Organic Free Radicals in Precambrian and Paleozoic Rocks: Origin and Significance

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Abstract

Fourteen Precambrian kerogens including seven isolated from stromatolites were studied by electron spin resonance (ESR). Organic free radicals were detected in only three of these kerogens: those from the Gunflint and Bitter Springs cherts and the Nonesuch shale. All three rocks are known to contain organically preserved microfossils. Comparative studies were conducted on the kerogens of eight fossiliferous Paleozoic rocks and a Jurassic anthracite. Careful measurements were made of g-values, line-widths, line-shapes, and integrated intensities of the observed signals. The kerogen radicals are believed to be polyaromatic structures with unpaired electrons stabilized as π electrons. The marked similarity of the ESR spectral parameters of the free radicals in Precambrian and Paleozoic kerogens and the Jurassic Vrška Čuka anthracite serves to strenghten the view that these radicals are relics of early biochemical processes.

It is suggested that chemical progenitors of Precambrian kerogens and associated free radicals are the corresponding sedimentary humic substances derived from algal and/or microbial sources. Interpretation of significant changes in spin concentration observed during pyrolysis of Precambrian kerogens containing radicals is based on published work on pure bituminous coal macerals (vitrinites and exinites) and anthracites. Experimental pyrolytic data and other evidence suggest that the Gunflint and Bitter Springs rocks have been exposed to temperatures of the order 100–150 °C during their burial histories through proximity to magmatic bodies and subsidence, respectively.

1 Introduction

Following a brief introduction to some of the basic aspects of electron spin resonance (ESR), the geochemical value of organic free radicals in the study of Precambrian kerogens is reviewed. The results of recent ESR studies on organic free radicals in selected Precambrian and Paleozoic kerogens are presented and discussed in terms of their structure, properties, origin, and implications for the origin of organic matter preserved in Precambrian sediments.

2 ESR and Organic Free Radicals

The electron has associated with it a magnetic moment and so it may be treated as a tiny bar magnet. Free electrons (in the absence of a magnetic field) are aligned at random, but in the presence of an external magnetic field, the lower energy state occurs when the electrons are aligned with the magnetic field. A higher energy state exists when the electrons line up in opposition to the magnetic field. The difference in energy between these two states (ΔE) is proportional to the applied field (H_o), thus

$$\Delta E = g \beta_e H_o.$$

The constant of proportionality (g) equals 2.0023 for a free electron and is called the spectroscopic splitting factor, or the g-factor. The value of g varies from 2.0023 when the unpaired electron is no longer free (i.e., when it is in a molecule). β_e is called the Bohr magneton: the magnetic moment of electron.

In quantum mechanical terms, the allowable electron spin states can only take one set of discrete values (i.e. $m_s = +1/2$ and $-1/2$). Electrons in the lower state, $m_s = -1/2$, can be excited to the upper state, $m_s = +1/2$ (Fig. 1 a) and for a given applied field the energy required for the transition will be

$$\Delta E = h\nu = g \beta_e H_o,$$

where ν is the frequency of the applied electromagnetic radiation. Since the energy gap is very small, the most convenient radiation frequencies occur when the magnetic field is about 0.35 T (3500 gauss) and lie in the microwave region of the electromagnetic spectrum (ca. 9 GHz).
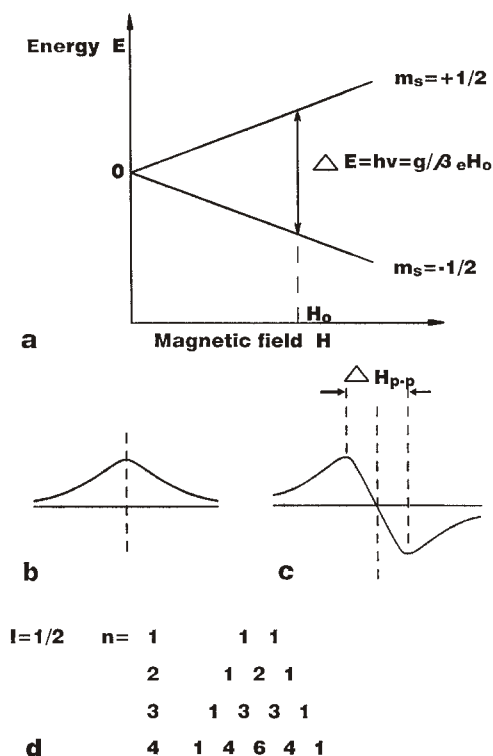
Fig. 1a–d. a Effect of an external magnetic field upon the energy levels of an electron and transition induced by an electromagnetic field. b Lorentzian zero derivative line-shape. c Lorentzian first derivative line-shape. d Line intensities for n (1–4) equivalent protons ($I = 1/2$)

The same molecular orbital (i.e., the spins of electrons are opposed); and hence the net magnetic moment of a pair is zero. Organic molecular species are known in which there is one unpaired electron in the molecule, and these are commonly known as "organic free radicals". Such radicals are paramagnetic and can be studied by ESR.

