Fourier transform infrared and electron spin resonance examinations of kerogen from the Gunflint stromatolitic cherts (Middle Precambrian, Ontario, Canada) and related materials

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Kerogen occurrences in stromatolitic cherts from the Middle Precambrian Gunflint Formation and related rocks have been investigated by the use of elemental analysis, Fourier transform infrared and electron spin reconance spectroscopies. Particular attention was paid to the structural properties of the Schreiber kerogen to allow comparison with biologically controlled kerogens from Paleozoic carbonaceous rocks. The low atomic H/C ratios (0.5) of the Schreiber kerogen indicates that this material has reached a high level of maturity. The Fourier transform infrared/electron spin resonance examinations revealed that the Schreiber kerogen contains predominantly aromatic/polyaromatic structures similar to those found in mature kerogens from Paleozoic carbonaceous rocks. The evidence from this organogeochemical comparison indicates that the Schreiber kerogen and mature kerogens from Paleozoic/Mesozoic carbonaceous rocks have sufficient similarity to suggest a similar origin. Consequently, this work gives strong support to the hypothesis that if the Schreiber kerogen is of biotic origin than it is derived from the remnants of various microbial organisms (mainly phytoplanktons) including a minor contribution of subtidal (stromatolite-building) cyanobacteria.

Keywords: kerogen, Gunflint stromatolitic cherts, electron spin resonance. Fourier transform infrared spectroscopy.

INTRODUCTION

Macrobiota

In marked contrast to the paucity of evidence of biological activity during Early Precambrian, Middle Precambrian sediments contain a wealth of paleobiological data. Of these occurrences, the most significant in terms of biological diversity and its preservation is the microbiota of the Gunflint Formation in unmetamorphosed black stromatolitic cherts of the Schreiber locality. The assem-

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blage of microscopic plants in the Schreiber stromatolitic cherts is composed predominantly of prokaryotic microorganisms, though the overwhelmingly dominant taxa are cyanobacteria, *i.e.,* filamentous *Gunflintia* and coccoid *Huroniospora.*[1–4] Although numerous other algae/bacteria occur in relatively small populations, the primary source of organic matter in the Schreiber cherts is presumably these two microorganisms. It is generally agreed that the Schreiber carbonaceous/fossiliferous cherts are the products of silicification of stromatolitic limestones deposited *via* the mediation of cyanobacteria in a marine subtidal environment.[2,5–7] The petrology of these cherts, and of associated sedimentary rocks, indicates a general absence of metamorphism; the brown-to-black kerogen suggests a mild thermal history.[2,8–10] Biogeochemical considerations of the Gunflint stromatolitic/algal rocks other than the Schreiber cherts suggest that marine subtidal cyanobacteria were also the prime builders of these sediments (Table I). Corroboratory evidence from geochemistry[2,11–16] and sedimentology[1–3,17,18] provide further evidence for the existence of biochemical activity during the Gunflint era (*ca.* 2 Ga ago).

Kerogen

Barghoorn *et al.*[13] have measured the stable carbon isotope ratios of kerogens from a wide variety of sediments of the Gunflint Formation. The $\delta^{13}C$ ratios of apparently syngenetic kerogen of black cherts from the Schreiber locality are found to be well within the range of values characteristic of organic materials of known photosynthetic origin or derivation and differ markedly from values typical of inorganically produced carbon compounds. [19,20]

In an earlier communication from this laboratory[21] it was suggested that kerogen from the Schreiber stromatolitic cherts is comparable to mature Paleozoic kerogens. However, this study was based on a single (Kussiella) type of the Schreiber carbonaceous chert from a single outcrop site and, as such, has a rather limited scope. It is the purpose of the present paper to report on a series of samples of various stromatolitic chert types distributed throughout the Schreiber deposit. In addition, this contribution examines the problem of the origin of kerogen from the Schreiber stromatolitic cherts in the light of some new geochemical data. The original hypothesis that the Schreiber kerogen is derived from Precambrian stromatolitic subtidal cyanobacteria is examined here by the parallel investigation of the kerogens from various Schreiber stromatolitic cherts and mature kerogens from Late Precambrian Bitter Springs stromatolite (0.9 Ga old, Australia), Paleozoic carbonaceous rocks including Late Devonian Sosnowiec stromatolite (0.3 Ga old, Poland) and Jurassic Vrška Čuka anthracite (0.19 Ga old, Serbia).

