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To cite this version:
Frédéric Delarue, Jean-Noël Rouzaud, Sylvie Derenne, Mathilde Bourbin, Frances Westall, et al.. The Raman-Derived Carbonization Continuum: A Tool to Select the Best Preserved Molecular Structures in Archean Kerogens. Astrobiology, Mary Ann Liebert, 2016, 16 (6), <10.1089/ast.2015.1392>. <hal-01321479>

HAL Id: hal-01321479
https://hal.sorbonne-universite.fr/hal-01321479
Submitted on 25 May 2016

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The Raman-Derived Carbonization Continuum: A Tool to Select the Best Preserved Molecular Structures in Archean Kerogens

Frédéric Delarue,1 Jean-Noël Rouzaud,2 Sylvie Derenne,3 Mathilde Bourbin,3 Frances Westall,4 Barbara Kremer,5 Kenichiro Sugitani,6 Damien Deldicque,2 and François Robert1

Abstract

The search for indisputable traces of life in Archean cherts is of prime importance. However, their great age and metamorphic history pose constraints on the study of molecular biomarkers. We propose a quantitative criterion to document the thermal maturity of organic matter in rocks in general, and Archean rocks in particular. This is definitively required to select the best candidates for seeking non-altered sample remnants of life. Analysis of chemical (Raman spectroscopy, 13C NMR, elemental analysis) and structural (HRTEM) features of Archean and non-Archean carbonaceous matter (CM) that was submitted to metamorphic grades lower than, or equal to, that of greenschist facies showed that these features had all undergone carbonization but not graphitization. Raman-derived quantitative parameters from the present study and from literature spectra, namely, R1 ratio and FWHM-D1, were used to draw a carbonization continuum diagram showing two carbonization stages. While non-Archean samples can be seen to dominate the first stage, the second stage mostly consists of the Archean samples. In this diagram, some Archean samples fall at the boundary with non-Archean samples, which thus demonstrates a low degree of carbonization when compared to most Archean CM. As a result, these samples constitute candidates that may contain preserved molecular signatures of Archean CM. Therefore, with regard to the search for the oldest molecular traces of life on Earth, we propose the use of this carbonization continuum diagram to select the Archean CM samples. Key Words: Archean—Early life—Kerogen—Raman spectroscopy—Carbonization. Astrobiology 16, xxx–xxx.

1. Introduction

The biological origin of some Archean carbonaceous matter (CM) is still debated (Schopf and Packer, 1987; Brasier et al., 2002; Lindsay et al., 2005; Marshall et al., 2012). Indeed, although most non-Archean CM is usually considered to be of biological origin, abiotic processes such as Fischer-Tropsch-type synthesis and siderite decomposition are often thought to account for Archean CM formations (van Zuilen et al., 2002, 2003; McCollom and Seewald, 2006; see van Zuilen et al., 2007, and references therein for more details about abiotic formation of CM). Molecular characterization of Archean CM has recently been recognized as a promising tool with which to discriminate between biotic and abiotic CM (Brocks et al., 2003; Marshall et al., 2007; Derenne et al., 2008). Unfortunately, in most samples, multiple sources of postdepositional CM and the extensive impact of metamorphism have resulted in the masking or elimination of molecular structures and a lack of univocal molecular biosignatures (Bourbin et al., 2012a; French et al., 2015). Quantifying the degree of alteration of Archean CM was thus of prime interest in the search for molecular...
biosignatures in the oldest cherts on Earth (Marshall et al., 2012). Indeed, as stressed by French et al. (2015), “future exploration for Archean biomarkers should screen for rocks with milder thermal histories.”

In this respect, the thermal alteration of CM is known to be driven by two reactions, namely, carbonization and graphitization (Oberlin, 1984, 1989). Carbonization is characterized by (i) chemical changes that consist of the relative enrichment of CM in aromatic structures (aromatization) due to the loss of oxygenated groups and other chemical groups containing heteroelements and aliphatic units, and (ii) structural changes resulting in the formation of nanometer-sized polyaromatic layers that tend to stack into structural units (Oberlin, 1984, 1989; Rouzaud et al., 2012, 2015). In natural environments, carbonization takes place in the 100–500°C temperature range (Mrozowski, 1988a, 1988b; Lahfid et al., 2010). Graphitization is a process whereby the aromatic skeleton is reorganized, yielding hexagonal graphite with triperiodic order and subsequent crystalline growth (Oberlin, 1984; Lahfid et al., 2010; Rouzaud et al., 2012, 2015; Charon et al., 2014). In natural carbons, graphitization takes place at higher temperature than carbonization and only in the presence of pressure (Oberlin 1984, 1989).

In recent years, Raman spectroscopy has become a favored technique with which to investigate CM evolution by way of carbonization and graphitization processes (Lahfid et al., 2010; Rouzaud et al., 2012, 2015; Charon et al., 2014). Raman spectra of CM exhibit two broad bands that are respectively assigned to defects (D) and graphite (G). Upon carbonization, these bands narrow, and their intensity ratios I(D)/I(G) increase, whereas I(D)/I(G) decrease during graphitization (Bernard et al., 2010; Rouzaud et al., 2012, 2015; Charon et al., 2014). Because carbon maturation is an irreversible process, CM records its highest thermal maturity stage (Beyssac et al., 2002).

In the present study, we investigated through Raman spectroscopy the chemical and structural features of kerogens isolated from cherts that underwent no, or low, metamorphism that ranges from prehnite-pumpellyite to greenschist facies and with ages that range from 0.05 to 3.5 Ga. The Raman spectroscopy data will be discussed in light of results from elemental analysis, solid-state 13C nuclear magnetic resonance (NMR), and high-resolution transmission electron microscopy (HRTEM). Utilizing data derived from Raman spectra in the literature, we propose a framework with which to select the most favorable samples in the search for molecular traces of life.

2. Material and Methods

2.1. Samples

Seventeen cherts of various ages, metamorphic facies, and geographical origins were studied. Cherts were selected because of their low porosity, which makes their organic matter less prone to postdeposition contamination. The sample characteristics are given in Table 1. All cherts underwent no, or low, metamorphism ranging from prehnite-pumpellyite to greenschist facies and with ages ranging from 0.05 to 3.5 Ga (Table 1).

