POLYAROMATIC UNITS FROM TAGISH LAKE INSOLUBLE ORGANIC MATTER. S. Derenne[1], J-N. Rouzaud[2], F. Robert[3] and S. Pizzarello[4], [1]LCBOP-BioEMCo, CNRS-ENSCParis, France (sylvie-derenne@enscp.fr), [2] Lab. Géologie, ENS Paris, France (rouzaud@geologie.ens.fr), [3] LEME, CNRS-MNHN Paris, France, [4] Department of Chemistry and Biochemistry, Arizona State University, Tempe, USA.

Introduction Carbonaceous chondrites are known to contain a substantial amount of carbon, mostly occurring as macromolecular insoluble organic matter (IOM). Mainly owing to limitations of analytical tools, the precise chemical structure of this IOM is not yet fully elucidated. However, the macromolecular network of the chondritic IOM is known to be based on aromatic moieties linked together by short aliphatic chains and functionalized bridges. Aromatic moieties from the Orgueil and Murchison meteorite IOM have been recently investigated through solid state ^{13}C NMR, thermal degradations and high resolution transmission electron microscopy (HRTEM). Taken together, these techniques pointed to polyaromatic units of relatively small size, highly substituted by short and branched alkyl chains. It must be noted that the two aforementioned meteorites are characterized by a low metamorphic grade. Indeed, an increase in the size of the polyaromatic units is commonly observed through thermal annealing upon laboratory or natural heating. In the present study, we have investigated the size of polyaromatic units in the IOM of another carbonaceous chondrite of relatively low metamorphic grade, Tagish Lake.

Tagish Lake was chosen for this study because it is unusual from several points of view when compared to other carbonaceous chondrites. First of all, the cold environment of the fall site, the rapid collection and the exceptional conditions of transportation and storage make the Tagish Lake meteorite especially suitable for organic studies. Moreover, this meteorite does not seem to fit in the present meteorite taxonomy. Indeed, the mineralogy, oxygen isotope and bulk chemical composition of the Tagish Lake meteorite fall between, rather than within, those of the CM and CI meteorites. The extent of its aqueous alteration leads to a classification as an ungrouped C2 chondrite or as the first example of a CI2 meteorite. Moreover, Tagish Lake was shown to be also unique in its organic chemistry and it is assumed that this carbonaceous chondrite may be one of the most primitive solar system materials [1]. Indeed, the soluble fraction is dominated by a few water-soluble organic compounds and is characterized by a virtual lack of amino acids. According to its solid state ^{13}C NMR spectrum [2], the macromolecular IOM of Tagish Lake was shown to be much more aromatic than that of Orgueil, Murchison and Allende. This highly aromatic character was confirmed by pyrolysis-gas chromatography-mass spectrometry [3]. Based on data obtained using the latter technique, a more condensed structure with larger aromatic moieties than in Murchison was anticipated for Tagish Lake. However, pyrolysis is known to induce aromatization and thus may be not be the most suitable technique to derive information on aromatic moieties. In contrast, HRTEM provides a direct imaging of the polyaromatic unit profile and was thus used in the present study coupled with image analysis. Indeed, thanks to image analysis, quantitative structural and microtextural data can be obtained [4]. They are required for a more complete interpretation of the complex images obtained on such disordered carbons. Results obtained for Tagish Lake are compared with those previously reported for Orgueil and Murchison [5].