EXPERIMENTAL

Samples

The collections upon which this study is based were made by A-S. Edhorn and S. Awramik at a series of localities along the strike of the Gunflint Formation. The samples were selected to represent a wide range of microfossiliferous stromatolite-related rocks. The sampling localities are indicated in
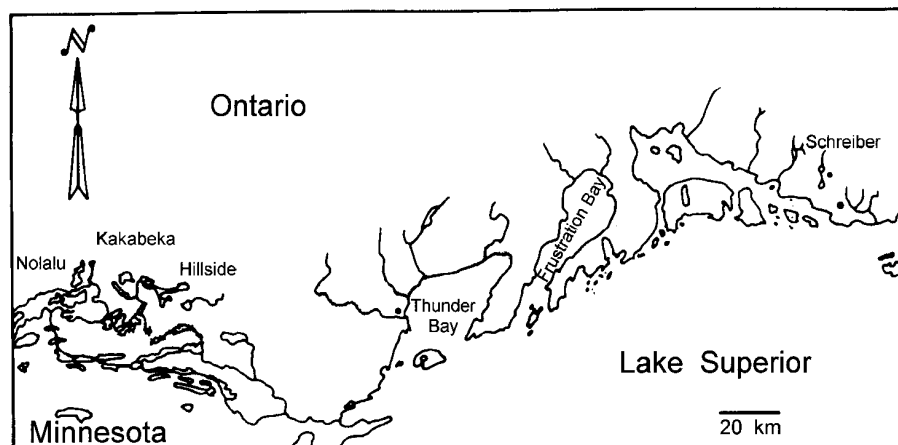
Fig. 1. Location map of the Gunflint Formation in W. Ontario (modified after Goodwin[17]).

Table I and on the map in Fig. 1. The regional geology of the Gunflint Formation has been summarized in detail by Goodwin,[17,22] Moorehouse,[1] Barghoorn and Tyler.[2] The Gunflint formation contains two cyclic units designated Lower and Upper member, respectively.[17] The Lower member consists of the following facies in ascending order: (1) black shale; (2) volcanoclastic shale; and, (3) taconite combined with banded chert and carbonates. The structurally preserved microflora originally described by Tyler and Barghoorn[23] were discovered in dense black stromatolitic cherts collected from the lower Gunflint outcrops at the Schreiber locality. The Upper member of the Gunflint formation is a repetition of the Lower member. Stromatolitic/non-stromatolitic rocks (listed in Table I) at localities other than Schreiber belong to the Lower or the Upper unit.

Samples were treated with maximum care to exclude contamination by handling or any other extraneous organic source before laboratory analysis. The rock samples were crushed to a fine powder (200–400 mesh) in a ball mill and stored in acid-cleaned vials.

Separation and extraction

The ground rock powders were treated with 20 % hydrochloric acid (HCl) to remove carbonates. After filtration and washing, the remaining minerals were acid leached by digestion for 72 h at room temperature using a 1:1 by volume mixture of concentrated hydrofluoric acid (HF): 48 % and HCl: 20 %. The mixture was filtered and the residue washed successively with boiling distilled water, and the pyrite was decomposed with $LiAlH_4$.[24] After drying, the insoluble organic concentrate was extracted with benzene/methanol azeotrope (6:1 v/v) until the solvent siphoning to the flask was clear. The material was dried at 80 °C and the resulting kerogen was stored in a desiccator.

Electron spin resonance (ESR)

The ESR measurements were made on the sealed, evacuated materials. The ESR experiments were performed on the samples (0.05–0.100 g) in a quartz or glass tube using a Bruker ER 200D ESR spectrometer employing 100 kHz modulation and a nominal frequency of 9.5 GHz interfaced to a HELP computer. All the tubes, containing the geological samples, were evacuated (before the ESR measurement) and sealed while still evacuated. The spin concentrations were calculated by double integration of the first derivative of a single line using the HELP computer system.

Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of the kerogens were obtained using KBr discs, using a Perkin-Elmer 1600 FTIR spectrometer. The aliphatic methyl/methylene (CH_3/CH_2) (2955 to 2920 cm^{-1}) bands of the FTIR spectra were studied by curve-fitting analysis.

Elemental (carbon/hydrogen) analysis

The kerogen samples were subjected to microanalysis for their C/H content in a Perkin-Elmer Model 240 elemental analyzer.

DEPOSITIONAL MILIEU: ANOXIC *vs.* OXIC

One of the requirements for the formation and preservation of both bioorganic substances (as the protokerogen precursor) and protokerogen during early diagenesis is anoxic conditions at the water/sediment interface and within the upper part of the sediment.[25] The abundance of pyrite, siderite and the presence of (brown to black) organic matter (predominantly kerogen) in the Schreiber cherts strongly suggest that their depositional environment was anoxic.[2,10,13,17,22,26] This type of environment is also suitable for the preservation/maturation of kerogen during the latter stages of diagenesis.[10]

Microscopic examination of Late Permian (0.25 Ga old, Harz Mountains) and Early Triassic (0.2 Ga old) stromatolites[27] and from modern (Shark Bay) stromatolites imply that cyanobacteria were, and presumably are responsible for these ancient and modern stromatolites (Table I). These organisms inhabited oxygenated bottom waters (with the O_2 content 5×10^{-3} mol dm^{-3}) of marine subtidal environments in which any bioorganic remains (the kerogen precursor) would have been destroyed soon after it had been buried through various oxidation reactions by free O_2. This may explain our failure to isolate kerogen from these stromatolites (Table I).