Normally, organic species containing unpaired electrons are unstable, rapidly decomposing, or dimerizing to give a new orbital. Organic free radicals can be relatively stable if the unpaired electrons are delocalized over an extensive conjugated system of double bonds, for example in certain aromatic molecules. These radicals normally are very short-lived but some may be trapped in the solid organic structure, effectively preventing dimerization. Such "trapped" organic free radicals are known to be very stable, although in some cases their ESR signal is broadened by oxygen, which is also paramagnetic.

3 Polyaromatic Paramagnetic Structures in Coals and Kerogens

The discovery of ESR absorption in natural carbons by Uebersfield et al. (1954) and Ingram et al. (1954) prompted researchers to apply the technique to coal and coal-like materials. Marchand et al. (1968) used ESR to demonstrate the presence of stable organic free radicals in kerogens (i.e., insoluble organic matter in carbonaceous sedimentary rocks).

It is generally thought that there are structural similarities between coals and kerogens, especially at higher levels of thermal maturation. Suggested structural models for both materials when relatively immature comprise polyaromatic centers crosslinked mainly by aliphatic bridges (Fig. 2a). With increasing rank the average number of stacked aromatic sheets further increases in coals, as well as in kerogens (Fig. 2b), until (through the catagenetic and metagenetic phases of maturation) a structure resembling graphite is approached.

The ESR spectral parameters of interest are the g-value of the organic free radicals in coals and kerogens, radical concentration, peak-to-peak line-width $\Delta Hp-p$ (of the first derivative signal) and in some cases, the spectral line-shape. The g-value is a parameter which is particulary sensitive to the chemical environment of the unpaired electron. The g-values of organic free radicals in coals and kerogens are greater than that of the free electron (2.0023) and range from 2.0027 to 2.0042 (Yen and Sprang 1977). Spin (radical) concentration is a measure of the number of unpaired
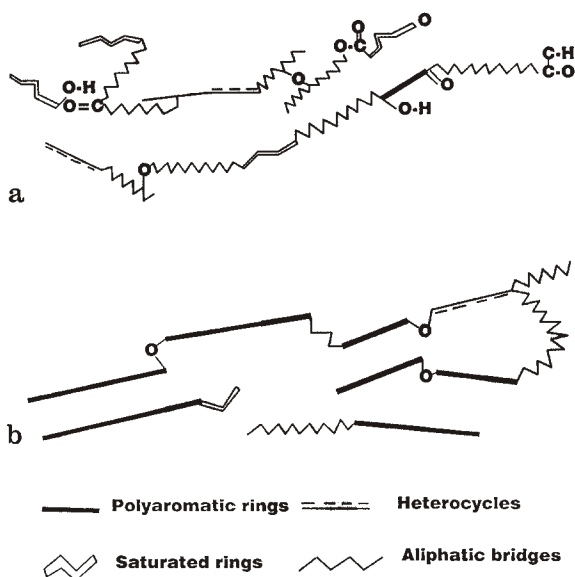
The intensity, or area, beneath the ESR absorption curve (Fig. 1b) is proportional to the number of unpaired spins in the sample. For instrumental purposes and for improved resolution, an ESR spectrum is usually recorded as the first derivative of the absorption spectrum (Fig. 1c) instead of absorption itself. The linewidth ΔH_{p-p} is the distance, in mT, between the two maxima (peak to peak) of the first derivative curve and thus represents the width of the absorption curve at the level of maximum slope.

The nucleus also has associated with it the property of spin. This is given by the nuclear spin quantum number I which may have values of 0, ½, 1, etc. In an atom subjected to an external magnetic field, the electron and nuclear spins will interact and this interaction yields $(2I + 1)$ ESR lines which are, to a first approximation, equally separated with a spacing a (hyperfine splitting constant). If there are n equivalent protons ($I = ½$), the number of lines will be $(n + 1)$. The relative intensities of these lines are given in Fig. 1d.