The Clarno Formation (ca. 0.05 Ga) is situated in the John Day Basin in northern Oregon, United States of America. It consists of thick layers of various rocks that range from volcanic to sedimentary and formed within an extensional basin or a series of basins near a volcanic arc complex. We examined a black chert sample (n°1; Table 1) that formed in a marsh environment in close proximity to hot springs. The hot springs provided silica, which precipitated to form bedded cherts (Arnold and Daugherty, 1964). Clarno black chert contains millimeter- to centimeter-scale permineralized fossils of organic materials such as wood tissue, fungi remnants, and diffused organic matter.

The Rhynie sample (n°2; Table 1) was collected in the Dryden Flags Formation, Aberdeenshire, North-East Scotland. This Devonian sample is characterized by a microcrystalline silica matrix that formed by way of a subaerial hot spring system (Rice et al., 1995). Formation of silica sinters favored the exceptional preservation remnants of continental life, and the studied sample contains a wide variety of CM from fungi, algae, spores, and woody remnants.

Zalesie Nowe, Zdanów (Poland), and Döbra cherts (Germany; n°3–5; Table 1) are early Silurian samples that are representative of typical Paleozoic primary cherts composed of cryptocrystalline and mostly homogeneous quartz with a small admixture of phyllosilicate minerals. The cherts are distinctly laminated and consist of well-defined, horizontally extended undulating laminae that are 10–40 μm thick and composed of amorphous dark brown to brownish-red organic material. Organic matter has been identified mostly as fossil remnants of algae and benthic cyanobacterial mats. Graftolites indicate a Llandovery (early Silurian) age for all samples.

The Gunflint cherts (n°6–8; Table 1) were collected in the Gunflint Formation, Port Arthur homocline, Ontario, Canada. This 1.9 billion-year-old formation is composed of alternation between banded iron formation rocks and silica cherts. The three studied black cherts are dominated by cryptocrystalline quartz. They also comprise spheric and filamentous structures.

The Rietgat sample (n°9; Table 1) was sampled in the Venterdorp Conglomerate Supergroup, Platberg Group (South Africa), which comprises a succession of volcanic and sedimentary rocks. The Rietgat sample (ca. 2.6 Ga) represents fluvial and/or lacustrine silicified sediments in which the occurrence of algal matter was suggested (Buck, 1980).

Farrel Quartzite samples (n°10–14; 3.0 Ga; Table 1) were collected from the Goldsworthy greenstone belt in the Pilbara Craton, Western Australia. Two samples (GFWEX1-1b, MGTKS1 up) are bedded black chert and contain microfossils (Sugitani et al., 2007, 2009; House et al., 2013, and references therein). They are assumed to have deposited in a shallow evaporitic basin with input of hydrothermal fluids (Sugahara et al., 2010). GGR2 is a black chert interbedded with sandstone from the lower unit of the Farrel Quartzite. ORW9 and GRW10 are laminated black cherts from the cherty succession, which conformably overlies the Farrel Quartzite that is assigned to the Cleaverville Formation.

The Josefsdal chert (n°15; 3.3 Ga; Table 1) was sampled from a chert horizon situated in the Barberton greenstone belt, Onverwacht Group, located in the upper part of the Josefsdal Valley, South Africa. The Josefsdal chert sample consists of silicified volcanoclastic sediments. It is laminated and contains phyllosilicate grains and silica veins (Westall et al., 2006).
Table 1. Characteristics of the Cherts Studied (Identified by Numbers 1 to 17)

| No. | Chert reference | Age (Ga) | Geological unit, locality | Estimated metamorphic grade | Described in |
|-----|-----------------|----------|---------------------------|-----------------------------|--------------|
| 1   | Clarno (PPRG456) | 0.05     | Clarno Formation, John Day Basin Tectonic Unit, Oregon, USA | n.m. | Walter et al., 1983 |
| 2   | Rhynie (1 of 9/13/83) | 0.4     | Rhynie, Dryden Flags Formation, Grampian Highlands, Aberdeenshire, Scotland | n.m. | / |
| 3   | Zalesie Nowe | 0.42 | Zalesie Nowe, Holy Cross Mountains, Bardo Syncline, Poland | p.p. to p.a. | Kremer and Kazmierczak, 2005 |
| 4   | Zdanow | 0.42 | Zdanow, Bardzkie Mountains, Sudetes Mountains, Poland | p.p. to p.a. | Kremer, 2006 |
| 5   | Döbra | 0.42 | Döbra, Franconian Forest, Bavaria, Germany | lower g.s. | Kremer et al., 2012 |
| 6   | Gunflint (3 of 06/30/84) | 1.9 | Gunflint Iron Formation, Port Arthur Homoclinc Tectonic Unit, Ontario, Canada | lower g.s. | Awramik and Barghoorn, 1977; Marin-Carbonne et al., 2012 |
| 7   | Gunflint (PPRG134) | 1.9 | Gunflint Iron Formation, Port Arthur Homoclinc Tectonic Unit, Ontario, Canada | lower g.s. | / |
| 8   | Gunflint (1 of 08/23/86) | 1.9 | Gunflint Iron Formation, Port Arthur Homoclinc Tectonic Unit, Ontario, Canada | lower g.s. | Beaumont and Robert, 1999 |
| 9   | Rietgat (SB023) | 2.65 | Rietgat Formation, Platberg Group, Ventersdorp Supergroup, South Africa | lower g.s. | / |
| 10  | Farrel Quartzite (GGR2) | 3.0 | Mount Goldsworthy–Mount Grant area, Pilbara Craton, Australia | lower to mid g.s. | / |
| 11  | Farrel Quartzite (GRW10) | 3.0 | Mount Goldsworthy–Mount Grant area, Pilbara Craton, Australia | lower to mid g.s. | / |
| 12  | Farrel Quartzite (ORW9) | 3.0 | Mount Goldsworthy–Mount Grant area, Pilbara Craton, Australia | lower to mid g.s. | / |
| 13  | Farrel Quartzite (GFWEX 1-1b) | 3.0 | Mount Goldsworthy–Mount Grant area, Pilbara Craton, Australia | lower to mid g.s. | / |
| 14  | Farrel Quartzite (MGTKS1 up) | 3.0 | Mount Goldsworthy–Mount Grant area, Pilbara Craton, Australia | lower to mid g.s. | / |
| 15  | Josefsdal (99SA07) | 3.3 | Josefsdal Valley, Kromberg Formation, Onverwacht Group, Barberton greenstone belt, South Africa | g.s. | Westall et al., 2006 |
| 16  | Middle Marker (07SA22) | 3.4 | Middle Marker, Komati Formation, Barberton greenstone belt, South Africa | g.s. | / |
| 17  | Dresser (PPRG006) | 3.5 | Dresser Formation (former Towers Formation), Warrawoona Group, Pilbara Block, Australia | p.p. to lower g.s. | Walter et al., 1983; Derenne et al., 2008 |