MATURITY OF KEROGEN

The finely disseminated kerogen of the Schreiber cherts ranges from 0.2 % to 0.9 % (Table II) which contains > 95 % structureless (amorphous) brown-black material and < 5 % inorganic insoluble fraction. Elemental analysis of the Schreiber kerogen samples are given in Table III. The low hydrogen content, and hence, low atomic H/C ratios (0.5)*, are characteristic of mature kerogen in the classification scheme reviewed by Tissot and Welte.[25] For comparison, elemental analyses of the Vrška Čuka anthracite, the kerogen from the Bitter Springs and Sosnowiec stromatolites are also listed. Surprisingly (other than the Schreiber cherts which belong to the Lower member of the Gunflint Formation), no kerogenous material was found in most of the microfossiliferous stromatolitic/non-stromatolitic rocks. This suggests that microbial productivity during deposition of the Lower unit was not widespread in the small and shallow Gunflint Basin. More work is needed to verify this observation. In general, the cherty bands of the Gunflint Formation are well-known to be remarkably free of organic carbon.[13]

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* The atomic H/C ratio in this case is insignificant for anything other than an indication of both maturity polyaromatic character of the Schreiber kerogen. Namely, the experimental error in the H analysis may be relatively large since the percentage of H is low.

TABLE II. Inorganic/oganic composition (wt %) of the Schreiber stromatolitic cherts

Rock sample	Iron oxides/carbonates	Silicates	Insoluble fraction*
Black (Kussiella-type) stromatolitic chert	7.3	91.0	0.9
Black (Gruneria-type) stromatolitic chert I	0.7	99.0	0.3
Black (Gruneria-type) stromatolitic chert II	10.8	89.0	0.2
Black (unnamed-type) stromatolitic chert I	4.5	95.0	0.6
Black (unnamed-type) stromatolitic chert II	2.8	97.0	0.2

* Kerogen + minor (< 5%) insoluble minerals: pyrite, fluorides *etc.*

The low atomic H/C ratios (0.5, Table III) of the Schreiber kerogen indicates that the degree of catagenesis is quite advanced, since similar values have been observed for kerogens of high maturity.[25] The extremely small concentrations (< 0.01 %) of soluble organic matter of the Schreiber cherts are, at least, consistent with such an interpretation. The low atomic H/C ratios are, also, evidence that the finely disseminated Schreiber kerogen has almost certainly undergone polyaromatization through extensive dehydrogenation. An atomic H/C ratio of 0.5 would be obtained from kerogen and coal in which the average structure was a polyaromatic hydrocarbon system containing more than 20 carbon atoms.[10]

TABLE III. Elemental analysis of the Schreiber and other kerogens [wt %, daf*]

Chert	C	H	H/C
Black (Kussiella-type) stromatolitic chert	82.5	3.5	0.5**
Black (Gruneria-type) stromatolitic chert I	87.0	4.0	0.5**
Black (Gruneria-type) stromatolitic chert II	82.0	3.5	0.5**
Black (unnamed-type) stromatolitic chert I	77.0	3.0	0.5**
Black (unamed-type) stromatolitic chert II	75.0	3.0	0.5**
Bitter Spring stromatolitic chert	66.0	4.0	0.7
Sosnowiec stromatolite	67.0	5.0	0.9
Vrška Čuka anthracite	88.0	3.7	0.5

* Dry ash free basis. ** High ash content (< 20 %) of this material indicates that actual value of its atomic H/C ratio could be higher.

FOURIER TRANSFORM INFRARED OF KEROGEN

The spectrum of the Schreiber kerogen from the Gruneria-type chert (Fig. 2a) is comparable to those from other types of the Schreiber stromatolitic cherts (Figs. 2b and 2c). The spectrum is dominated by a strong band centered in the 1590–1605

cm^{-1} region which is characteristic of solid carbonaceous systems and is generally assigned to large polyaromatic carbon skeletons.[28] The weak band at *ca.* 1700 cm^{-1} is usually ascribed to carbonyl groups. The three considerably reduced absorption bands in the 3100 cm^{-1} to 2700 cm^{-1} zone indicate the presence of aliphatic structures in the kerogen[29] and the weak absorption at 3030 cm^{-1} is related to aromatic/polyaromatic structures.[28] Further evidence for aromatization/polyaromatization is seen from the weak absorption bands in the 900–700 cm^{-1} region.[28] In fact, the FTIR spectrum of kerogen from the Schreiber cherts resembles those of the kerogens from the Bitter Springs chert (Fig. 2d), the Sosnowiec stomatolite (Fig. 2e), the Vrška Čuka anthracite (Fig. 2f) and the kerogens from Paleozoic/Mesozoic sedimentary rocks.[9,29]