In normal covalently bonded organic molecules all the electrons occur in pairs. Each pair is contained by

Fig. 2a, b. Simplified structural models for the macro-molecular structure of kerogen. **a** Immature and **b** very mature. (Tissot and Welte 1978)

spins (electrons) in a given amount of sample. The spectral line-width, $\Delta Hp - p$, in the case of both coals and kerogens, is probably determined by the proximity of the unpaired electron to nuclei with magnetic moments, such as proton and nitrogen (hyperfine interactions). Typical ESR spectra of both coal and kerogen samples are single symmetric curves without hyperfine structures. Spectral line-shapes in these samples are largely affected by unresolved hyperfine structure and anisotropic effects. Because of the complex mixture of compounds present in both coals and kerogens, the g-value, line-width and line-shape are composite properties of all the organic free radicals present in a sample. The position and characteristics of the ESR signal envelope are greatly influenced by the relative concentrations of the different radicals.

Although the exact nature of the paramagnetic species responsible for the ESR signal has not been established unambiguously, various ESR parameters indicate that unpaired electrons, at least in coals and kerogens of high rank, are associated with similar polyaromatic clusters. For these reasons, it seems preferable to refer to free radicals in coals and kerogens as polyaromatic paramagnetic structures (PPS). The term PPS also encompasses polyaromatic charge transfer (CT) complexes (Premović 1982; Pryor et al. 1983). Unpaired electrons of most PPS are stabilized, as π electrons.

Free electron transfer between adjacent aromatic sites is possible and results in exchange effects. Where the exchange frequency is small, compared with the hyperfine splitting constants of protons, the envelope formed by unresolved hyperfine lines adopts a Gaussian shape (Fig. 1 b). On the other hand, if the exchange frequency is much larger than the hyperfine splitting constants and exchange narrowing occurs, the line-shape is Lorentzian (Fig. 1 c). Thus line-shape and line-width together indicate the exchange phenomenon, and the size and compactness of the aromatic clusters. PPS trapped in the matrix of coals and kerogens owe their stability to the immobility of the solid structure of these materials and an inaccessibility to oxygen.

Ignoring natural radiolytic processes there are two possibilities for the formation of PPS in kerogens: (1) PPS formed during diagenesis, or (2) PPS formed during catagenesis (Austen et al. 1966). The second possibility is consistent with the well-documented increase of radical concentration with kerogen rank (Marchand and Conrad 1980) and would also account for the variation of g-values observed by Durand et al. (1977).

The main chemical progenitors of PPS in humic coals (e.g., the Vrška Čuka anthracite) are lignins (Rex 1960; Steelink 1964; Hatcher et al. 1981, 1982). These compounds are phenolic polymers of relatively high chemical stability which occur as major components of the conductive tissues of vascular plants. From an evolutionary viewpoint, lignins first appeared in brown algae (Reznikov et al. 1978).

The composition of a kerogen depends firstly on the nature of its precursor organisms and in part on its progress towards the final stage of maturation (i.e., graphitization). Kerogens may originate from either higher plant debris or microbial remains, or from a mixture of both types of material (Tissot and Welte 1978). At low maturity levels, both bacterial and algal kerogens are complex organic materials containing aliphatic and aromatic moeities (McKirdy et al. 1980), whereas vascular plant kerogens comprise predominantly polyaromatic structures. Thus chemical distinction between higher plant and microbial kerogens is clear at low levels of maturation but is difficult to make in very mature materials. For this reason, it is important to first establish the rank of Precambrian (and Paleozoic) kerogens before interpreting their ESR characteristics.

4 Samples and Methods

The 25 kerogens considered in this paper (Table 1) include seven isolated from stromatolites and range in

Table 1. Evidence of biological activity in selected Precambrian and Paleozoic Rocks

Lithology and rock	Region	Geologic period	Age [Ga]	B	Cb	G	F	V	PPS
Onverwacht Series: Kromberg stromatolitic chert Hooggenoeg stromatolitic chert	S. Africa	E. Precambrian	3.4						
Fig Tree shale	S. Africa	E. Precambrian	3.1						
Pongola stromatolitic limestone	S. Africa	E. Precambrian	3.0						
Soudan shale	USA	E. Precambrian	2.7						
Bulawayan Group: Huntsman stromatolitic limestone Cheshire stromatolitic limestone	Zimbabwe	E. Precambrian	2.7						
Gunflint stromatolitic chert	Canada	M. Precambrian	1.9	+	+				+
Michigamme coaly rock	USA	M. Precambrian	1.7						
Sudbury anthraxolite	Canada	M. Precambrian	1.7						
Onwatin slate	Canada	M. Precambrian	1.7						
Paradise Creek stromatolitic chert	Australia	L. Precambrian	1.6	+	+		+		?
Nonesuch shale	USA	L. Precambrian	1.1	+	+	+	+		+
Bitter Springs stromatolitic chert	Australia	L. Precambrian	0.9	+	+	+	+		+
Zvonce black shale	Serbia	M. Silurian	0.4	+	+	+	+		+
Rhynie chert	Scotland	E. Devonian	0.4	+	+	+	+	+	+
Sosnowiec stromatolitic limestone	Poland	L. Devonian	0.4	+	+	+	+		+
Sosnowiec limestone	Poland	L. Devonian	0.4	+	+	+	+		+
Antrim black shale	USA	L. Devonian	0.4	+	+	+	+	+	+
Silicified wood	Croatia	Permian	0.26				+	+	+
Tasmanite	Australia	Permian	0.26	+				?	+
Torbanite	Scotland	Permian	0.26			+		?	+
Vrška Čuka anthracite	Serbia	Jurassic	0.19					+	+