The cherts were collected by J.W. Schopf, S.M. Awramik, B. Kremer, K. Sugitani, and F. Westall. The metamorphic facies are indicated as follows: n.m. = non-metamorphosed; p.p. = prehnite-pumpellyite; p.a. = pumpellyite-actinolite; g.s. = greenschist.
The Middle Marker chert (n=16; 3.4 Ga; Table 1) was sampled in the Barberton greenstone belt, South Africa. It consists of silicified detrital sediment comprising volcanic grain, fluid inclusions, and CM flocules (Bourbin et al., 2012b).

The Dresser chert (n=17; 3.5 Ga; Table 1) was collected in the Towers Formation at North Pole B Deposit Mine, Warrawoona Group, Pilbara Craton, Australia (Walter et al., 1983). This sample is a secondary chert that formed by the accumulation of carbonate sediments that were then silicified by hydrothermal fluids. This chert is characterized by microcrystalline silica with dispersed CM.

2.2. Methods

The kerogen was isolated from the cherts by using the classical HF/HCl protocol (Durand and Nicaise, 1980). The samples were crushed in a mechanical crusher, which was previously cleaned with ethanol. The soluble compounds were first extracted by using a dichloromethane/methanol (2/1: v/v) solvent mixture. The remaining powder was then submitted to a first acidic treatment with HCl 6 N and then to a second acidic treatment with a HF (40%)/HCl (6 N; 2/1: v/v) mixture. A final acidic treatment was then conducted with HCl 6 N at 60°C to dissolve any fluorides that may have been formed during the previous acidic treatment.

Ash content and elemental analyses for carbon (±0.4%) and hydrogen (±0.2%) contents were conducted by the SGS Company using calcination at 1000°C and thermal conductivity, respectively.

Cross-polarization/magic angle spinning (CP/MAS) solid-state 13C NMR spectroscopy was run on a Bruker Avance 400 spectrometer using a 14 kHz spinning rate to spin out chemical anisotropy and avoid spectrum disturbance by spinning side bands. Recycle and contact times were 10 s and 1 ms, respectively.

Raman spectra were obtained with a Renishaw InVIA microspectrometer, equipped with a 514.5 nm Spectra Physics argon laser at 20 mW. The laser was focused on the sample by using a DMLM Leica microscope with a 100× objective. The laser power at the sample surface was set at below 1 mW to prevent thermal alteration. The signal was detected by a Peltier cooled RENCAM CCD detector. The spectrometer was calibrated with a silicon standard before each session. As proposed by Sadezky et al. (2005), Raman spectra were decomposed into a combination of five Lorentzian/Gaussian bands (namely, D1, D2, D3, D4, and G; Fig. 1). In this decomposition, the height of the D1 band (occurring at ca. 1350 cm⁻¹) was fixed to be that of D, and the heights of the D2 to D5 bands were adjusted to obtain the best fit. Various Raman parameters can be determined: the full width at half maximum of the D1 (FWHM-D1) and of the G (FWHM-G) bands, and the intensity (band height) ratio of the defect (D1) and the graphite (G) bands, termed the R1 ratio (Beyssac et al., 2002).

As the heights of D and D1 are usually identical, R1 ratios may be directly determined graphically from literature Raman spectra and then compared to our data. FWHM-D1 values were also graphically estimated when values were lacking in the literature. The graphical procedure involves two biases in the determination of these parameters. First, it may enhance error in the estimation of the FWHM-D1 as D3, D4, and D5 bands are not considered. Second, it may underestimate the R1 ratio when a D2 is well defined. To assess the reliability of R1 and FWHM-D1 graphical determination, we compared the values obtained by both graphical determination and spectra decomposition. Results obtained from the two procedures were highly correlated for both R1 ($R^2=0.96$) and FWHM-D1 ($R^2=0.94$), validating the graphical determination of these parameters. HRTEM observations were carried out with a Jeol 2011 microscope operating at 200 keV. An image analysis technique that was initially developed for HRTEM images of disordered industrial carbons was then applied (Rouzaud and Clinard, 2002).

3. Assessment of the Thermal Maturity

H/C atomic ratios are known to decrease with the thermal maturation of kerogens (Lis et al., 2006; Vandenbroucke and Largeau, 2007). In the present sampling set, H/C varies from 1.32 to 0.28 (Table 2). For the three samples dated at 0.42 Ga (n=3–5; Table 2), a classical decrease in H/C with metamorphism grade was observed. However, such a trend is not visible when comparing the lower greenschist samples (n=6–9) with the lower to mid-greenschist samples (n=10–14) or with the greenschist samples (n=15 and 16). In addition, the Middle Marker (n=16) and the Gunflint (n=8) samples exhibit anomalously high H/C values (1.32 and 0.75, respectively) especially when considering their NMR-derived aromaticity (98% and 92%, respectively; Table 2; Fig. 2a). This illustrates the fact that hydrogen-rich minerals may survive the acidic treatment. Indeed, ash contents often exceed 50% in kerogen residues (n=8, 9, 10, 12, 13, 15, and 16; Table 2). However, it must be noted that within a given metamorphic grade (such as the Farrel Quartzite samples that underwent greenschist facies metamorphism), no relationship exists between ash content and H/C ratio. In all samples except Middle Marker, the H/C ratio remains lower than 1 even though the ash content is quite high, which indicates that the samples underwent early catagenesis to
### Table 2. Results from Elemental Analyses, $^{13}$C NMR, Raman Spectroscopy, and HRTEM on the Studied Cherts

