CHARACTERIZATION OF THE ORGANIC MATTER IN AN ARCHEAN CHERT (WARRAWOONA, AUSTRALIA).

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Introduction: The question of the origin of life on Earth is one of the most debated scientific questions to date. To address this important issue, a special attention has been paid to the oldest archean rocks and especially to their carbonaceous matter. The discovery of microstructures in cherts from the Warrawoona group created a considerable interest in the organic matter contained in this deposit. Based on microscopic studies, these microstructures were considered to correspond to the oldest microfossils on Earth (3.465 billion years old) and to be derived from photosynthetic filamentous cyanobacteria [1]. The occurrence of carbonaceous material associated with these structures, revealed by laser Raman microspectroscopy, was put forward as an additional evidence for a biogenic origin of the aforementioned microfossils [2]. However, this biogenicity has been recently debated since it was shown that similar structures can be formed through abiotic reactions and the microstructures were even considered as secondary artifacts formed from amorphous carbon under hydrothermal conditions [3, 4, 5]. Taken together, these results emphasize the necessity for reliable biomarkers for this ancient organic matter. To this end, we have undertaken a multidisciplinary study of the insoluble organic matter isolated from a chert of the Warrawoona Group using high resolution transmission electron microscopy and several spectroscopic techniques (Fourier transform infrared, solid state nuclear magnetic resonance and electron paramagnetic resonance).

Sample: The sample (PPRG 006) was collected in the "lower chert" of the Towers Formation at North Pole B Deposit Mine. The metamorphism is prehnite-Pumpellyite to lower grennschist. The nitrogen and organic carbon contents are 22 and 121 ppm, respectively with the following isotope compositions, $\delta^{13}C$ = - 32.7 ‰ and $\delta^{15}N$ = -4.4 ‰.

The insoluble organic matter was isolated from the bulk sample using the classical demineralization procedure via HF/HCl. The recovery yield of this acid treatment is 150 ppm in agreement with the low carbon content of the bulk chert.

Results: In a preliminary study, the organic matter was analysed in situ by electron paramagnetic resonance [6]. This technique allows the characterization of the free radicals. Organic free radicals are formed through homolytic cleavage of C-X bonds (X = H, C, O, …) hence a single electron in a dangling bond. The evolution of the EPR signal with temperature definitely shows that the organic matter has not reached the graphite stage. Moreover, it did not reveal the occurrence of diradicaloids as recently discovered in the insoluble organic matter of meteorites. This may be due to differences in the size of the aromatic moieties building up the macromolecular network of the two types of samples. In this study, we also showed that the evolution of the EPR signal of cherts of biogenic origin with thermal stress resulted in a signal similar to that of Warrawoona. In the present study, the organic matter is examined again by EPR after being isolated by HF/HCl treatment. The g-factor (given by the center of the EPR line) at 2.0031 reveals a substantial contribution of heteroelements (oxygen, sulfur, possibly nitrogen) to the free radicals. The intensity of the EPR signal gives a spin concentration of $4.3 \pm 0.7\ 10^{19}$ spins/g in the organic matter. This value is in the range of the spin concentrations measured for terrestrial kerogens.

High resolution transmission electron microscopy (HRTEM) is a powerful tool for the direct observation of the polyaromatic skeleton of carbonaceous materials. Examination of the organic matter isolated from the chert of Warrawoona firstly confirms that this material has not reached the graphite stage as indicated by EPR. Secondly, it reveals the presence of polyaromatic structural units formed by the stacking of a few layers. These units are locally oriented in parallel to form domains, a few nanometers large. The misorientation of these domains allows for a mesoporous microtexture (Figure 1). Such structural structural and microtextural organization is similar to what is usually observed in mature kerogens. Indeed, especially when compared with what we previously observed in the insoluble organic matter of the meteorites, the mean size of the aromatic layers is much longer in the chert. Such an increase in the fringe length may reflect high and/or long thermal event or high pressure. Image analysis is under progress to determine the structural parameters and their distribution and to compare them with homogeneous series of increasing natural or artificial metamorphism.

Fourier transform Infrared (FTIR) spectroscopy gives information on the nature of the functional groups in organic macromolecules. The spectrum clearly shows an absorption in the 2850-2950 cm^{-1} range due to CH stretching vibrations in aliphatics. The pattern of this band is similar to that usually observed in mature terrestrial kerogens and, in contrast, strongly differs from that observed in carbonaceous chondrites. The main difference relies on the CH_3/CH_2 ratio, i.e. the branching level, in these aliphatic chains that mainly act as linkages between the aromatic moieties. Other bands of lower intensity can be observed at 1660 and 1730 cm^{-1}, possibly due to C=O groups. The aromatic carbons are responsible for the band at 1590 cm^{-1}.

Solid state ^{13}C NMR provides information on the environment of the carbon atoms and allows to distinguish the different types of carbons. It is here performed for the first time on such a sample using cross polarization sequence and magic angle spinning. This sequence results in an enhancement of the signal thanks to polarization transfer from hydrogens to carbons. The use of this sequence was required due to the low amount of material. The main drawback of this sequence is that no precise quantitative data, i. e. relative abundance of the different types of carbons, can be derived from the spectrum. Three main peaks can be identified: a broad one ranging from 150 ppm to 100 ppm corresponding to aromatic carbons, a thinner one centered at 70 ppm corresponding to carbons linked to oxygen and/or nitrogen atom through a single bond and a broad one between 40 and 0 ppm. This latter peak is assigned to aliphatic carbons and it shows a shoulder at 15 ppm corresponding to methyl groups. The two broad peaks are roughly of similar intensity whereas that of the peak around 70 ppm is weaker. It must be emphasized that the relative intensity of the aromatic peak leads to a strong underestimation of the actual contribution of the aromatic carbons in the macromolecule. This is especially true due to the large size of the polyaromatic units inferred from HRTEM.

Conclusion: The combination of analytical techniques leads to important information on the chemical structure of the insoluble organic matter isolated from the Warrawoona chert. This organic matter has not reached the graphite stage. It is similar to a mature kerogen, based on a macromolecular network of large polyaromatic units but still contains a substantial amount of heteroelements. C-O bonds and aliphatic chains contribute to this structure. A pyrolytic study is under progress to add information at the molecular level to these spectroscopic and microscopic data.

This chemical structure is consistent with a biological origin and is sharply different from the chemical structure of the insoluble organic matter of the carbonaceous chondrites. However, an abiotic origin cannot be completely excluded for the organic matter of the Warrawoona chert on the basis of the above results.

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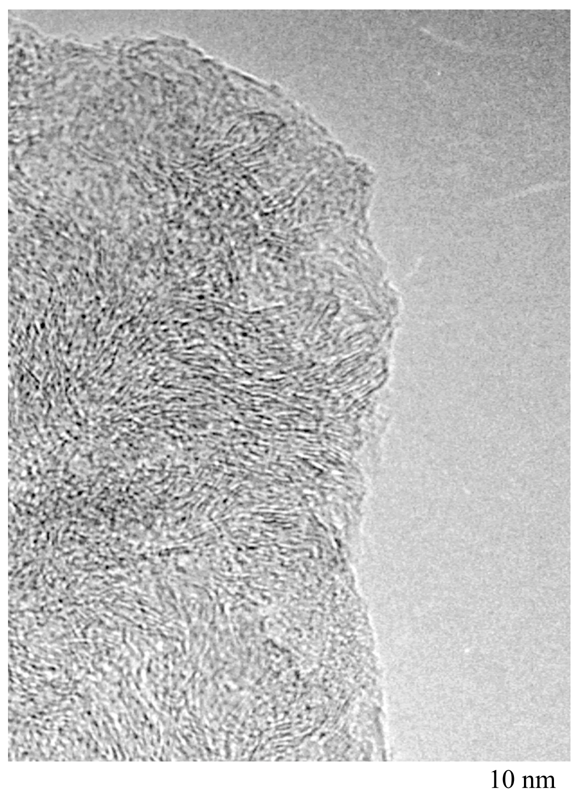

Figure 1: HRTEM image of the organic matter isolated from the Warrawoona chert.