The FTIR spectra of three kerogen samples from the Schreiber (Cruneria-, Kussiella- and unnamed-type) stromatolitic cherts, expanded for the region of 3100 cm^{-1} to 2700 cm^{-1}, are shown in Figs. 3a–c. For comparison, the expanded scale spectra for the Sosnowiec kerogen is given in Fig. 3d and for the Vrška Čuka
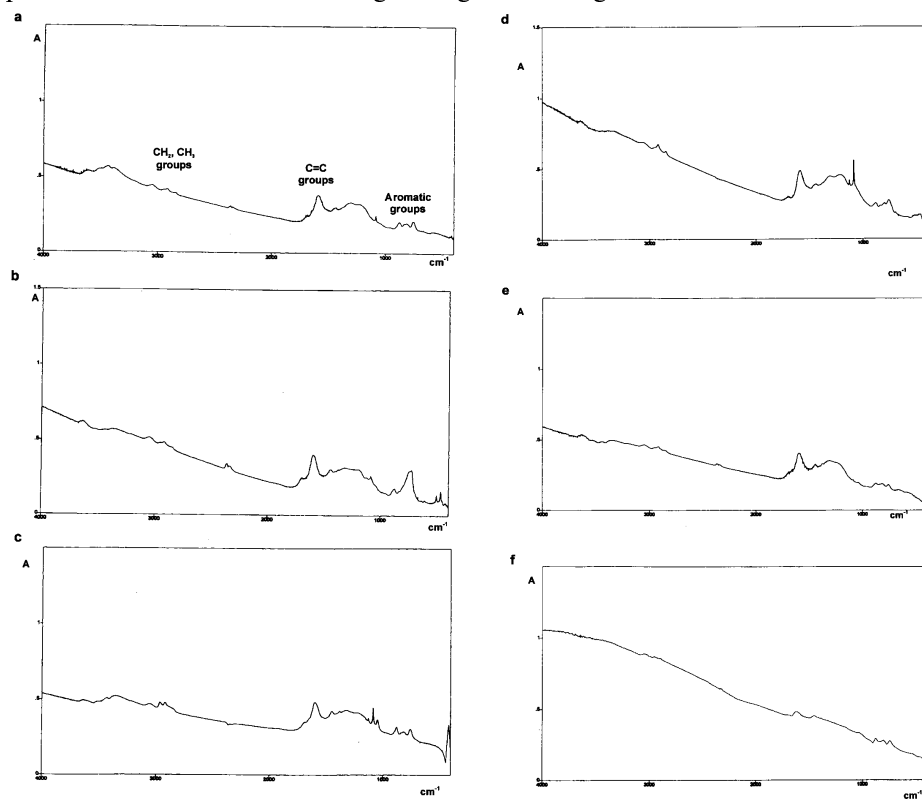

Fig. 2. The FTIR spectrum of kerogen isolated from: the Gruneria-type (a); Kussiella-type (b); unnamed-type (c) cherts; the Bitter Springs chert (d); the Sosnowiec stromatolite (e), and the Vrška Čuka anthracite (f).

anthracite in Fig. 3e. As in most mature kerogens, there are three principal bands, near 2955 cm^{-1}, 2920 cm^{-1} and 2860 cm^{-1}, that can be clearly assigned to CH_3/CH_2 groups attached to alkyl chains/aromatic rings. In general, from the curve-fitting analysis of the FTIR bands of kerogen, a series of relationships (defined as ratios of integrated absorbance areas) may be used to quantify the structural characteristics. The relationship used here was the CH_3/CH_2 ratios = 2955 cm^{-1} band/2920 cm^{-1} band. For most of the kerogenous materials (Schreiber cherts, Vrška Čuka anthracite, Bitter Springs and Sosnowiec kerogens) the CH_3/CH_2 ratio is between 0.4 do 0.5 (Table IV). This is probably due to loss of alkyl chains and conversion of various aromatic methylene structures to polyaromatic rings[30] during catagenesis of the Schreiber kerogen. An exception is the kerogen from one of the unnamed-type cherts, which has an exceptionally high content of methyl structures (the CH_3/CH_2 ratio > 1.0, Fig. 3f/Table IV), probably due to differences in the microbial precursor(s) and/or in the geological conditions of kerogen formation.

TABLE IV. The CH_3/CH_2 ratio of the Schreiber and other kerogens*

Chert	The CH_3/CH_2 ratio (± 0.1)
Black (Kussiella-type) stromatolitic chert	< 0.5
Black (Gruneria-type) stromatolitic chert I	0.4
Black (Gruneria-type) stromatolitic chert II	0.4
Black (unnamed-type) stromatolitic chert I	> 1.0
Black (unnamed-type) stromatolitic chert II	0.4
Bitter Springs stromatolitic chert	0.4
Sosnowiec stromatolite	0.5
Vrška Čuka anthracite	0.4

* Evalauated as the FTIR 2955 cm^{-1} band /2920 cm^{-1} band ratio (see above).