| $^{13}$C NMR | Elemental analyses | Raman spectroscopy | HRTEM La (Å) | FWHM-G | FWHM-D1 | R1 ratio |
| --- | --- | --- | --- | --- | --- | --- |
| Age (Ga) | H content (%) | C content (%) | H/C atomic ratio | Ashes (%) | Aromatic carbon (%) | |
| 1 | Charon | 2.82±0.2 | 0.4 | 3 | n.d. | 57 | 45 |
| 2 | Rhione | 2.13±0.2 | 0.4 | 3 | n.d. | 57 | 45 |
| 3 | Zelenie Nowe | 2.47±0.2 | 0.4 | 3 | n.d. | 57 | 45 |
| 4 | Doba | 2.19±0.2 | 0.4 | 3 | n.d. | 57 | 45 |
| 5 | Gunflint | 2.64±0.2 | 0.4 | 3 | n.d. | 57 | 45 |
| 6 | Gunflint | 2.80±0.2 | 0.4 | 3 | n.d. | 57 | 45 |
| 7 | Rekkel | 2.62±0.2 | 0.4 | 3 | n.d. | 57 | 45 |
| 8 | Rekkel | 2.62±0.2 | 0.4 | 3 | n.d. | 57 | 45 |
| 9 | GORM | 2.62±0.2 | 0.4 | 3 | n.d. | 57 | 45 |
| 10 | GORM | 2.62±0.2 | 0.4 | 3 | n.d. | 57 | 45 |
| 11 | Farrel Quartzite | 3.0 | 0.1 | 3 | n.d. | 57 | 45 |
| 12 | Farrel Quartzite | 3.0 | 0.1 | 3 | n.d. | 57 | 45 |
| 13 | Farrel Quartzite | 3.0 | 0.1 | 3 | n.d. | 57 | 45 |
| 14 | Farrel Quartzite | 3.0 | 0.1 | 3 | n.d. | 57 | 45 |
| 15 | Farrel Quartzite | 3.0 | 0.1 | 3 | n.d. | 57 | 45 |
| 16 | Farrel Quartzite | 3.0 | 0.1 | 3 | n.d. | 57 | 45 |
| 17 | Farrel Quartzite | 3.0 | 0.1 | 3 | n.d. | 57 | 45 |

n.d. = not determined.

### Notes
- The Dresser sample is characterized by a surprisingly low aromaticity (57%) for Archean kerogens. The Dresser sample, on the other hand, presents a surprisingly low aromaticity (57%) for an Archean Sample. However, this result is consistent with the release of significant amounts of aliphatic moieties by pyrolysis (Derenne et al., 2008). Such aliphaticity may reflect the input of poorly ordered CM through hydrothermal circulation as recently demonstrated in the Apex chert (Marshall et al., 2012; Sforna et al., 2014) or late pyrobitumen generation formed through carbonization (Bernard et al., 2012).

Full width at half maximum of the D1 and G bands, together with the R1 ratios, was determined for each spectrum (Fig. 2b; Table 2). In this sample set, the R1 ratio clearly distinguishes non-Archean (0.47–0.97) from Archean samples (1.2–2.17; Fig. 3a). A similar distinction can be reached with FWHM-D1 (Archean FWHM-D1 = 59–87 cm$^{-1}$) and non-Archean FWHM-D1 = 126–249 cm$^{-1}$). A decrease in FWHM-G with increasing sample age and metamorphism was observed, although this parameter is less efficient in distinguishing between Archean and non-Archean cherts (Fig. 3b). FWHM-D1 and FWHM-G were previously reported to decrease with increasing natural carbonization (Wopenka and Pasteris, 1993; Bernard et al., 2010; Rouzaud et al., 2012). The gradual increase in the D1 band preponderance over the G band is consistent with the creation of defects inside the aromatic planes of the kerogen but without significant growth of the latter, which demonstrates that graphitization has not yet occurred. All samples fall into the range of FWHM-D1 (from ca. 300 to ca. 50 cm$^{-1}$) and R1 ratio values (from ca. 0.5 to 2) corresponding to carbonization as previously defined for numerous natural and anthropogenic carbonaceous matters (Charon et al., 2014; Romero-Sarmiento et al., 2014). Nonetheless, FWHM-D1 and R1 ratios alone are not straightforward when distinguishing between samples that have undergone either the end of carbonization or the early beginning of graphitization when FWHM-D1 remains stable and R1 ratio decreases (Beyssac et al., 2002). A HRTEM analysis is therefore required, as it provides an estimation of the mean length of polyaromatic layers and allows for distinction between carbonized and graphitized CM (Boulmier et al., 1982; Charon et al., 2014).