Material and method: Tagish Lake was provided by M. Zolensky from the NASA JSC and IOM was isolated using the classical HF/HCl treatment. HRTEM observations were performed using a Philips CM 20 microscope, operating at 200 kV. For sample preparation, we used a classical grinding under alcohol in an agate mortar. After ultrasonic treatment of the alcoholic suspension thus obtained, a droplet was deposited on a lacey carbon grid and dried. Using the edges of the thinnest fragments deposited across the holes minimizes risks of fringe superimposition. Raw HRTEM images obtained with a 300,000 x magnification are recorded on classical 8 x 10 cm negatives. A 20 x 20 nm representative area is sampled and digitalised on 1024 x 1024 pixels with a resolution of 4000 ppi; one pixel then corresponds to 0.019 nm as calibrated with a graphite 002 lattice fringe image (with the adopted value of 0.3354 nm for the interlayer spacing). Some criteria then have to be taken into account to avoid artifacts: (1) the aromatic layers being constituted of aromatic rings with a size of 0.246 nm, all the shorter fringes have to be eliminated; (2) the C-C bond being 0.142 nm, a fringe crossed by segments smaller than this value will be considered as rectilinear; (3) van der Waals forces being supposed as negligible between graphene layers spaced by more than 0.7 nm (twice the d_{002} graphite value), pairs of fringes with greater spacing or forming an angle broader than 15° were considered as two single layers. At least several hundreds of fringes are usually measured and characterized, i.e. many more than the hundred ones that are classically measured using a measuring magnifier. The length of all the fringes, L, *i.e*. the extent of the aromatic layers, was individually measured. L distribution was obtained from these measurements and the average value of fringe lengths $\overline{L}$ was also calculated. Coherent domains are defined by the parts of the polyaromatic planes that are involved in the stacking of parallel planes (with a 15° tolerance). In addition, coherent domains formed by stacked polyaromatic layers could be distinguished from single layers. They are thus characterized by their diameter La and height Lc along with the number N of stacked layers and interlayer spacings d (Fig.1). Whereas X-ray diffraction and ^{13}C NMR only give access to averaged data, the distribution of these parameters could be determined thanks to the procedure of image analysis discussed above, and average values were calculated: $\overline{La}$, $\overline{Lc}$, $\overline{N}$ and $\overline{d}$, respectively.

Results: From image analysis of figure 2, the distribution of the fringe lengths L shows that the polyaromatic layers in the IOM of Tagish Lake are of small size, since the average length of the aromatic layers, both single and stacked, $\overline{L}$, is only 0.6 nm. This average size corresponds to 2 to 3 rings in diameter, i.e. a total number of ca. 10 rings per layer. When the coherent domains are concerned, the average value of their diameter $\overline{La}$ is even lower with 0.3 nm.

The number of stacked layers N is also small as most of the basic structural units, i.e. the coherent domains formed by stacked layers, comprise only two stacked polyaromatic layers. The mean $\overline{N}$ value (~ 2.2 layers/stack) is low. As far as the coherent domains formed by the stacking of polyaromatic layers are concerned, the interlayer spacing shows an average of 0.46 nm, i. e. far from graphite. This low stacking along with the relatively high interlayer spacing reveals a low level of organization in Tagish Lake IOM. This is further confirmed by a substantial amount of single layers, i.e. not stacked, of 58 %.

When Tagish Lake is compared with Orgueil and Murchison, it appears that the IOM of the three carbonaceous chondrites comprise polyaromatic units of similar size and that the coherent domains exhibit similar features. The rather high interlayer spacing should reflect the occurrence of heteroelements in the IOMs and also the high level of substitution exhibited by these polyaromatic units as revealed by solid-state ^{13}C NMR and pyrolysis.

The rather poor organization of the polyaromatic units in the IOMs, is confirmed by the high amount of single layers even if the latter seems to decrease from Orgueil to Murchison and Tagish Lake.

As a result, although NMR revealed an increase in aromaticity from Orgueil and Murchison to Tagish Lake, confirmed by a decrease in H/C ratio from elemental analysis, no major difference in aromatic size could be inferred from HRTEM observations. This is consistent with recent EPR analyses which revealed the occurrence of diradicaloids in these three samples [6]. Diradicals formed from small aromatic moieties are more stable than those with larger polyaromatic units and similar features were noted for the diradicaloids in the three carbonaceous chondrites, pointing to similar size for the polyaromatic units bearing the free radicals. .

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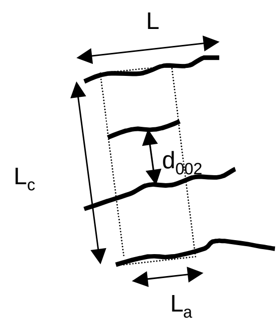

Fig. 1 Schematic representation of an aromatic unit showing the measured parameters

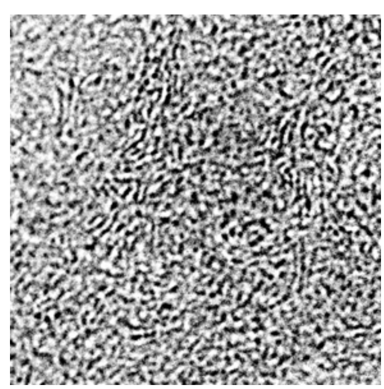

Fig.2: HRTEM image of Tagish Lake IOM (square size: 16 nm x 16 nm)