B: bacteria; Cb: cyanobacteria; G: green algae; F: fungi; V: vascular plant.

age from Early Precambrian to Devonian. For comparison, ESR data on the Jurassic Vrška Čuka anthracite and a Permian silicified wood are also included. The microbial origin of the Precambrian samples was established on the basis of their pre-Devonian age. In the case of kerogens isolated from younger sedimentary rocks, recognition of their precursor biota depended on paleontological and other organic geochemical evidence.

The basic instrumentation and experimental procedures for the ESR analysis of kerogen have been described by Premović (1986) and Premović et al. (1989). Kerogen was separated from acid-resistant mineral grains by the chloroform sink-float technique of McKirdy and Powell (1974). The limit of PPS detection for the ESR spectrometer employed is about 10^{14} spins g^{-1}.

# 5 ESR of Precambrian and Paleozoic Kerogens

It can be seen from Table 2 that, unlike the Precambrian kerogens, all the Paleozoic and younger materials contain relatively high concentrations of PPS ($> 10^{18}$ spins g^{-1}). PPS could not be detected in all but three of the Precambrian kerogens, viz. those from the Gunflint and Bitter Springs cherts and the Nonesuch shale. They are, in fact, the most characteristic structural feature of these three kerogens (Jovanović 1989). Their PPS concentrations are comparable with those found in much younger Paleozoic materials Jurassic Vrška Čuka anthracite (Table 2). Figures 3 and 4 show representative ESR spectra of Precambrian and younger materials, respectively, which contain PPS. These spectra are devoid of any hyperfine structure and comprise single, nearly Lorentzian, symmetrical signals (except that of tasmanite which is slightly asymmetric). They have g-values between 2.0027 to 2.0037 and line-widths (ΔH_{p-p}) between 0.32 mT to 0.62 mT. The nearly Lorentzian shape of the signals indicates that exchange and/or delocalization narrowing occur.

The Precambrian kerogens containing PPS in Table 2 have attained very high levels of maturation. This conclusion is based on several lines of geochemical evidence. Firstly, their atomic hydrogen/carbon (H/C) ratios are lower than 0.7 (Jovanović 1989). The various kerogen types (e.g., vascular plant versus algal), seem to be structurally equivalent at H/C ratios less than 0.7 (Hayes et al. 1983). Secondly, their spin concentrations are high (10^{18} spins g^{-1}). It has been shown (Pusey 1973; Hwang and Pusey 1973; Durand

Table 2. ESR parameters of PPS in selected Precambrian and Paleozoic kerogens

Lithology and rock unit	Atomic H/C ratio[a]	g ± 0.0003	ΔHp-p ± 0.05 mT	Spin concentration × 10^{18} spins per gram
Gunflint stromatolitic chert	0.50	2.0027	0.32	16
Nonesuch shale	n.a.[b]	2.0037	0.50	4
Bitter Springs stromatolitic chert	0.68	2.0032	0.34	2
Zvonce black shale	n.a.	2.0037	0.55	9
Rhynie chert	0.86	2.0036	0.59	7
Sosnowiec stromatolitic limestone	0.88	2.0030	0.42	4
Sosnowiec limestone	n.a.	2.0030	0.44	11
Antrim black shale	n.a.	2.0034	0.52	8
Silicified wood	n.a.	2.0035	0.47	1
Tasmanite	1.52	2.0036	0.56	0.4
Torbanite	1.56	2.0036	0.62	0.3
Vrška Čuka anthracite	0.51	2.0034	0.49	45

