

## Preliminary comparison of precambrian and paleozoic kerogens from cherts. Spectroscopic evidence for aliphatic composition

PAVLE I. PREMOVIĆ, STOJAN R. STOJKOVIĆ, RONALD J. PUGMIRE\*  
and WARNER R. WOOLFENDEN\*\*

Department of Chemistry, Faculty of Science, University of Niš, YU-18000 Niš, Yugoslavia and  
\*Department of Fuels Engineering and\*\* Department of Chemistry, University of Utah,  
Salt Lake City, Utah 84112, USA

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Carbon-13 solid state nuclear magnetic resonance data on kerogen (in whole rock sample) of Middle Precambrian Gunflint chert reveal an aliphatic-type structure characteristic of algal kerogens. This is confirmed by Fourier transform infrared analysis of isolated kerogen. Similar results are obtained for the kerogens of both Late Precambrian Paradise Creek and Early Carboniferous Kiesel-schiefer cherts inferring the presence of a similar type of structure, rich in aliphatic carbons.

It is important to understand the nature of Precambrian kerogens because these materials may provide cogent evidence of the existence of life forms during the Precambrian. Obviously, when examining kerogen in a given Precambrian geologic matrix, one must analyze with as many chemical methods and techniques as possible to accumulate evidence for a biological vs. abiological origin. In our initial investigation of the Middle Precambrian Gunflint chert (*ca.* 1.9 Ga) we applied electron spin resonance (ESR) spectroscopy to study aromatic paramagnetic structures (condensed aromatic ring systems) incorporated in the chert kerogen. We found that these structures were identical to those found in much younger carbonaceous sedimentary rocks in which their origin is biologically controlled.<sup>1</sup> To extend this study, we have analyzed the Gunflint kerogen by Fourier transform (FT) infrared (IR) spectrometry and <sup>13</sup>C nuclear magnetic resonance (NMR) for solids. For comparison, studies were conducted on the Late Precambrian Paradise Creek (*ca.* 1.6 Ga) and Carboniferous Kiesel-schiefer (*ca.* 0.35 Ga) cherts.

### EXPERIMENTAL

Black stromatolitic Gunflint chert was collected near Schreiber, Ontario (Canada), at the type locality for many of the twelve species of microscopic plants recognized in the well-documented Gunflint microbiota.<sup>2</sup> Geochemistry, sedimentary and stable isotope studies provide further evidence for biological activity during the Gunflint era.<sup>2,3</sup> Black chert of the Paradise Creek formation, from Queensland (Australia) contains nanofossils in cherty blebs associated with branched stromatolites, comprising colonies analogous to living *Eucapsis*, a member of the blue-green algal family *Chroococcaceae*.<sup>4</sup> The Carboniferous chert Kiesel-schiefer from Harz (Germany) is more

coarsely bedded and are thought to represent silicified marine deposit.<sup>5</sup> According to Hoss<sup>5</sup> this rock contains many organically preserved microorganisms such as planktons, bacteria and algae. The origin, lithology, mode of preservation of organic constituents, as well as the (mild) thermal history of the three deposits appear to be quite similar.<sup>5,6</sup>

The extraction and fractionation procedure was similar to that used by Saby<sup>7</sup> and Premović.<sup>8</sup> Powdered rock (10 g) was extracted with benzene/methanol (1:3 v/v) for 90 h in a Soxlet apparatus. The extract constitutes the soluble organic fraction of the total sample. The residue remaining in the Soxlet thimble was treated with boiling hydrochloric acid (HCl, 4M) to remove most of the carbonates. Carbonate removal was checked by IR analysis. The insoluble residue constitutes the whole chert kerogen. This material was demineralized further by repeated treatment with boiling HF/HCl (22M and 0.25 M, respectively.) This acid mixture removes silicates<sup>7</sup> and the removal was checked by IR analysis. The final residue (0.1–0.3% of total sample) is isolated kerogen. It contained only small traces of inorganic materials, including pyrite, as confirmed by electron microscopy and microprobe analysis.

Carbon-13 NMR spectra of the whole chert kerogen were taken at 25.15 MHz with cross polarization (CP) and magic angle spinning (MAS) at room temperature on a Bruker CXP-100 spectrometer.<sup>9</sup> The isolation of kerogen from the silicic matrix, although desirable in the <sup>13</sup>C NMR analysis of kerogens, was not feasible in this case because of the small chert sample available (100 g).

