THE HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY: A POWERFUL TOOL FOR STUDYING THE ORGANIZATION OF TERRESTRIAL AND EXTRA-TERRESTRIAL CARBONS. J.-N. Rouzaud1, A. Skrzypczak2, L. Bonal1, S. Derenne2, E. Quirico1 and F. Robert4, 1Laboratoire de Géologie, ENS, 24 rue Lhomond, 75231, Paris Cedex 5, France (rouzaud@geologie.ens.fr), 2Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, 75231 Paris cedex 05, France (audrey-skrzypczak@enscp.fr, sylvie-dermenne@enscp.fr), 3Laboratoire de Planétologie de Grenoble (eric.quirico@obs.ujf-grenoble.fr, lydie.Bonal@obs.ujf-grenoble.fr), 4LEME, Muséum National d’Histoire Naturelle de Paris, 61, rue Buffon, 75005, Paris, France (robert@mnHN.fr).

**Introduction:** Unlike crystalline carbon phases (graphite, diamond) in highly metamorphised carbonaceous rocks, natural carbons are usually more or less disordered materials. They generally exhibit a polyaromatic structure, and the mutual orientation of the aromatic units gives rise to a multiscale organization. Most natural carbons (coals, kerogens, chondritic insoluble organic matter (IOM), …) exhibit such organization. Whereas graphite and diamond are easily characterized by Raman microspectrometry or X-Ray diffraction, disordered carbons are especially difficult to study. They are not crystallized enough to be studied by X-ray diffraction, and too organized to be investigated by the classical methods used in organic geochemistry. For instance, reliable IR spectra are difficult to obtain on these very absorbent and feature-poor carbons and a controversy arises about interpretation of NMR data, as a large part of carbon atoms in large polyaromatic structure and/or highly cross-linked small structures can hardly be detected. In contrast, High Resolution Transmission Electron Microscopy (HRTEM) makes possible the imaging of the profile of the polyaromatic layers, allowing a better knowledge of the skeleton of such carbons. The multiscale organization (structure and microtexture) can be then directly imaged over 3 orders of magnitude (µm-nm). At the structural scale (0.1-1 nm), disordered carbons are composed of basic structural units (BSU) corresponding to nm-sized polyaromatic structures, single or stacked by 2 or 3 [1,2]. The microtexture corresponds to the spatial arrangement of the BSUs in the nm-µm range. Various microtextures can be obtained from different precursors submitted to different conditions of formation in laboratory or in geological or planetological conditions: lamellar pyrocarbons (cracking of hydrocarbon gases on a support), porous carbons with a ‘crumpled sheet microtexture’ in high rank coals (anthracites), mature kerogens, and industrial cokes, concentric nanoparticles (soots obtained by homogeneous hydrocarbons cracking (engine soots, industrial carbon blacks, hydrogenated carbon nanoparticles from laser pyrolysis) [1-3]. 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. Moreover, meaningful relationships can be thus obtained between multiscale organization and numerous properties (graphitizability, reactivity, optical properties…). From decades, such relationships were successfully applied to various industrial carbon materials. Nowadays, beyond the material field, carbon organization provides original clues on the universe science field, especially on the origin and the history of natural terrestrial and extra-terrestrial carbons. In the present work, we have used this approach to study disordered natural carbons from (i) meteorites of low metamorphic grade and (ii) from Precambrian sediments. Unmetamorphised and metamorphosed well-known meteorites were used to check the efficiency of TEM to study the evolution with the metamorphism degree of the organisation of extra-terrestrial carbon fractions. To contribute to address the question of the origin of life on Earth, the same characterization was applied to the carbonaceous matter from archean rocks. The microtexture could allow distinguishing pyrocarbons obtained from an abiotic process from classical kerogens from biological precursors.

**Experimental:**

**Sampling:** Unmetamorphised meteorites as Orgueil (CI1) and Murchison (CM2) and three CV3 chondrites (Kaba, Léoville, Allende) were investigated. Insoluble organic matter isolated from the Warrawoona Archean chert (3.465 billion years old) [4] was also studied to contribute to the debate about their biotic or abiotic origin [4,5].

**HRTEM technique and image analysis:** HRTEM allows direct imaging of the polyaromatic layers and reveals their multiscale organization. However, up to now, the information from such complex images was mainly qualitative, whereas quantitative structural and microtextural data are required. Consequently, we developed image analysis techniques to obtain more quantitative data on synthetic carbons [3,6]. After skeletonization of images, our software allows analyzing each fringe individually and in relation with its neighbours and to specifying the boundaries of coherent domains and the proportion of non-stacked layers (Figure 1). De-averaged structural data can then be
derived, giving for instance the distributions of: L the fringe length (i.e. the polyaromatic layer extent) and d the interlayer spacings, Lc and La the height and the diameter of the coherent domains respectively.

Figure 1. HRTEM image analysis of the insoluble carbon from the Orgueil meteorite (CI1). a: raw HRTEM image; b: corresponding skeletonized image (image size: 10 nm x 10 nm); c: limits of a coherent domain, definition of the structural parameters.

**Results:** Carbons from meteorites. The polyaromatic carbon of unmetamorphised (Orgueil, Murchison) may represent a link between the interstellar medium and the solar system [7]. As seen by HRTEM (Figures 1a and 1b), the polyaromatic layers within these objects are short (< 1nm), frequently unstacked and the microtexture is strongly disordered. Their structure is similar to the one observed for low-temperature analogues of cosmic carbon dust, obtained by laser pyrolysis [3]. Our image analysis shows that more than 70 % of the domains comprise only two stacked polyaromatic layers and ca. 20 % are made up of three layers, and the interlayer spacing ranges then from 0.35 to 0.65 nm with an average of 0.47 and 0.49 nm for Orgueil and Murchison respectively, i.e. far from graphite (0.3354 nm). Carbons from meteorites of increasing metamorphic rank are clearly more organized, as illustrated by the Figure 2 obtained on the Allende CV3 meteorite; the aromatic layers are much longer (until a few nm, with a mean value of 0.7 nm), better stacked (55% of unstacked layers, stacks formed by 3 to 6 layers, with a mean value of 2.4 and the mean interlayer spacing is here 0.43 nm). Moreover, the structural evolution observed in Kaba, Leoville and Allende allows a CV3 petrographic classification versus from Kaba to Allende, via Leoville, perfectly consistent with Raman data [9].

Figure 2. HRTEM image of the insoluble carbon from the Allende meteorite (CV3); image size: 10nm x 10nm

Archean organic matter. Examination of the structure of organic matter isolated from the Warrawoona chert shows this carbon was significantly more metamorphised than the previously presented carbons as illustrated by the Figure 3. The carbon microtexture is here made of stacks of large layers: the mean layer diameter obtained from image analysis is about 1 nm, and more than 10 layers can be piled up. Despite the NMR and IR data detecting a substantial amount of C-O bonds and aliphatic chains between large polyaromatic units, the TEM data shows this carbon very similar to a classical very mature type II kerogen. However the organization degree is far to have reached the graphite crystalline state. The Warrawoona carbon is microtexturally different of usual lamellar pyrocarbons obtained by abiologic hydrocarbon cracking. This strengthens a probable biogenic origin for this Warrawoona carbon.

Figure 3: HRTEM image of the organic matter isolated from the Warrawoona chert; image size: 10nm x 15nm.

**Conclusion:** HRTEM appears as a powerful technique to access the organization of natural terrestrial or extra-terrestrial carbons. These preliminary data are very promising as structural and microtextural information is revealed. The suggested interpretations in terms of precursor nature, metamorphism degree and possible formation processes will be further investigated using image quantification techniques.