High-resolution transmission electron microscopy is a relevant tool with which to investigate the multiscale organization of CM (structure and nanostructure) by direct imaging of the profile of the polyaromatic layers (Boulmier et al., 1982; Oberlin, 1984, 1989; Buseck and Huang, 1985; Bustin et al., 1995; Rouzaud et al., 2015, and references therein). The structure corresponds to organization at the atomic scale that results from the existence of polyaromatic layers, single or stacked, to form structural units; the fringe mean length then corresponds to the crystallite size $\text{La}$ measured by Raman spectroscopy. The nanostructure is the organization from the nanometer to the micrometer scales. This results from the mutual orientation of layers or structural units to give domains of molecular orientation. The nanostructure provides information on the geochemical maturity, as shown for kerogens (Boulmier et al., 1982;
HRTEM images (Fig. 2c) reveal significant differences in multiscale organization within the studied series. Some samples such as Clarno are made of randomly oriented small (subnanometric) layers, indicating a low degree of thermal maturity. Others such as Middle Marker are made of much larger layers (some nanometers), which are stacked by 5 to 10 to form structural units. Moreover, the latter are locally oriented in parallel and form domains of molecular orientation. This means that these samples reached the metagenesis stage. Such characteristics are found for the oldest samples (Farrel Quartzite, Josefsdal, and Middle Marker) as well as for the most metamorphosed sample (Dobra), whereas the other samples appear much more disordered (see Clarno as an example in Fig. 2c). The mean length \( L_a \) derived from HRTEM image analysis ranges from ca. 5 Å up to 9 Å in the set of studied samples (Table 2; Fig. 3c). Thus, in agreement with Raman data, none of these samples underwent real graphitization (Tuinstra and Koenig, 1970; Ferrari and Robertson, 2000; Bernard et al., 2010; Charon et al., 2014), that is, a physical process corresponding to the triperiodic structure development and crystal growth that leads to the formation of perfectly stacked (along the A-B sequence) polyaromatic layers with mean length \( L_a \) up to 1000 nm (Oberlin, 1989). The increase in both \( L_a \) and \( R_1 \) similarly reflects the increase in metagenesis and early metamorphism for the most mature (Fig. 3c). Temperature is a key controlling factor; time, pressure, and the source of the organic precursor are known to affect FWHM-D1 and the R1 ratio during carbonization (Lahfid et al., 2010; Charon et al., 2014). Positions of samples within the FWHM-D1 versus the R1 ratio diagram (Fig. 3a) clearly indicate that all Archean samples are still in the carbonization stage, which is in good agreement with their metamorphism facies. Hence, this implies that Archean kerogens recorded a more extensive carbonization than those that are non-Archean, which is in agreement with their higher metamorphic grade and age (Table 2) without having reached the graphitization stage.

4. Implications in the Search for Traces of Life

To test the general character of the aforementioned changes in CM structures as a consequence of carbonization, FWHM-D1 and R1 values taken from literature spectra on various Archean and non-Archean CM were added to the present set of results (Fig. 3). Data about graphitized kerogens from the 3.8 billion-year-old Isua Supracrustal Belt and Akilia rocks (van Zuilen et al., 2007; Papineau et al., 2010) were also added to highlight the impact of early “real”
graphitization on FWHM-D1 and R1 ratio. These partially graphitized samples do not lie on the carbonization continuum reported in Fig. 4 and thus record strong structural changes, definitively altering the structure of original organic matter.

Literature Raman spectra of CM have been recorded by using a wide range of excitation laser energy (from 458 to 785 nm), and the relative intensities of the bands are known to strongly depend on the excitation laser energy (Mernagh et al., 1984). However, no substantial differences in the determination of the R1 ratio were reported when comparing spectra obtained with a 514.5 nm laser (as in the present study) or with a 532 nm laser (Aoya et al., 2010). As a result, literature Raman spectra acquired with a 514.5 or 532 nm laser were used in the following to obtain FWHM-D1 and R1 values and Fig. 4.

Taken together, the FWHM-D1 and R1 values confirmed the previously observed trend (Fig. 4). It must be noted that the same trend was observed on chondrites of petrologic type 3 (Bonal et al., 2007; Busemann et al., 2007), definitely showing that the carbonization continuum cannot be used to argue the biogenicity of CM (Pasteris and Wopenka, 2003). Regardless of the mineralogical context, two carbonization stages can be distinguished on the trend reported in Fig. 4. The first carbonization stage is characterized by a large range of FWHM-D1 values, which may reflect a precursor effect, the latter having a higher impact on carbonaceous organization (structure and nanostructure) at low temperature constraints (Lahfid et al., 2010). The beginning of the second stage of carbonization starts when R1 ratio reaches a value of ca. 0.8 to 1. Calibrating a Raman spectra–derived geothermometer on metasediments from the Glarus Alps (Cenozoic), Lahfid et al. (2010) pointed out that R1 ratio reached a value of 1 at about 300°C. Such a temperature seemed consistent with the metamorphism grade of studied rocks, which suggests that most Archean rocks were exposed to temperatures of roughly 300°C.

Full width at half maximum of the D1 band and R1 values also highlighted two groups of CM that merit further discussion (Fig. 4). A first group of CM falls at the outer limit of the carbonization/graphitization continuum, as the members of this group exhibit unusual and very high R1 ratio (≥2.5; Fig. 4). They comprise “coccoid-like” abiotic CM from the Cleaverville Formation (3.0 Ga; Ueno et al., 2006) and some CM from the Kromberg and Hooggenoeg Formation cherts (3.48–3.26 Ga; Hofmann et al., 2014). Although these high R1 values reflect a strong thermal alteration, this is not necessarily the case for all CM from South African Archean rocks that have undergone variable degrees of regional metamorphism (van Zuilen et al., 2007). However, an intense hydrothermal activity was recorded for the samples as presented in Fig. 4 (Sugitani et al., 1996; Hofmann et al., 2014; Westall et al., 2015). Although high R1 values are likely to reflect a strong carbonization, we question the impact of hydrothermal fluids on the structure of CM. Despite the fact that hydrothermal circulation can supply low ordered CM in comparison to syngenetic CM (Marshall et al., 2012; Sforna et al., 2014), the impact of hydrothermal fluids on syngenetic CM structure remains poorly constrained. Hence, to the best of our knowledge, it seems that CM with high R1 ratio was altered, which makes these samples unsuitable for classical biomarker analysis.
although some CM with high R1 ratio may contain other biosignatures (morphological, geochemical and organic, e.g., Westall et al., 2011). As a result, CM with high R1 values must be avoided in the search for molecular evidence of life. A second group of samples comprise some Archean CM from the Apex Basalt chert (3.49 Ga; Brasier et al., 2002; Schopf et al., 2002; Sforna et al., 2014) and microbially induced sedimentary structures (MISS) from the Dresser Formation (3.48 Ga; Noffke et al., 2013). These sample types exhibit a high FWHM-D1 and low R1 values compared to other Archean CM (see Fig. 4 inset), and they are therefore located at the boundary between Archean and non-Archean samples despite their old age. Their relatively low R1 values (0.72 to 1) suggest that this Archean CM underwent milder carbonization. In turn, this should favor the conservation of molecular remnants of early traces of life.