[a] Dry, ash-free corrected kerogen data.
[b] Not analyzed.
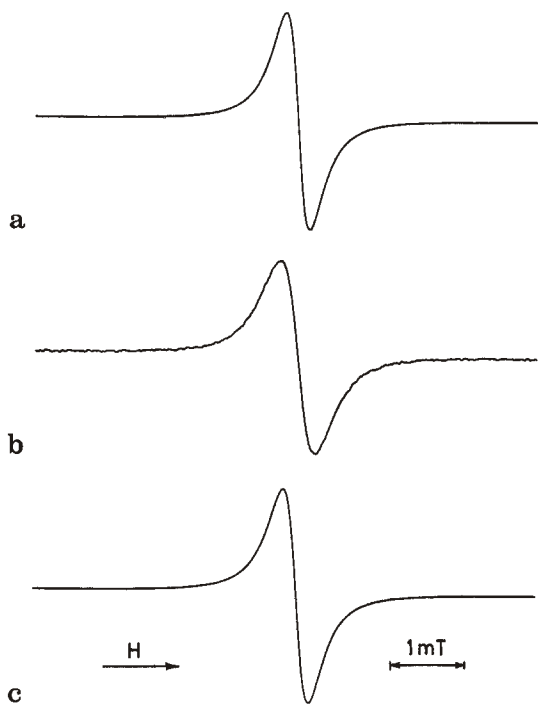
Fig. 3 a–c. ESR spectra of Precambrian kerogen PPS. **a** Gunflint chert. **b** Nonesuch shale. **c** Bitter Springs chert

et al. 1977) that spin concentration increases smoothly as the kerogen matures. The very large number of measurements available for correlative studies has made the spin concentration an extremely reliable indicator of kerogen maturity below a rank equivalent to 2% vitrinite reflectance (Durand et al. 1977). Finally, their infrared (IR) spectra are characterized by strong but featureless absorption throughout the range 650–4000 cm^{-1}. Similar spectra were observed for coals of very high rank (e.g., the Vrška Čuka anthracite: Komatinović 1984).

Undoubtedly, the most intriguing result of the present investigation is the striking similarity between the ESR spectral features of PPS in the Precambrian and younger kerogens listed in Table 2. This suggests that the Precambrian kerogens containing PPS, or at least that part of their structure with unpaired spins, may be inherited directly from their microbial precursors.

6 Humic Substances and the Origin of Kerogen-Hosted PPS

Most students of the subject now agree that Devonian and younger kerogens consist of diagenetically altered humic substances (i.e., humic and fulvic acids: Tissot and Welte 1978). Numerous attempts have been made to devise a structural formula representative of humic substances, but none has proved entirely satisfactory (Stevenson 1982). Humic substances cannot be considered true phenolic polymers because other widely diverse structures, such as aliphatic and polyaromatic hydrocarbons, are also present in their macromolecular skeletons.

Four major pathways by which the decomposition products of plants and microorganisms may give rise to humic substances are illustrated in Fig. 5. Briefly, these are as follows:

1. Lignins are degraded by microorganisms and the residues become part of the humic macromolecular structure (Flaig 1972).