Three FTIR bands are observed in the 900 cm^{-1} to 700 cm^{-1} region for the Schreiber kerogen samples, as illustrated in Fig. 4a for the kerogen from the unnamed-type chert rich in methyl moieties (Fig. 3f). These bands are assigned to aromatic/polyaromatic structures with isolated aromatic hydrogens (870 cm^{-1}), two adjacent hydrogens per ring (815 cm^{-1}) and four adjacent aromatic hydrogens (750 cm^{-1}).[31] Similar FTIR spectra were recorded for the Schreiber kerogen from the Gruneria-type (Fig. 4b), and Kussiella-type (Fig. 4c) stromatolitic cherts, the Sosnowiec kerogen (Fig. 4d), and the Vrška Čuka anthracite (Fig. 4e). The curve-fitting analysis revealed the presence of other minor overlapping bands in the 900 cm^{-1} to 700 cm^{-1} zone. The number of adjacent hydrogens per ring provides an estimate of the degree of aromatic substitution/polyaromatization. The Schreiber kerogen has the most intense bands at 870 cm^{-1} and 750 cm^{-1} (Figs. 4a–4c), attributed to average aromatic sizes of 3 to 4 rings or more. Thus, condensed aromatic nuclei (3 to 4 rings) should be present in the Schreiber kerogen. Overall, the FTIR spectrum supports the concept of an aromatic/polyaromatic macrostruc-
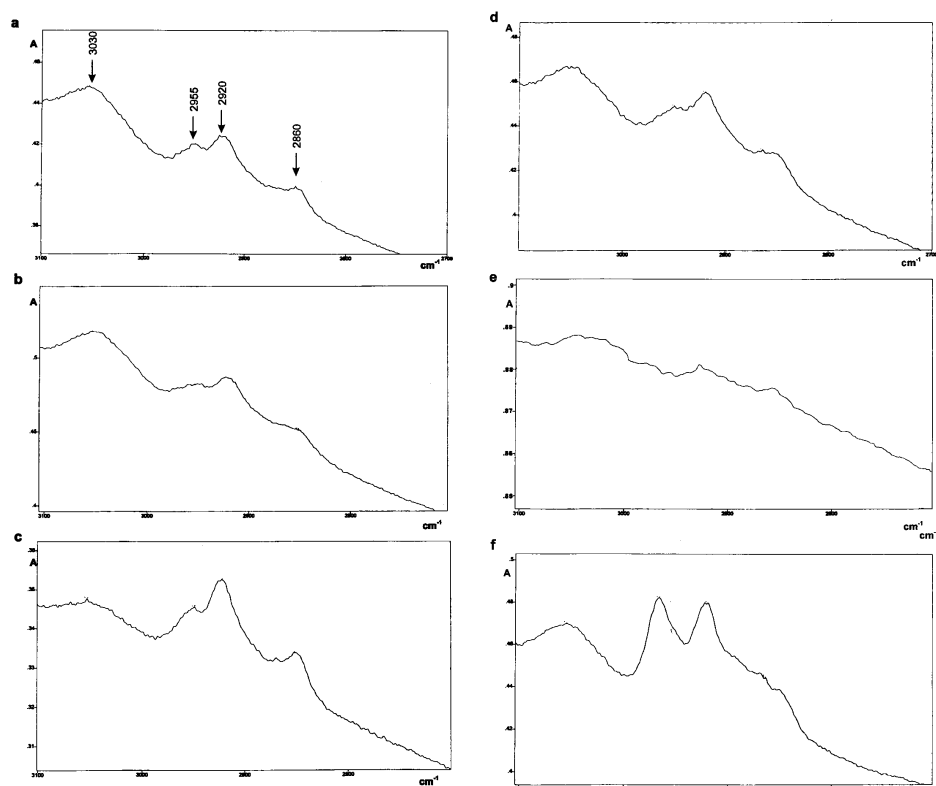
Fig. 3. The FTIR spectrum (3100–2700 cm⁻¹) of kerogen from: the Gruneria-type (a); Kussiella-type (b); unnamed-type (c) cherts; the Sosnowiec stromatolite (d), the Vrška Čuka anthracite (e), and unnamed-type (rich in methyl groups) chert (f).

ture, in accord with mature kerogen assignment based on elemental analysis. This finding is in a good agreement with previous observations that the Schreiber kerogen has reached its aromaticity with increasing natural maturation as evidenced by the higher content of polyaromatic structures. The close geochemical similarity between the kerogens from different types of Schreiber cherts strongly suggests that the kerogen in these rocks has a common origin.