5. Conclusion

Combining Raman spectroscopy, $^{13}$C NMR, HRTEM, and elemental analyses highlights the impact of carbonization in the structural order of non-Archean and Archean kerogens. The quantitative parameters FWHM-D1 and R1 ratio derived from literature Raman spectra indicate that most non-Archean CM underwent a first carbonization stage, whereas most Archean samples underwent a second carbonization stage. The latter is characterized by an increase in the R1 ratio, which probably reflects two stages of heteroatom release.

The existence of CM with unusually high R1 ratio values was highlighted. In some cases, hydrothermal activity is presumed to play a key role in maturation of CM by favoring the rise of defects in polyaromatic layers. In the carbonization continuum, some Archean samples fall at the

FIG. 4. Compilation of R1 ratio and FWHM-D1 estimated on Archean and non-Archean CM from this study and from literature Raman spectra (Roberts et al., 1995; Brasier et al., 2002; Schopf et al., 2002; Marshall et al., 2005; Ueno et al., 2006; Westall et al., 2006; van Zuilen et al., 2007; Igisu et al., 2009; Javaux et al., 2010; Papineau et al., 2010; Sugitani et al., 2010; Marshall et al., 2012; Schiffbauer et al., 2012; Lepot et al., 2013; Noffke et al., 2013; She et al., 2013; Hofmann et al., 2014). Non-Archean and Archean samples from this study are, respectively, represented by empty and gray circles, whereas those from the literature are respectively indicated by empty and gray triangles. Graphitized CM is represented by black triangles. Number 1 corresponds to samples with unusual high R1 (Ueno et al., 2006; Hofmann et al., 2014) discussed in the text. Number 2 indicates Archean CM with low structural order discussed in the text [D = CM from the Dresser Formation characterized in Noffke et al. (2013); A = CM from the Apex Basalt chert characterized in Brasier et al. (2002), Schopf et al. (2002), and Sforna et al. (2014)].
boundary defined by CM of nonquestionable biological origin. Definitely non-graphitized, these samples are the best candidates to consider in the search for molecular biomarkers.

Acknowledgments

The authors are thankful to F. Delbes (UPMC) and J.J. Pantel for his help in sample crushing, to C. Anquetil and F. Costa-Torro (CNRS) for running $^{13}$C NMR measurements, and to E. Charon for calibrating the Raman spectrometer. This work was supported by the PNP (Programme National de Planétologie) program of the CNRS (Centre National de la Recherche Scientifique), the National Science Centre grant NN307468938 (BK) and by the ERC project “PaleoNanoLife.” We also acknowledge the anonymous reviewers for their constructive comments.

Disclosure Statement

No competing financial interests exist.

References

Aoya, M., Kouketsu, Y., Endo, S., Shimizu, H., Mizukami, T., Nakamura, D., and Wallis, S. (2010) Extending the applicability of the Raman carbonaceous-material geothermometer using data from contact metamorphic rocks. Journal of Metamorphic Geology 28:895–914.

Arnold, C.A. and Daugherty, L.H. (1964) A fossil Dennstaedtioid fern from the Eocene Clarno Formation of Oregon. Contributions from the Museum of Paleontology, University of Michigan 19:65–88.

Awramik, S.M. and Barghoorn, E.S. (1977) Gunflint microbial mats. Precambrian Res 5:121–142.

Beaumont, V. and Robert, F. (1999) Nitrogen isotope ratios of kerogens in Precambrian cherts: a record of the evolution of atmosphere chemistry? Precambrian Res 96:63–82.

Bernard, S., Beyssac, O., Benzerara, K., Findling, N., Tzvetkov, G., and Brown, G.E., Jr. (2010) XANES, Raman and XRD study of anthracene-based cokes and saccharose-based chars submitted to high-temperature pyrolysis. Carbon 48:2506–2516.

Bourdier, S., Wirth, R., Schreiber, A., Schulz, H.M., and Horsfield, B. (2012) Formation of nanoporous pyrobitumen residues during maturation of the Barnett Shale (Fort Worth Basin). Int J Coal Geol 103:3–11.

Beyssac, O., Goffe, B., Chopin, C., and Rouzaud, J.N. (2002) Raman spectra of carbonaceous material in metasediments: a new geothermometer. Journal of Metamorphic Geology 20:859–871.

Bonan, L., Bourrot-Denise, M., Quirico, E., Montagnac, G., and Lewin, E. (2007) Organic matter and metamorphic history of CO chondrites. Geochim Cosmochim Acta 71:1605–1623.

Boulmier, J.L., Oberlin, A., Rouzaud, J.-N., and Villey, M. (1982) Natural organic matters and carbonaceous materials: a preferential field of application for transmission electron microscopy. In Scanning Electron Microscopy, edited by A.M.F. O’Hare, SEM Inc., Chicago, pp 1523–1538.

Bourbin, M., Derenne, S., and Robert, F. (2012a) Limits in pyrolysis-GC-MS analysis of kerogen isolated from Archean cherts. Org Geochem 52:32–34.

Bourbin, M., Derenne, S., Gourier, D., Rouzaud, J.N., Gautret, P., and Westall, F. (2012b) Electron paramagnetic resonance study of a photosynthetic microbial mat and comparison with Archean cherts. Orig Life Evol Biosph 42:569–585.

Brasier, M.D., Green, O.R., Jephcoat, A.P., Kleppe, A.K., Van Kranendonk, M.J., Lindsay, J.F., Steele, A., and Grassineau, N.V. (2002) Questioning the evidence for Earth’s oldest fossils. Nature 416:76–81.

Buck, S.G. (1980) Stromatolite and ooid deposits within the fluvial and lacustrine sediments of the Precambrian Venterdsorp Supergroup of South Africa. Precambrian Res 12:311–330.

Buseck, P.R. and Huang, B.J. (1985) Conversion of carbonaceous material to graphite during metamorphism. Geochim Cosmochim Acta 49:2003–2016.