2. Phenolic compounds released from lignins during microbial metabolism undergo enzymatic conversion to quinones, which then polymerize in the presence or absence of amino acids to form humic materials (Hurst and Burgess 1967).
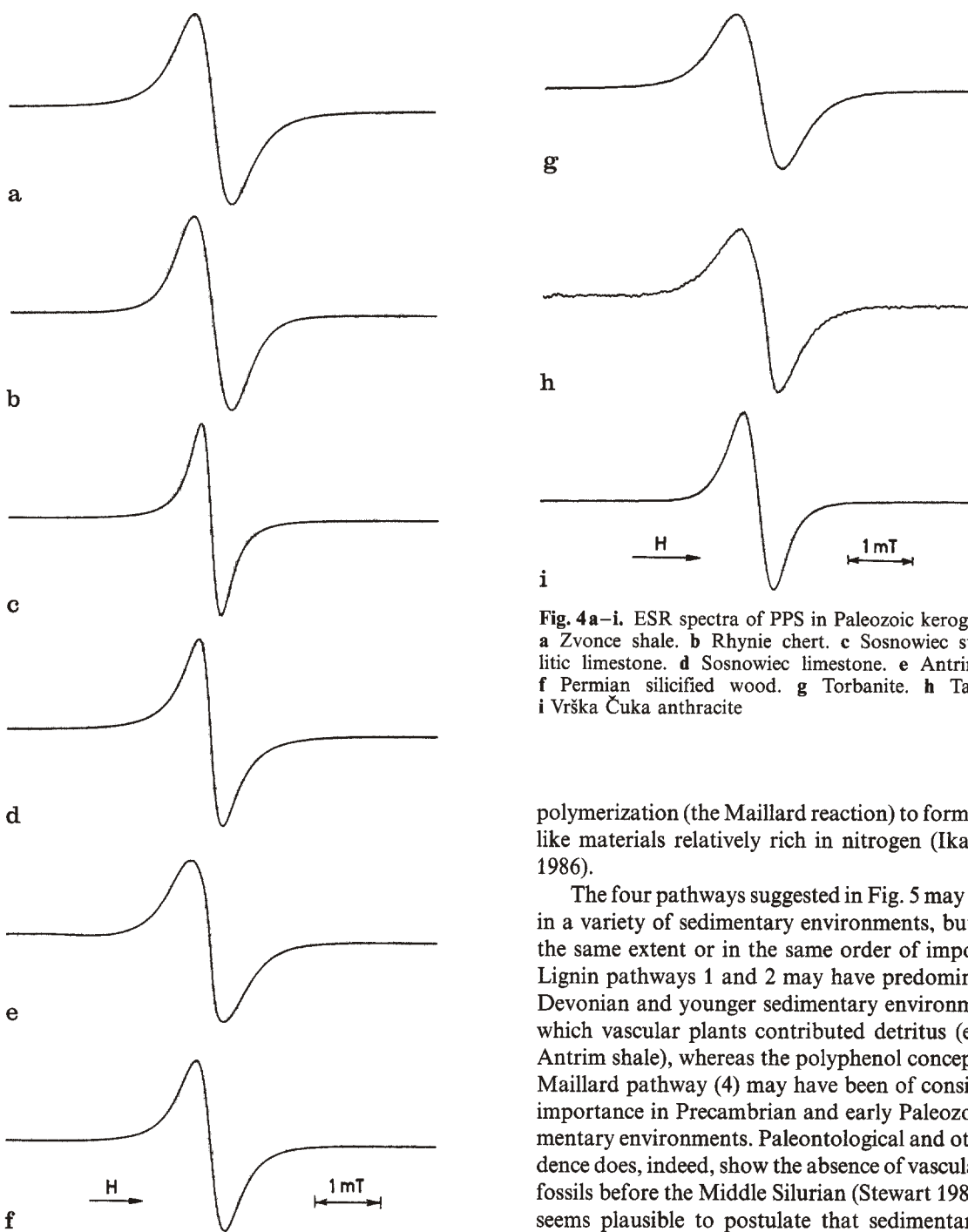
Fig. 4a–i. ESR spectra of PPS in Paleozoic kerogens.
a Zvonce shale. **b** Rhynie chert. **c** Sosnowiec stromatolitic limestone. **d** Sosnowiec limestone. **e** Antrim shale. **f** Permian silicified wood. **g** Torbanite. **h** Tasmanite. **i** Vrška Čuka anthracite

polymerization (the Maillard reaction) to form humic-like materials relatively rich in nitrogen (Ikan et al. 1986).

The four pathways suggested in Fig. 5 may operate in a variety of sedimentary environments, but not to the same extent or in the same order of importance. Lignin pathways 1 and 2 may have predominated in Devonian and younger sedimentary environments to which vascular plants contributed detritus (e.g., the Antrim shale), whereas the polyphenol concept (3) or Maillard pathway (4) may have been of considerable importance in Precambrian and early Paleozoic sedimentary environments. Paleontological and other evidence does, indeed, show the absence of vascular plant fossils before the Middle Silurian (Stewart 1983), so it seems plausible to postulate that sedimentary (marine or terrestrial) humic substances during the Precambrian and early Paleozoic were derived from the remnants of nonlignin-bearing (or nonvascular) organisms, i.e., algae and/or bacteria. If this concept is correct then highly branched aliphatic structures would constitute a much larger fraction of pre-Devonian kerogens, as these chemical structures account for a major portion of humic substances derived from algal and/or microbial sources (Hat-

3. Polyphenols are produced by microorganisms from non-lignin organic sources (e.g., cellulose). The polyphenols are then enzymatically oxidized to quinones and transformed to humic substances (Kononova 1966).

4. Reducing sugars and amino acids, as by-products of microbial metabolism, undergo nonenzymatic
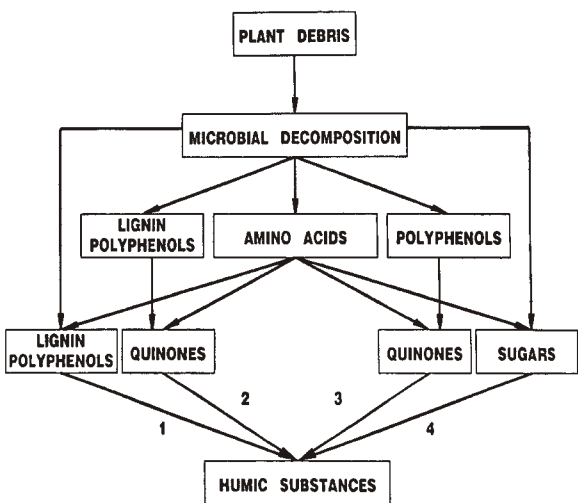
Fig. 5. Mechanisms for the formation of humic substances

with condensed aromatic ring system which also incorporate some alicyclic rings. The fact that their ESR parameters are similar to those of the kerogen PPS listed in Table 2 suggests that the same structural type may be present in the kerogens. It is clear that these humic PPS (semi-quinone radicals in a polyaromatic ring systems) are much less aromatic (i.e., less mature) than the kerogen PPS (carbon radicals in a polyaromatic ring systems) (Ishiwatari 1974). Nevertheless, it is not unreasonable to suggest that Precambrian kerogens containing PPS (or, at least, those parts of their macromolecular skeletons which are paramagnetic) may be relics of sedimentary humic substances.