The isolated kerogen sample was mixed with anhydrous potassium bromide (KBr) and pressed into disc (2.5 mg/150 mg KBr) with a load of 200 MPa. The spectra were recorded on a Bruker ISF 113 v FTIR spectrometer.

## RESULTS AND DISCUSSION

Our analysis indicates that the rock samples of 98% silicic component (mainly, cryptocrystalline quartz) contain 0.1–0.3% indigenous organic matter. Since the rocks were found to contain only traces of soluble organic substances (*ca.* 10<sup>-4</sup>%) it is clear that its original bioorganic material has suffered complete diagenetic conversion to insoluble organic material and gases – process analogous to coalification. On the other hand, petrologic and geologic evidence suggest that most, presumably all, of the organic materials in these sedimentary rocks are indigenous and syngenetic.<sup>6</sup>

Fig. 1a shows a typical <sup>13</sup>C spectrum of kerogen in the Gunflint chert sample taken with CP/MAS. The poor signal to noise is due to the low organic carbon content in the chert sample. Kerogen of the Paradise Creek chert has essentially an identical spectrum, Fig. 1b. These spectra exhibit only limited fine structure consisting of the typical broad bands (*ca.* 0–110 ppm) which are due to sp<sup>3</sup> hybridized carbons (*ca.* 80%) and the broad band (*ca.* 20%) due to sp<sup>2</sup> hybridized carbons (*ca.* 100–220 ppm). The broad resonance band from 0–50 ppm arises from overlapping of individual resonance lines due to saturated hydrocarbon structure. In typical coals and shales the maximum for this band is centered near 30 ppm indicative of the presence of a relatively large amount of hydroaromatic structure or the presence of linear and branched alkyl groups. The shoulder at *ca.* 70–80 ppm is characteristic to carbon adjacent to oxygen. The broad featureless band in the 150–220 ppm range arises from sp<sup>2</sup> hybridized carbon adjacent to oxygen (phenols and phenolic ethers) and carbonyls (carboxylic acids, esters and aldehydes).

Assignments for the IR absorptions are based on the work of Bent and Brown<sup>10</sup> and Painter *et al.*,<sup>11</sup> on coal macerals, and Rouxhet and Robin<sup>12</sup> on kerogen (these are: 740 cm<sup>-1</sup>, aromatic CH bending; *ca.* 1200 cm<sup>-1</sup>, contributions from C-C skeletal vibrations, C-OR stretching and C-OH deformation; 1375 cm<sup>-1</sup>, CH<sub>3</sub> deformation; 1450 cm<sup>-1</sup>, CH<sub>2</sub> and CH<sub>3</sub> deformation; 1600 cm<sup>-1</sup>, C=C stretching in aromatic rings and polyaromatic structures; 1700 cm<sup>-1</sup>, C=O stretching; 2850 and 2920 cm<sup>-1</sup>, aliphatic CH<sub>2</sub> stretching; *ca.* 3400 cm<sup>-1</sup>, OH stretching).

The FTIR spectrum of the Gunflint chert kerogen, Fig. 2a, has some general features characteristic for the IR spectra of the high rank vitrinites<sup>10,11</sup> and sporinites<sup>10</sup> and mature kerogens.<sup>12</sup> Strong absorption bands at  $2924 \pm 1 \text{ cm}^{-1}$ , as well as a weak band at  $1460 \pm 5 \text{ cm}^{-1}$  demonstrate a hydrocarbon structure with prominent alkyl chains. Extensive chain branching in this kerogen is indicated by an additional absorption at  $2960 \pm 1 \text{ cm}^{-1}$ . This band can be assigned to methyl ( $\text{CH}_3$ ) groups and both the  $2924 \text{ cm}^{-1}$  and  $2853 \text{ cm}^{-1}$  band are ascribed predominantly to methylene ( $\text{CH}_2$ ) groups although the aliphatic CH mode at  $2924 \text{ cm}^{-1}$  is also characteristic of  $\text{CH}_3$  groups attached directly to aromatic units.

Some degree of aromatization of the Gunflint chert kerogen, as indicated by an earlier ESR study,<sup>1</sup> is reflected by a strong absorption at  $1620 \pm 5 \text{ cm}^{-1}$  corresponding to an aromatic stretching mode in structures in which there is the possibility of intensity enhancement due to the presence of phenolic groups or due to the linkage of aromatic entities by  $\text{CH}_2$  and possibly ether bridges. Further FTIR evidence for aromatization was seen in a number of weak absorptions in the  $600\text{--}900 \text{ cm}^{-1}$  region related to various aromatic CH (out of plane bending). Support for

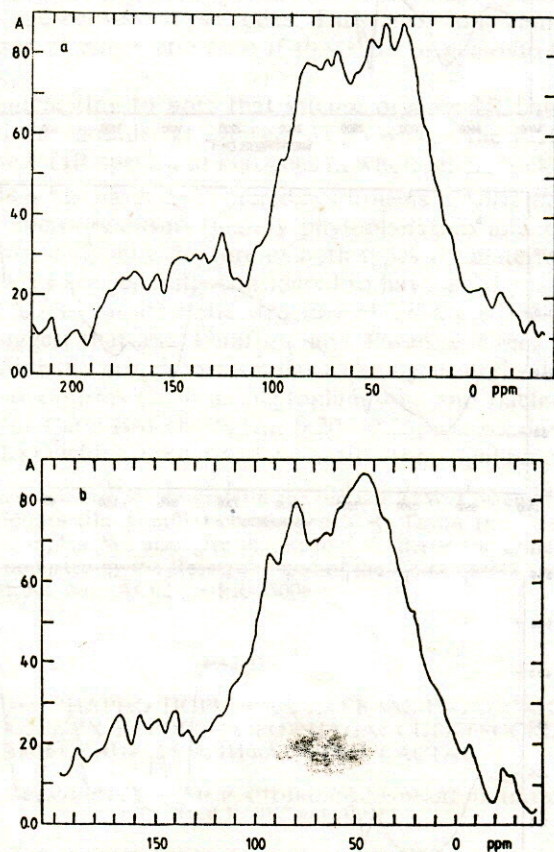


Fig. 1. Carbon-13 NMR spectra of kerogens in whole sediment (powdered) samples of: (a) the Gunflint chert (209008 scans) and (b) the Paradise Creek chert (243017 scans). A is the NMR absorption in arbitrary units.

the relatively low aromatic nature of the sample is provided by the  $^{13}\text{C}$  NMR data in Fig. 1a. The FTIR data of coal macerals of high rank<sup>10,11</sup> and mature kerogens,<sup>12</sup> are similar to the FTIR spectrum of the Gunflint chert kerogen in the absence of the C=O absorption at  $1700\text{--}1720\text{ cm}^{-1}$ . This absence of carbonyl and carboxyl groups in the FTIR is an indication that extensive diagenetic evolution of the kerogen in question may have occurred as expected in view of the age of the chert.

We also obtained FTIR data on kerogen of both the Paradise Creek chert, Fig. 2b, and the Kieselschiefer, Fig. 2c. What is striking is the similarity in the FTIR absorption patterns of these two kerogens and Gunflint chert kerogen. The signi-

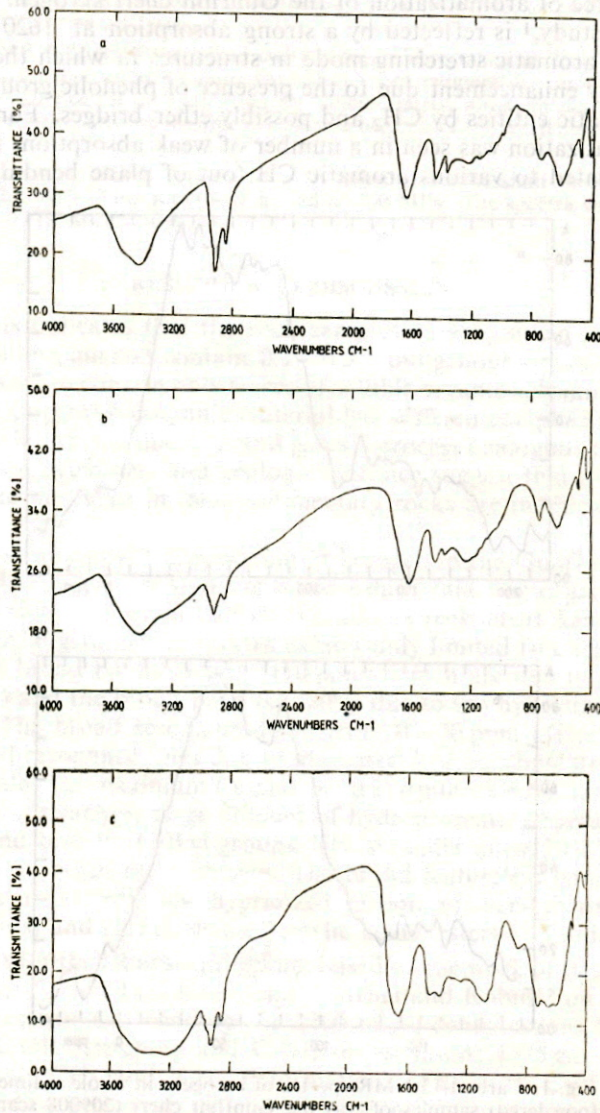


Fig. 2. FTIR spectra of isolated kerogen of: (a) the Gunflint chert, (b) the Paradise Creek chert; and (c) the Kieselschiefer.