Busemann, H., Alexander, C.M.O.D., and Nittler, L.R. (2007) Characterization of insoluble organic matter in primitive meteorites by microRaman spectroscopy. Meteorit Planet Sci 42:1387–1416.

Bustin, R.M., Ross, J.V., and Rouzaud, J.N. (1995) Mechanisms of graphite formation from kerogen—experimental evidence. Int J Coal Geol 28:1–36.

Charon, E., Aleon, J., and Rouzaud, J.N. (2014) Impact delivery of organic matter on the acapulcoïd-lodranite parent-body deduced from C, N isotopes and nanostructures of carbon phases in Acapulco and Lodran. Geochim Cosmochim Acta 142:224–239.

Derenne, S., Robert, F., Skrzypczak-Bonduelle, A., Gourier, D., Binet, L., and Rouzaud, J.-N. (2008) Molecular evidence for life in the 3.5 billion year old Warrawoona chert. Earth Planet Sci Lett 272:476–480.

Durand, B. and Espitalié, J. (1976) Geochemical studies on organic-matter from Douala Basin (Cameroon). 2. Evolution of kerogen. Geochim Cosmochim Acta 40:801–808.

Ferrari, A.C. and Robertson, J. (2000) Interpretation of Raman spectra of disordered and amorphous carbon. Physical Review B 61:14095–14107.

French, K.L., Hallmann, C., Hope, J.M., Schoon, P.L., Zumbehere, J.A., Hoshino, Y., Peters, C.A., George, S.C., Love, G.D., Brocks, J.J., Buick, R., and Summons, R.E. (2015) Reappraisal of hydrocarbon biomarkers in Archean rocks. Proc Natl Acad Sci USA 112:5915–5920.

Hofmann, A., Bolhar, R., Orberger, B., and Foucher, F. (2014) Cherts of the Barberton greenstone belt, South Africa: petrology and trace-element geochemistry of 3.5 to 3.3 Ga old silicified volcaniclastic sediments. South Afr J Geol 116:297–322.

House, C.H., Oehler, D.Z., Sugitani, K., and Mimura, K. (2013) Carbon isotopic analyses of ca. 3.0 Ga microstructures imply planktonic autotrophs inhabited Earth’s early oceans. Geol 41:651–654.

Igisu, M., Ueno, Y., Shimojima, M., Nakashima, S., Awramik, S.M., Ohta, H., and Maruyama, S. (2009) Micro-FITR spectroscopic signatures of bacterial lipids in Proterozoic microfossils. Precambrian Res 173:19–26.

Javaux, E.J., Marshall, C.P., and Bekker, A. (2010) Organic-walled microfossils in 3.2-billion-year-old shallow-marine siliciclastic deposits. Nature 463:934–938.

Kremer, B. (2006) Mat-forming coccoid cyanobacteria from early Silurian marine deposits of Sudetes, Poland. Acta Palaeontol Pol 51:143–154.
Kremer, B. and Kazmierczak, J. (2005) Cyanobacterial mats from Silurian black radiolarian cherts: phototrophic life at the edge of darkness? Journal of Sedimentary Research 75:897–906.

Kremer, B., Bauer, M., Stark, R.W., Gast, N., Altermann, W., Gursky, H.-J., Heckl, W.M., and Kazmierczak, J. (2012) Laser-Raman and atomic force microscopy assessment of the chlorococcacean affinity of problematic microfossils. J Raman Spectrosc 43:32–39.

Lahfid, A., Beyssac, O., Deville, E., Negro, F., Chopin, C., and Marshall, C.P., Love, G.D., Snape, C.E., Hill, A.C., Allwood, Lis, G.P., Schimmelmann, A., and Mastalerz, M. (2006) D/H ratios and hydrogen exchangeability of type-II kerogens with increasing thermal maturity. Org Geochem 37:342–353.

Marshall, A.O., Emry, J.R., and Marshall, C.P. (2012) Multiple generations of carbon in the Apex chert and implications for preservation of microfossils. Astrobiology 12:160–166.

Marshall, C.P., Javaux, E.J., Knoll, A.H., and Walter, M.R. (2005) Combined micro-Fourier transform infrared (FTIR) spectroscopy and micro-Raman spectroscopy of Proterozoic acritarchs: a new approach to palaeobiology. Precambrian Res 138:208–224.

Marshall, C.P., Love, G.D., Snape, C.E., Hill, A.C., Allwood, A.C., Walter, M.R., Van Kranendonk, M.J., Bowden, S.A., Sylvia, S.P., and Summons, R.E. (2007) Structural characterization of kerogen in 3.4 Ga Archaean cherts from the Pilbara Craton, Western Australia. Precambrian Res 155:1–23.

McCollom, T.M. and Seewald, J.S. (2006) Carbon isotope composition of organic compounds produced by abiotic synthesis under hydrothermal conditions. Earth Planet Sci Lett 243:74–84.

Mernagh, T.P., Cooney, R.P., and Johnson, R.A. (1984) Raman-spectra of graphon carbon-black. Carbon 22:39–42.

Mrozowski, S. (1988a) Electron-spin-resonance studies of carbonization and coalification processes. 1. Carbonaceous compounds. Carbon 26:521–529.

Mrozowski, S. (1988b) Electron-spin-resonance studies of carbonization and coalification processes. 2. Biological materials. Carbon 26:531–541.

Noffke, N., Christian, D., Wacey, D., and Hazen, R.M. (2013) Microbially induced sedimentary structures recording an ancient ecosystem in the ca. 3.48 billion-year-old Dresser Formation, Pilbara, Western Australia. Astrobiology 13:1103–1124.

Oberlin, A. (1984) Carbonization and graphitization. Carbon 22:521–541.

Oberlin, A. (1989) High resolution TEM studies of carbonization and graphitization. In Chemistry and Physics of Carbon, edited by P.A. Thrower, Marcel Dekker, New York, pp 1–143.