POLYAROMATIC CLUSTERS AND PARAMAGNETIC STRUCTURES

Although the exact nature of the polyaromatic paramagnetic structures (PPS) in kerogen has not been established unambiguously,[10] various ESR considerations imply that these species in kerogens of high rank are associated with polyaromatic clusters. For this reason, the PPS content of kerogen is used as a measure of its content of polyaromatic clusters and, hence, maturity. It has been shown[32–35] that the PPS content increases with increasing maturity of the kerogen. The very large number of measuremints available for correlative studies have made the PPS content an extremely reliable indicator of the kerogen maturity.[34]
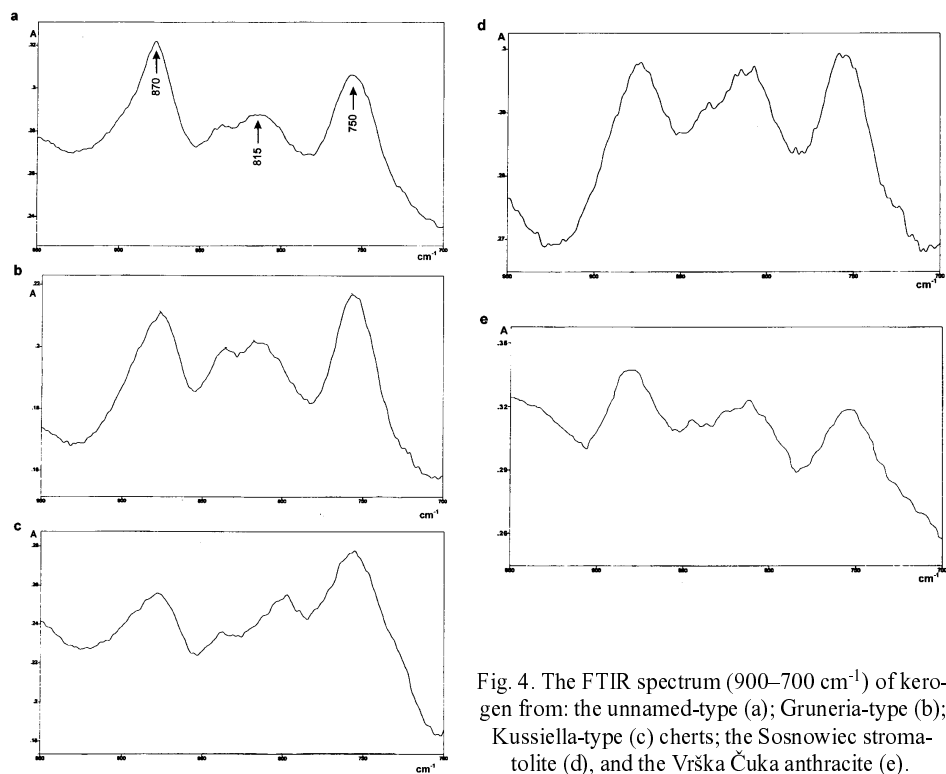
Fig. 4. The FTIR spectrum (900–700 cm^{-1}) of kerogen from: the unnamed-type (a); Gruneria-type (b); Kussiella-type (c) cherts; the Sosnowiec stromatolite (d), and the Vrška Čuka anthracite (e).
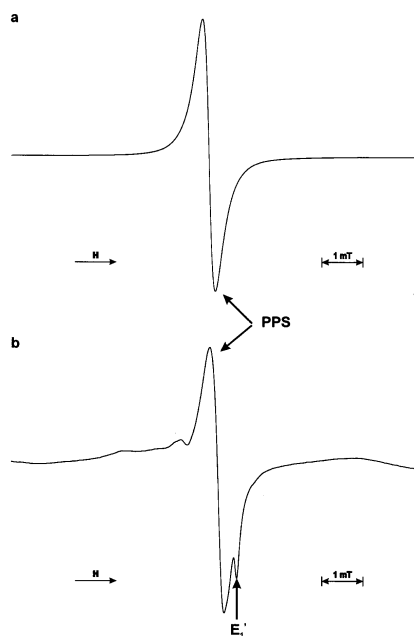

Fig. 5. The ESR spectrum of: PPS of kerogen of the Kussiella-type chert (a), and E$_1$' center of the Schreiber stromatolitic chert (b).

Kerogen isolated from the Schreiber stromatolitic cherts contains an exceptionally high concentration ($>10^{19}$ spins g^{-1}) of PPS (Table I). Such a high concentration of PPS of the Schreiber kerogen is consistent with the high degree of aromatization/polyaromatization indicated by the elemental/FTIR data. The ESR spectrum of the kerogen from the Schreiber stromatolitic cherts (Fig. 5b) is similar to the spectrum of the Kussiella-type chert shown in Fig. 5a. This is the most unique feature of this material. The presence of a high concentration of PPS in the kerogen may be interpreted only in terms of the initial formation of complex organic substances enriched with PPS, which were subsequently transformed during diagenesis/catagenesis into mature kerogen enriched with both polyaromatic moieties and PPS.[10] Similar kerogens have been reported in the geological cherts from the late Precambrian Bitter Springs (0.9 Ga, Australia) and the Late Devonian Rhynie chert (0.39 Ga, Scotland),[10] although PPS enrichment has not been found in any of several hundred Paleozoic/Mesozoic chert specimens examined by us. Further, no other carbonaceous cherts of Early/Middle Precambrian contain kerogen rich in PPS.[10] Therefore, the formation of the Schreiber kerogen may be an extraordinary local rather than a global Precambrian event. Evidence consistent with this interpretation is also available from comparably aged Michigamme anthracite (Middle Precambrian, *ca.* 1.7 Ga old. USA) and related Sudbury and Onwatin anthraxolites (Middle Precambrian, *ca.* 1.9 Ga old, Canada). Namely, solid state ^{13}C-NMR and ESR analyses did not reveal either the presence of polyaromatic kerogen or PPS in these materials. Generaly, the kerogens isolated from Paleozoic/Mesozoic carbonaceous sedimentary rocks contain lower PPS concentrations (*ca.* 10^{16} –10^{18}) than the Screiber kerogen. This is to be expected given the geological/thermal history of the Schreiber kerogen for *ca.* 1.9 Ga.[10]

