based paleothermometer. This approach finds an unexpected application in archeology (e.g., the study of fire marks in prehistoric caves).



## 1. Introduction

Carbon Science spreads over numerous fields including Earth Sciences and Astronomy as well as the material sciences and industrial products. It is traditionally connected to fossil fuels, i.e. coal and oil, and their derived industrial carbon materials, i.e. coke and graphite, generated by various pyrolysis-based processes. Such geomaterials are involved in a large part of the heavy industry ranging from iron and steel making, to electrometallurgy, etc. Moreover, during the past few years, very promising nanomaterials emerged such as carbon nanotubes, graphene, etc. Such carbon materials are at the core of human activities, yet they are responsible for large $CO_2$ emission and severe pollutions in polyaromatic hydrocarbons, soot nanoparticles, etc. Conversely some of the carbon materials, i.e. active chars, are specifically prepared to remediate such pollutions. Carbon materials are thus at the crossroad of problems linked to resources, energy, and environment. A naturalist makes use of the original fossil fuel for a better understanding of the origin and history of the Earth and the solar system; moreover, he is today expected to extrapolate his knowledge to work on energy resources questions such as fossil fuels (conventional or not) and to contribute to resolving environment questions such as decontamination of irradiated nuclear graphite waste. The originality of our approach is to combine in a single material science strategy both categories of natural and anthropogenic carbons usually studied separately, by using a common approach based on their specific multiscale organization. The nanostructure, i.e. their organization at the nanometer scale, is usually the pertinent scale for establishing a double correlation between the nature of their precursors and the formation conditions in Nature or in the laboratory on the one hand, and their global properties on the other one. In order to reveal the message

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carried by carbons, and to understand and forecast their properties, one must visualize the multi-scale organizations of natural and anthropogenic carbons and, if possible, to quantify them.

According to their formation conditions, carbons show very variable organization states (Delhaes, 2009). Thermodynamically stable crystalline forms such as graphite, which is stable at high temperature and low pressure (whereas diamond is stable at high pressure), are well-known, but strictly amorphous carbon forms exist as well. These crystalline and amorphous forms are often the only ones to be considered by researchers who are not specialists of Carbon Sciences. There is however a huge variety of chemically pure and more or less disordered carbons, characterized by various multi-scale organizations. Carbon Science researchers call them "microtextured" carbons, or, to adopt the up-to-date term, "nanostructured" carbons. Each of these organizations is an indicator of the formation conditions (such as precursor nature, temperature, pressure, irradiations, etc.) in the laboratory and in the industry, but also in Nature. A better understanding of the mechanisms responsible for the occurrence of the carbon multi-scale organizations is also a compulsory step when preparing materials with predetermined properties (such as optical properties, chemical reactivity, adsorption, mechanical and transport properties, etc.).

The classical diffraction techniques, giving only averaged structural information such as elemental cell and crystallite size, are often not adapted to the study of carbons, which are usually disordered. In contrast, only High-Resolution Transmission Electron Microscopy (HRTEM) is able to image directly the nanostructure and distinguish various disordered carbons. Moreover Raman microspectrometry has emerged as a technique of choice in the early 1980s to access quantitative results. Raman microspectrometry is now more and more systematically used to characterize natural or industrial carbons, but, up to now, these studies are mostly devoted to the most graphitized carbons.

Reminders on the multi-scale organization of carbons will be first recalled, especially on the notion of nanostructure. Then, the original and extremely fruitful coupling of HRTEM mode imaging and structural characterization by Raman microspectrometry will be presented. This will be illustrated by two examples at the interface between the fields of energy resources and environment, that are directly concerned by the "Bernard and Odile Tissot" *Grand Prix* awarded by the French Academy of Sciences in 2014. The first two examples consist in:

- an original $^{14}C$ decontamination process of irradiated nuclear graphite waste, based on a selective carboxy-gasification;
- a contribution to the study of non-conventional sources of hydrocarbons such as oil and gas shales where it will be demonstrated that hydrocarbons are trapped in the organic nanoporosity.

Disordered carbon multi-scale organization will be used for a somewhat unexpected application: the study of fire marks in prehistoric caves. In this third example, a novel paleothermometer based on the Raman microspectrometry of wood chars is specifically proposed.

## 2. Some background in Carbon Sciences; notion of nanostructure

Carbon materials can be either crystalline (graphite or diamond), or amorphous or disordered, depending on their conditions of formation in Nature, in the laboratory or in the factory. By definition, crystals feature a three-periodic order. As an example, graphite results from the stacking of polyaromatic planes now known as "graphene" layers according to an A-B sequence (Fig. 1a), which is responsible for its hexagonal structure. In contrast, amorphous carbons do not exhibit any order, even at a local scale and the distribution of carbon atoms is completely random. However, most real carbons are neither crystallized, nor amorphous, but show a multi-scale organization. Their structure at the atomic scale corresponds to a turbostratic, i.e. biperiodic stacking of a few nanometer-sized layers (Fig. 1b). The stacks constitute the Basic Structural Units (BSU) of such carbons (Oberlin, 1989). Their dimensions usually give evidence of the highest treatment temperature (HTT) reached during their preparation. We call here "nanostructure" the mutual orientation in space of the BSU; this neologism corresponds to the term "micro-texture" previously used by the Oberlin school. Different nanostructures can be generated according to the formation conditions. For instance the BSU in chars are locally oriented in parallel and form orientation domains, the extent of which depends on the chemical composition of the precursor, and especially of its oxygen/hydrogen atomic ratio (Oberlin, 1989). The random three-dimensional distribution of such domains is responsible for a porous nanostructure previously called "crumpled sheet" (Oberlin et al., 1980) shown in Fig. 1c. Such a nanostructure is characteristic of wood-based chars, but also of blast furnace cokes. The pore wall extent corresponds to the domain dimension ranging from a few nanometers for wood-based chars, up to a few micrometers for blast furnace cokes. Numerous other nanostructures can be obtained according to the conditions of industrial carbon material production. For instance, the fibrous nanostructure corresponds to domains which are preferentially parallel to the carbon fiber axis. An example of concentric nanostructure is the onion-like organization of soot, as proposed by Heidenreich et al., 1968 is shown in Fig. 1d.

We should keep in mind that diffraction techniques, i.e. X-ray, electron or neutron diffractions, as well as Raman spectroscopy, only give information on structure and allow the description of an averaged BSU. In contrast, TEM is the only tool giving access to the carbon multi-scale organization and especially nanostructure. With the so-called high-resolution mode of TEM (HRTEM), it is possible to image directly the aromatic, i.e. graphene, layer profile and, therefore, to access the nanostructure. Illustrations are presented in Figs. 3, 5 and 6, respectively, corresponding to virgin and neutron irradiated nuclear graphite (Fig. 3a and b respectively), mature kerogen (Fig. 5a), anthropogenic fire byproducts such as wood-chars (Fig. 6a and b, and