7 The Origin of Marine Humic Substances

cher 1980). Clearly, identification of particular types of microbial progenitor(s) for Precambrian kerogens and their constituent PPS would greatly advance our efforts at reconstruction of the paleoenvironments inhabited by Precambrian microbiota.

Although it is widely believed that there was no land-plant cover prior to the evolution of vascular plants, this conclusion has not been universally accepted. According to Jackson (1973), late Precambrian continents were colonized by green algae. Subsequently, during the early Paleozoic, higher plants may have evolved from these terrestrial green algae, their phenolic secondary metabolites being the evolutionary precursors of lignins. Jackson based his view on quantitative ultraviolet/visible (UV/VIS) and IR spectrophotometric analyses of bitumens extracted from a suite of carbonaceous sedimentary rocks varying in lithology and depositional environment and ranging in age from Early Precambrian to Miocene, with the majority of his samples being of pre-Paleozoic age. Unfortunately our knowledge of paleosols, especially those of Precambrian age, is so meager (Retallack 1981) that it is impossible to say whether or not the geological record bears out Jackson's hypothesis.

Sedimentary humic substances, regardless of chemical composition or place of origin, contain relatively high concentrations of very stable organic free radicals, of the order of 10^{18} spins g^{-1}. An ESR spectrum of sedimentary humic substances consists generally of a single near-Lorentzian profile without hyperfine structure. The g-values and line-widths of these paramagnetic species range from 2.0032 to 2.0035 and 0.36 mT (Ishiwatari 1974), respectively. According to Ishiwatari, organic free radicals in sedimentary humic substances are possibly associated

Lignins have been implicated as a major source material for terrestrial humic substances (Flaig et al. 1975). However, humic materials can accumulate in marine sediments lacking a lignin input (Vasilevskaya et al. 1977; Ertel and Hedges 1984). Elemental and carbon isotopic compositions (Nissenbaum and Kaplan 1972; Stuermer et al. 1978) and spectroscopic properties (Huc and Durand 1977; Hatcher et al. 1981) of marine humic substances differ significantly from those of terrigenous humic materials, indicating that the bulk of the carbon found in many recent marine sediments originates from autochthonous (mainly planktonic and/or bacterial) sources. Moreover, phenolic constituents are less abundant in marine than in terrigenous humic substances (Tissot and Welte 1978).

The amino-carbonyl reaction of sugars with amino acids (Maillard reaction) has been postulated to be of importance in the formation of terrestrial humic substances (Ikan et al. 1986). Most investigators, however, agree that this reaction contributes very little (if any) to the genesis of marine humic material (Stevenson 1975). The evidence supporting this view is diverse, but the most persuasive argument is that the sugar-amino condensation proceeds rather slowly at the temperatures normally found at the seawater/sediment interface or within the sediment. Another unattractive feature of this reaction is that, even at relatively high temperatures (say 90 °C), it requires molar concentrations of reactants (sugars, amino acids etc.) in order to proceed at a moderate rate and yield significant amounts of macromolecular humic-like material (Maillard 1912; Enders and Theis 1938; Hodge 1953; McWeeny et al. 1974; Stevenson 1975).
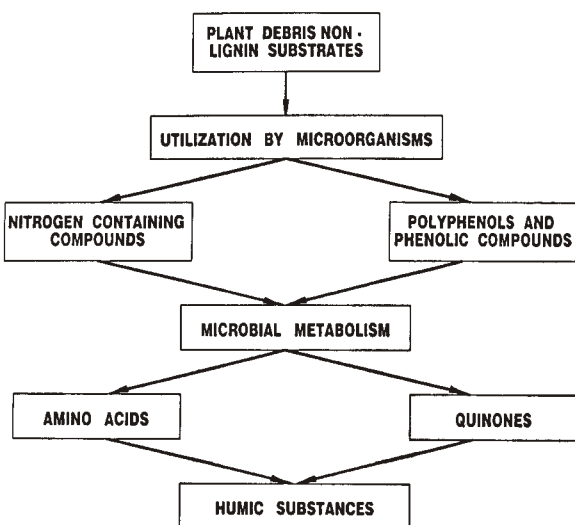
Fig. 6. Schematic representation of the nonlignin polyphenol theory of humic formation