When an evacuated Schreiber kerogen sample was exposed to air or O_2, the PPS ESR signal intensity was reduced within minutes and its linewidth was slightly broadened. A similar (but much less pronounced) effect was observed for Jurassic Vrška Čuka anthracite, which contained predominantly polyaromatic structures[10] but, no such changes were noticed for algal koregens: *e.g.,* Permian torbanite kerogen (0.26 Ga old, Scotland) with a highly aliphatic macrostructure.[36] Initial ESR intensity of the Schreiber kerogen is partly restored by either re-evacuation or flushing with N_2. A satisfactory explanation can be given if it is assumed that O_2 is physically absorbed on the surface of the kerogen particles. In this case O_2 reduces the PPS ESR spectrum by formation of a complex between O_2 and the highly polyaromatized Schreiber kerogen macrostructure. Similar results have been reported by others and assigned to complex formation between O_2 and structures containing highly delocalized unpaired spins.[37] In contrast to the Schreiber kerogen samples, the Schreiber whole-chert samples show neither changes in line intensity nor linewidth during the air/O_2 experiments. This indicates that PPS are not located at or very near surfaces of quartz grain boundaries and other readily accessible sites, including the internal surfaces of pores. The ESR features observed on exposure of

the Schreiber kerogen and related materials to air/O_2 will be discussed in detail elsewhere.

Our ESR results on untreated Schreiber cherts show also the presence of a very narrow readily saturated signal, which we assign to the E_1' center in quartz (Fig. 5b). This center has an electron at an oxygen vacancy, first observed by Weeks.[38] The formation process of the E_1' center is still an unresolved problem. From experimental results of artificial irradiation and heating, Griffiths *et al.*[39] concluded that the E_1' center is suitable for the dating of cherts. Odom and Rink[40] showed the correlation between the E_1' intensity and the geologic age in the Ma to Ga range pointing out the possibility that the range of ESR dating might be extended to one billion years. They proposed that α-recoil nuclides within the quartz matrix create E_1' centers. Recently, Toyoda and Ikeya[41] calculated the accumulated doses of natural quartz from radiometric ages and annual doses given by external β- and γ-rays. According to these authors, the relative amount of E_1' centers observed in their experiment is consistent with those in natural quartz samples. These authors concluded that: (a) external β- and γ-rays create E_1' centers in quartz, but this does not eliminate the possibility that internal α-recoil nuclides also produce this center in quartz and (b) the ESR signal of E_1' center could only be observed in quartz samples older than several million years because the formation efficiency of E_1' centers is very low.

ORIGIN OF THE SCHREIBER KEROGEN

The commonly accepted interpretation of the origin of syngenetic geoorganic matter within the Middle Precambrian Schreiber cherts focuses on the biological activity on the level of marine subtidal (stromatolite-building) cyanobacteria with relatively low organic productivity.[42] Contradictions to this view exist, however. For example. Premović[10] previously suggested that the presence of predominantly polyaromatic kerogen within the stromatolitic cherts from the Schreiber locality does not corroborate with this view. Consistent with, and in part supportive of this interpretation are the following biogeochemical rationalization.

Modern kerogen studies indicate that marine organic matter, as the precursor of the kerogen isolated from Paleozoic/Mesozoic sedimentary rocks, are mainly derived from the organic remains of microflora (predominantly phytoplanktons) other than subtidal (stromatolite-building) cyanobacteria.[43] The marked similarity between the kerogen from the Schreiber carbonaceous cherts and the corresponding analogs from Paleozoic carbonaceous rocks (in which their origin, nature and early diagenesis were clearly controlled by a number of microorganisms, including phytoplanktons, fungi and bacteria[10]) supports such a notion. For example, late Precambrian Bitter Springs stromatolitic chert contains kerogen, but its microflora is considerably more advanced than that of Gunflint biota and includes many species similar to extant eukaryotic algae. In addition, Paleozoic Sosnowiec stromatolite also contains kerogen, but the organic

matter in this rock is largely derived from (colonial) green algae (Table I). In fact, modern stromatolite studies imply that eukaryotic algae, besides stromatolitic cyanobacteria, can participate in stromatolitic construction.[44,45] The consequence of this rationalization is that most of the microplant organisms living in the Schreiber Basin deposition may have been obliterated by the effect of microbial activity. According to Awramik and Barghoorn,[4] two different types of microfossil assemblages are recognized in the Schreiber carbonaceous cherts: one stromatolitic dominated by subtidal cyanobacteria (the *Gunflintia/Huroniospora* assemblages), while the other is non-stromatolitic possibly planktonic cyanophytes (the *Eoastrion* assemblage). In addition, these rocks contain a microbiota with a high percentage of morphological entities of unknown affinity. The identification of specific microfossils makes possible the conclusion that certain types of microplants were present in the Schreiber environment of deposition, however, an absence cannot be interpreted as a proof of the absence of these organisms.

The contribution of cyanobacterial remains to the Schreiber kerogen, however, should not be overlooked. Resistant biopolymers have been identified in the cell walls of cyanobacteria.[46] It is probable that similar resistant macromolecular materials in subtidal stromatolitic cyanobacteria could also contribute to the Schreiber kerogen. This material in both existing and fossil cyanobacteria is an insoluble biopolymer (termed algaenan) that is rich in aliphatic structures. Similar algaenans have been found in algal coals torbanite.[47] Such highly aliphatic, resistant biomacromolecules in cyanobacterial cell walls could probably be important precursors of the aliphatic network of young Schreiber kerogen and may also contribute to the aliphatic content of mature Schreiber kerogen, which is rather low.

In view of the above consideration, it seems likely that the Schreiber kerogen is derived from the remains of various microplants, as well as stromatolitic subtidal cyanobacteria. By far the most compelling evidence for this contention is the presence of amorphous/polyaromatic kerogen (similar to that isolated from the Schreiber cherts) in the non-stromatolitic carbonaceous chert which occurs at the so-called Frustration Bay locality (Fig. 1) of the upper Gunflint Formation. Available data suggest that this rock was also deposited in a shallow, subtidal marine environment.[6,48] According to Awramik,[6,48] the Frustration Bay carbonaceous chert contains abundant remains of planktonic cyanophytes of the *Eoastrion* assemblage, and lacks the remnants of subtidal (stromatolite-building) cyanobacteria such as *Huroniospora/Gunflintia*.[13]

CONCLUSIONS

From our continuing detailed study of the kerogens separated from the Schreiber carbonaceous cherts (PIP for 20 years) and, in light of our present investigation of these materials, we conclude that:

1. Black stromatolitic cherts (Middle Precambrian Gunflint Formation) at the Schreiber locality contain 0.2 to 0.9 % kerogen;

2. the Schreiber kerogen is composed of > 95 % amorphous brown-to-black material; and

3. organogeochemical evidence (*e.g.*, the low atomic H/C ratio, ESR and FTIR analyses) suggests that the Schreiber kerogen is similar to mature kerogen from Paleozoic/Mesozoic carbonaceous rocks and Jurassic anthracite, which also contain predominantly polyaromatic structures including PPS.

И З В О Д

ФУРИЈЕОВА ТРАНСФОРМАЦИОНА ИНФРАЦРВЕНА СПЕКТРОФОТОМЕТРИЈА И ЕЛЕКТРОНОСПИНСКА РЕЗОНАНТНА СПЕКТРОМЕТРИЈА КЕРОГЕНА ИЗ ГАНФЛИНТ СТРОМАТОЛИТСКОГ РОЖНАЦА (СРЕДЊИ ПРЕКАМБРИЈУМ, ОНТАРИО, КАНАДА) И СЛИЧНИХ МАТЕРИЈАЛА

ПАВЛЕ И. ПРЕМОВИЋ, ГОРАН С. НИКОЛИЋ, МИРОСЛАВ П. ПРЕМОВИЋ и ИВАНА Р. ТОНСА

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Проучавано је присуство керогена у строматолитским рожнацима из средњег прекамбријума из Ганфлинт формације и сличних стена помоћу елементарне анализе, Фуријеове трансформационе инфрацрвене спектрофотометрије и електроноспинске резонантне спектрометрије. Посебна пажња је посвећена структурним особинама Шрајбер-керогена које су поређене са структурама истих материјала (биолошког порекла) у палеозоијским угљеничним стенама. Низак атомски H/C однос (0,5) Шрајбер-керогена показује да је овај материјал достигао висок степен зрелости. Фуријеовом трансформационом инфрацрвеном спектрофотометријом и електроноспинском резонантном спектометријом је утврђено да Шрајбер-кероген углавном садржи ароматичне и полиароматичне структуре сличне онима у зрелим керогенима из палеозојских угљеничних стена. Ови резултати указују да Шрајбер-кероген и зрели керогени из палеозоијских/мезозоијских угљеничних стена имају много сличности па према томе и слично порекло. Овај рад иде у прилог хипотези да уколико је Шрајбер-кероген биолошког порекла онда вероватно потиче од остатка различитих микробиолошких организама (углавном фитопланктона) укључујући плитководне строматолитске цијанобактерије.

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