ficant content of organic materials derived from marine (plant) organisms, (algae phytoplanktons and bacteria) in the Kieselschiefer, and its origin as a silicified deposit<sup>5</sup> suggest that features similar to those of marine (plant) kerogen might be expected. While more work is required for verification, it is interesting to speculate that the FTIR spectrum of the Kieselschiefer kerogen resembles those of the much older Precambrian sedimentary rocks that a similar type of biologic source could be inferred.

It is worth noting here that organic paramagnetic structures observed by ESR in the Paradise Creek chert and the Kieselschiefer are identical and at the same level of spin concentration (*ca.*  $10^{16}$  spins  $g^{-1}$ ). However, their ESR parameters ( $g = 2.00263 \pm 0.00005$  and linewidth  $\Delta H_{p-p} = 0.12 \pm 0.01$  mT), saturation behaviour with microwave power, ESR behavior on laboratory heating and temperature dependence of spin concentration<sup>13</sup> are distinctively different than those of the Gunflint chert.<sup>1</sup>

A comparison of the FTIR spectrum of the Kieselschiefer kerogen with those from much older Precambrian chert kerogens studied does not reveal significant differences in the degree of geochemical maturation, as might be expected from the great differences in age between these rocks. Thus, age alone cannot be the factor controlling the degree of diagenetic even if this span of geologic time is measured in billions of years.

Finally, it is interesting to note that intense organic IR bands at  $2924\text{ cm}^{-1}$  and  $2853\text{ cm}^{-1}$  (and the shoulder at  $2960\text{ cm}^{-1}$ ), as well as the  $1620\text{ cm}^{-1}$  band can be readily seen in the FTIR spectra of kerogens in whole silicic rock samples studied.

Organic geochemists have characterized kerogens as originating from remnants of algae and microorganisms (mainly phytoplanktons and bacteria) or remnants of higher plants, or from a mixture of both types of materials.<sup>14</sup> Of the two extremes, algal kerogens are generally considered to have an aliphatic-type structure and higher plant kerogens an aromatic structure.<sup>14</sup> Thus our <sup>13</sup>C NMR CP/MAS and FTIR results suggest that the Gunflint and Paradise Creek chert kerogens, containing mainly aliphatic groups, are similar to kerogens derived from algal organisms and/or microorganisms (such as phytoplanktons and bacteria). In fact, the aromaticity values for these two cherts (*ca.* 0.20–0.25) are similar to those of the Green River oil shales<sup>15</sup> which are derived primarily from algal remains.<sup>16</sup>

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#### ИЗВОД

### ПРЕЛИМИНАРНО ПОРЕЂЕЊЕ ПРЕКАМБРИЈАНСКИХ И ПАЛЕОЗОЈСКИХ КЕРОГЕНА РОЖНАЦА: СПЕКТРОСКОПСКЕ ЧИЊЕНИЦЕ ЗА АЛИФАТИЧНИ САСТАВ

ПАВЛЕ И. ПРЕМОВИЋ, СТОЈАН Р. СТОЈКОВИЋ, РОНАЛД Џ. ПАГМАЈЕР\*  
и ВОРНЕР Р. ВУЛФЕНДЕН\*\*

*Одељење за хемију, Филозофски факултет, Универзитет у Нишу, 18000 Ниш, Југославија и \*Одељење за гориво  
инжењерство и \*\*Одељење за хемију, Универзитет у Јути, Соли Лејк Сити, Јута 84112, САД*

GUNFLINT

<sup>13</sup>C нуклеарна магнетна резонанција керогена у целом узорку Ганфлинт рожнаца из средњег прекамбријума открива алифатични тип структуре карактеристичан за алгалне

FOULIER

PARADISE

керогене. Ово је потврђено Фуријеовом инфрацрвеном анализом изолованог керогена. Слични резултати су добијени за керогене Парадајз крик рожнаца (касни прекамбријум) и Кизелшифер — рожнаца (рани карбон). Ови резултати указују на присуство сличног типа структура у овим рожнацима, богатим алифатичним угљеником.

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KIESELSCHIEFER

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