Papineau, D., De Gregorio, B.T., Cody, G.D., Fries, M.D., Mojzsis, S.J., Steele, A., Stroud, R.M., and Fogel, M.L. (2010) Ancient graphite in the Eourchean quartz-pyroxene rocks from Akilia in southern West Greenland I: Petrographic and spectroscopic characterization. Geochim Cosmochim Acta 74:5862–5883.

Pasteris, J.D. and Wopenka, B. (2003) Necessary, but not sufficient: Raman identification of disordered carbon as a signature of ancient life. Astrobiology 3:727–738.

Rice, C.M., Ashcroft, W.A., Batten, D.J., Boyce, A.J., Caulfield, J.B.D., Faillick, A.E., Hole, M.J., Jones, E., Pearson, M.J., Rogers, G., Saxton, J.M., Stuart, F.M., Trewin, N.H., and Turner, G. (1995) A Devonian auriferous hot-spring system, Rhyne, Scotland. J Geol Soc London 152:229–250.

Roberts, S., Tricker, P.M., and Marshall, J.E.A. (1995) Raman spectroscopy of chitinozoans as a maturation indicator. Org Geochem 23:223–228.

Romero-Sarmiento, M.-F., Rouzaud, J.-N., Bernard, S., Deldicque, D., Thomas, M., and Littke, R. (2014) Evolution of Barnett Shale organic carbon structure and nanostructure with increasing maturation. Org Geochem 71:7–16.

Rouzaud, J.N. and Clinard, C. (2002) Quantitative high-resolution transmission electron microscopy: a promising tool for carbon materials characterization. Fuel Processing Technology 77:229–235.

Rouzaud, J.N., Deldicque, D., and Velde, B. (2012) Raman microspectrometry study of carbonization processes. First promising application in archaeology [abstract 956]. In Carbon 2012 Conference Proceedings, Krakow, Poland.

Rouzaud, J.N., Deldicque, D., Charon, E., and Pageot, J. (2015) Carbons at the heart of questions on energy and environment: a nanostructural approach. Comptes Rendus Geosciences 347:124–133.

Sadezky, A., Muckenhuber, H., Grothe, H., Niessner, R., and Poschl, U. (2005) Raman micro spectroscopy of soot and related carbonaceous materials: spectral analysis and structural information. Carbon 43:1731–1742.

Schiffbauer, J.D., Wallace, A.F., Hunter, J.L., Jr., Kowalewski, M., Bodnar, R.J., and Xiao, S. (2012) Thermally induced structural and chemical alteration of organic-walled microfossils: an experimental approach to understanding fossil preservation in metasediments. Geobiology 10:402–423.

Schopf, J.W. and Packer, B.M. (1987) Early Archean (3.3–3.5-billion-year-old) microfossils from Warrawoonga group, Australia. Science 237:70–73.

Schopf, J.W., Kudryavtsev, A.B., Agresti, D.G., Wdowiak, T.J., and Czaja, A.D. (2002) Laser-Raman imagery of Earth’s earliest fossils. Nature 416:73–76.

Sfrona, M.C., van Zuilien, M.A., and Philippot, P. (2014) Structural characterization by Raman hyperspectral mapping of organic carbon in the 3.46 billion-year-old Apex chert, Western Australia. Geochim Cosmochim Acta 124:18–33.

She, Z., Strother, P., McMahon, G., Nittler, L.R., Wang, J., Zhang, J., Sang, L., Ma, C., and Papineau, D. (2013) Terminal Proterozoic cyanobacterial blooms and phosphogenesis documented by the Doushantuo granular phosphorite I: In situ micro-analysis of textures and composition. Precambrian Res 235:20–35.

Sugahara, H., Sugitani, K., Mimura, K., Yamashita, F., and Yamamoto, K. (2010) A systematic rare-earth elements and yttrium study of Archean cherts at the Mount Goldsworthy greenstone belt in the Pilbara Craton: implications for the origin of microfossil-bearing black cherts. Precambrian Res 177:73–87.
Sugitani, K., Horiuchi, Y., Adachi, M., and Sugisaki, R. (1996) Anomalously low Al2O3/TiO2 values for Archean cherts from the Pilbara block, western Australia—possible evidence for extensive chemical weathering on the early Earth. Precambrian Res 80:49–76.

Sugitani, K., Grey, K., Allwood, A., Nagaoka, T., Mimura, K., Minami, M., Marshall, C.P., Van Kranendonk, M.J., and Walter, M.R. (2007) Diverse microstructures from Archaean chert from the Mount Goldsworthy–Mount Grant area, Pilbara Craton, Western Australia: microfossils, dubiofossils, or pseudofossils? Precambrian Res 158:228–262.

Sugitani, K., Grey, K., Nagaoka, T., and Mimura, K. (2009) Three-dimensional morphological and textural complexity of Archean putative microfossils from the northeastern Pilbara Craton: indications of biogenicity of large (> 15 µm) spheroidal and spindle-like structures. Astrobiology 9:603–615.

Tuinstra, F. and Koenig, J.L. (1970) Raman spectrum of graphite. J Chem Phys 53:1126–1130.

Ueno, Y., Isozaki, Y., and McNamara, K.J. (2006) Coccolid-like microstructures in a 3.0 Ga chert from Western Australia. Int Geol Rev 48:78–82.

van Zuilen, M.A., Lepland, A., and Arrhenius, G. (2002) Reassessing the evidence for the earliest traces of life. Nature 418:627–630.

van Zuilen, M.A., Lepland, A., Arrhenius, G., and Versteegh, M. (2003) Graphite and carbonates in the 3.8 Ga old Isua Supracrustal Belt, southern West Greenland. Precambrian Res 126:331–348.

van Zuilen, M.A., Chaussidon, M., Rollion-Bard, C., and Marty, B. (2007) Carbonaceous cherts of the Barberton greenstone belt, South Africa: isotopic, chemical and structural characteristics of individual microstructures. Geochim Cosmochim Acta 71:655–669.

Wopenka, B. and Pasteris, J.D. (1993) Structural characterization of kerogens to granulite-facies graphite—applicability of Raman microprobe spectroscopy. Am Mineral 78:533–557.

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Submitted 31 July 2015
Accepted 23 December 2015