So, there remains to be considered the polyphenol concept (pathway 3 in Fig. 5). A schematic representation of the polyphenolic synthesis of humic substances from non-aromatic substrate by microorganisms is shown in Fig. 6. Numerous phenolic compounds are produced from nonaromatic carbon sources (e.g., polysaccharides) through biosynthesis by microorganisms such as fungi, actinomycetes, and bacteria (Martin and Haider 1971; Steinbrenner and Matschke 1971). The resulting phenolic products (and any uncombined higher plant phenols present) are oxidized to quinones, either by enzymes or autooxidation. The oxidative coupling of phenolic substances and quinones results in the formation of humic-like polymers or melanins (Martin et al. 1972), in which the ESR signal is due to the presence of PPS of the semiquinone type (Schnitzer and Skinner 1969; Rifaldi and Schnitzer 1972; Saiz-Jimenez and Shafizadeh 1985). During diagenesis other materials (including carbohydrates, nitrogenous compounds, and lipids) may be incorporated into the developing polymer (Stevenson 1982). In addition, microorganisms may synthesize intra- and extracellular humic-like materials (Turner 1971). It appears that the PPS content of lignin-derived humic substances is higher than that of the marine humic polymers. In other words, the PPS contents of terrestrial and marine humic substances may reflect their different origins (Steelink 1966; Schnitzer 1971). These immature marine humic PPS are very stable (even in air) and can survive the geochemical processes of humification and diagenesis (immature kerogen PPS) until they are finally converted through catagenesis into mature kerogen PPS.

Although the role of polyphenol mechanism 2 (see Fig. 5) in the synthesis of marine humic substances is unclear, indirect evidence that polyphenols (structurally similar to lignins) contribute to their formation has come from comparative studies of chemical structures of terrestrial and marine humic acids (Hatcher 1980; Hatcher et al. 1981). These studies indicate that complex (highly branched) aliphatic structures constitute a large fraction of both terrestrial and marine humic materials, although overall the former are more aromatic. The authors concluded that similar source materials and/or mechanisms are involved in humic substance genesis in both marine and terrestrial aquatic environments. Recently, Ertel and Hedges (1984) used copper (II) oxide oxidation to examine the distribution of lignin structural units in terrestrial and marine humic substances. No lignin-derived phenols were detected in the marine materials: the sensitivity of the methods employed was about 4 ppm. A similar absence of these compounds in marine humic substances was reported by Vasilevskaya et al. (1977). Thus, one may reasonably conclude that marine humic substances (including those of Precambrian age) could result mainly from polycondensation of the organic residues of microbial (fungal, actinomycete and bacterial) metabolism.

8 Paleontology and Geochemistry of Precambrian Rocks: Origin of Kerogen and Associated PPS

8.1 The Early Precambrian (3.4–2.5 Ga)

Rocks of the Onverwacht and Fig Tree Groups contain possible microfossils resembling modern coccoid or unicellular cyanobacteria (e.g., Muir and Grant 1976; Knoll and Barghoorn 1977). The Pongola and Bulawayan stromatolitic limestones comprise laminae with a microstructure suggestive of construction by finely filamentous organisms of cyanobacterial affinity (Schopf 1972). Similar taxa are suggested for thread-like microfossils in carbonaceous sediment of the Soudan Iron Formation (Cloud and Licari 1968). However, the simple morphology of these microstructures, and their similarity to structured organic matter of nonbiological origins, make their unequivocal identification as fossil entities virtually impossible (Walter 1983; Schopf and Walter 1983).

The origin of Precambrian sedimentary humic substances as outlined in Fig. 6 requires both algal or bacterial residues and heterotrophic microorganisms for the decomposition and conversion of these rem-

nants into the major biochemical components (poly-phenols, phenols, sugars, and amino acids). In parti-cular, the polyphenol theory requires appropriate microorganisms for enzymatic conversion of phenolic compounds into quinones.

Lack of detectable PPS in the Early Precambrian kerogens listed in Table 2 suggests either that they are of nonbiological origin or, as is more likely in view of their extreme thermal alteration (atomic H/C < 0.2: McKirdy and Hahn 1982; Hayes et al. 1983), that their condensed polyaromatic structures approach that of graphite.

8.2 The Middle Precambrian (2.5–1.7 Ga)

Unmetamorphosed black siliceous stromatolites (cherts) of the Gunflint Formation near Schreiber, Ontario, contain a diverse assemblage of prokaryotic microorganisms including representatives of several extant cyanobacterial families (Chroococcaceae, Oscillatoriaceae, