



## Molecular evidence for life in the 3.5 billion year old Warrawoona chert

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### ABSTRACT

The biological origin of organic matter in the oldest siliceous sediments (cherts) is still debated. To address this issue, the insoluble organic matter (kerogen) was isolated from a chert of the Warrawoona group. The chemical structure of the kerogen was investigated through a combination of analytical techniques including solid-state <sup>13</sup>C nuclear magnetic resonance and pyrolysis. Although dominated by aromatic hydrocarbons, the pyrolysate comprises a homologous series of long chain aliphatic hydrocarbons characterized by odd-over-even carbon number predominance. This distribution is only consistent with a biological origin. As kerogen must be contemporaneous of the solidification of the chert, this observation should be regarded as an evidence for the presence of life on Earth, 3.5 By ago.

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### 1. Introduction

Cherts are amongst the oldest sedimentary rocks on Earth and offer a remarkable record of well-preserved microfossils throughout the Precambrian. Based on spectroscopic and morphological observations, microstructures in the 3.5 By old Apex chert from the Warrawoona group in Australia have been attributed to fossil cyanobacteria and thus would constitute the oldest evidence for life on Earth (Schopf, 1993). In addition to morphological criteria, the carbonaceous nature of the microstructures established by Laser Raman microspectroscopy was considered as an evidence for their biogenicity (Schopf et al., 2002). However, the validity of this criterion as evidence for life has been questioned and it is now accepted that Raman spectroscopy alone cannot assess biogenicity (Pasteris and Wopenka, 2002). Moreover, it was shown that abiotic synthesis (Fischer–Tropsch) is able to yield organic microstructures exhibiting similar morphological features and Raman spectra as the putative microfossils from the Apex chert (Brasier et al., 2002; Garcia-Ruiz et al., 2003). Carbon isotope composition was also often put forward as an additional criterion of the biological origin of the organic matter in the Archean cherts (Mojzsis et al., 1996; Schidlowski, 2001). However, once again, this

approach was shown not to be univocal, as abiotic processes can lead to similar fractionation (Horita and Berndt, 1999; Van Zuilen et al., 2002; McCollom and Seewald, 2006). More recently, the wide diversity in the morphological features of the stromatolites from Strelley Pool chert and the continuity in the carbonaceous matter record in rocks >3.0 By suggested that most OM in these rocks was produced by living organisms (Allwood et al., 2006; Tice and Lowe, 2006).

A new criterion, in the form of an indisputable biomarker, is therefore needed in order to resolve the debate about when life first appeared on Earth. Biomarkers characteristic of cyanobacteria were reported in the soluble organic fraction of the ca. 2.7 By old shales from Hamersley Basin in Australia (Brocks et al., 1999). However, evidence drawn from soluble organic matter is disputable because there are several potential sources of post-depositional contamination, notably subsurface biological activity and groundwater penetration. Although such issues have been carefully evaluated in the case of Hamersley Basin shales (Brocks et al., 1999), the synchronism between the formation of soluble molecular fossils and the host rock remains difficult to demonstrate (Brocks et al., 2003a; Brocks et al., 2003b). In contrast, it is generally accepted that the insoluble macromolecular organic matter characterized by covalent bonds is syngenetic with the host rock hence an increasing interest for this organic fraction (Brocks et al., 2003a; Marshall et al., 2006; Marshall et al., 2007). We have therefore isolated the kerogen from a chert of the lowest metamorphic grade from the Warrawoona Group and investigated its chemical structure using a combination of spectroscopic and pyrolytic tools.

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## 2. Methods

The sample (PPRG 006 from Precambrian Palaeobiology Research Group collection, courtesy of W. Schopf) was selected for this study from a large collection of cherts on the basis of its isotopic composition (see below). It was collected in the lower chert horizon of the Towers Formation in the North Pole B Deposit Mine from the upper lip of the open cut on the west side; Marble Bar 1:250,000 map sheet grid ref n°. 223357 (Walter et al., 1983). The North Pole Dome, from which the sample was collected, is situated 30 km NW of the Apex cherts in the Marble Bar region. Since 1983, the Towers Formation cherts at The North Pole Mine have been reassigned to the Dresser Formation, which has an age of ca. 3.490 By (van Kranendonk, 2006).

The insoluble organic matter was isolated from the ground chert as follows: stirring at room temperature for several hours in dichloromethane/methanol, 2/1, v/v in order to remove soluble organics, followed by demineralization using the classical HF/HCl treatment (Durand and Nicaise, 1980) and further solvent extraction. After each treatment, the insoluble residue was recovered by centrifugation.

Variable amplitude cross-polarization/magic angle spinning (VACP/MAS) solid-state  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum was obtained at 100.62 MHz for carbon (Bruker Avance 400 spectrometer, recycle time 5 s, contact time 1 ms), using a high spinning rate (20 kHz) to spin out chemical anisotropy and avoid spectrum disturbance by spinning side bands.

Curie point pyrolysis-gas chromatography/mass spectrometry (CuPy-GC/MS) was performed with a Fischer 0316 flash pyrolyser. The sample (ca. 2 mg) was pyrolysed for 10 s using ferromagnetic tubes with a Curie temperature of 650 °C under a 5 ml min $^{-1}$  He flow. The pyrolyser was directly coupled to the GC/MS: a HP-5890 gas chromatograph (30 m CPSil5CB capillary column, i.d. 0.25 mm, film thickness 0.5  $\mu\text{m}$ ) and a HP-5889A mass spectrometer (electron energy 70 eV, ion source temperature 205 °C, scanning from 40 to 650 a.m.u., 0.7 scan/s). The GC oven was programmed from 100 to 300 °C at a rate of 2 °C min $^{-1}$  after a first stage at 100 °C for 10 min.

High resolution transmission electron microscopy (HRTEM) observations were carried out using a Jeol 2011 microscope operating at 200 keV. Image analysis was conducted after skeletonization as described by Rouzaud and Clinard (2002).

## 3. Results and discussion

Demineralization of 149.5 g of crude rock yielded 32.7 mg of kerogen, i. e. 218 ppm. The carbon content (53.4%) of the isolated kerogen indicates that most of the initial carbon of the rock is recovered in this insoluble fraction, since the crude rock contains 121 ppm of carbon (Beaumont and Robert, 1999). The elemental composition gives an atomic H/C ratio of 0.62, indicating a rather aromatic character. This kerogen concentrate also contains mineral phases, such as titanium and chromium oxides, as revealed by SEM-EDS. These oxides, which are known to survive HF / HCl treatment,

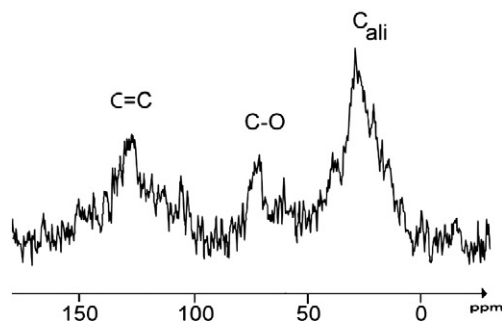


Fig. 1. Solid state variable amplitude CP-MAS  $^{13}\text{C}$  NMR spectrum of the kerogen from the Warrawoona chert.

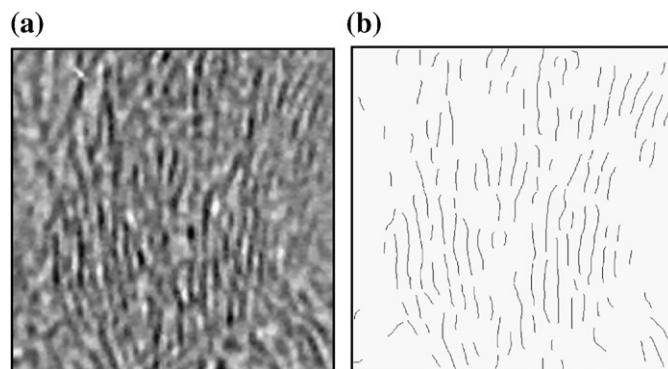


Fig. 2. HRTEM image (10 $\times$ 10 nm) of the kerogen from the Warrawoona chert and corresponding skeletonized image.

were previously observed by Kato and Nakamura (2003) on crude cherts from Warrawoona.

The solid-state  $^{13}\text{C}$  cross-polarization/magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectrum of the isolated kerogen (Fig. 1) is dominated by a broad signal centered at 29 ppm due to aliphatic carbon atoms and shows two relatively minor peaks at 70 and 130 ppm, assigned to C–O and unsaturated carbons, respectively. Although solid-state CP/MAS  $^{13}\text{C}$  NMR is known to overestimate aliphatic carbons, it must be noted that the presence of alkyl chains is also observed through Fourier transform Infrared (FTIR) spectroscopy (not shown). Indeed, the spectrum of the Warrawoona chert exhibits the typical bands for  $\text{CH}_2$  and  $\text{CH}_3$  in the 2850–2965  $\text{cm}^{-1}$  range. The 2925  $\text{cm}^{-1}$  and 2850  $\text{cm}^{-1}$  bands are due to asymmetrical and symmetrical stretching vibrations of  $\text{CH}_2$  groups. The asymmetrical stretching band of the  $\text{CH}_3$  groups can be clearly seen at 2965  $\text{cm}^{-1}$ . A band at 1585  $\text{cm}^{-1}$  reflects the stretching vibration of aromatic C=C whereas carbonyl functions are detected at 1710  $\text{cm}^{-1}$ . The broad band around 1160  $\text{cm}^{-1}$  may be due either to ether functions or to residual silica. The NMR spectrum strongly differs from those of mature kerogens, for which the 30 ppm peak is virtually absent due to thermal release of alkyl chains upon maturation (Miknis et al., 1982). As a result, the NMR spectrum of the Warrawoona chert indicates that this material, although 3.5 By old, did not experience any severe, thermally induced chemical modification.

This may appear at variance with the Archean age of the sample. However, the Warrawoona Group has been described as the one which underwent the lowest metamorphism and which contains the best preserved Archean stratigraphic succession on Earth (Van Kranendonk et al., 2002). Moreover, the carbonaceous matter structure, which cannot be used to determine the biological origin (or not) of the sample, can provide powerful information about its thermal history as recently stressed by Tice and Lowe (2006). Indeed, large “graphitic domains” are commonly reported when the sample reached the metamorphic grade of prehnite–pumpellyite (Wedeking and Hayes, 1983). In contrast, our observations of the PPRG 006 sample through high resolution transmission electron microscopy (HRTEM) (Fig. 2) and further image analysis showed relatively large aromatic units but no such “graphitic domains” (PPRG 006 exhibits a mean layer extent about 1.1 nm, corresponding to about 15 fused aromatic rings (Rouzaud et al., 2005)). It must be noted that the occurrence of these large aromatic units is not at variance with the presence of aliphatic carbons in the FTIR and NMR spectra as the latter cannot be detected through HRTEM. However the organization degree is far from having reached the graphite crystalline stage. Indeed, the interlayer spacing is 0.39 nm, significantly higher than the graphite value (0.3354 nm). These observations are in perfect agreement with a recent study of the Apex chert through TEM and electron energy loss spectroscopy (EELS) (de Gregorio and Sharp, 2006). Taken

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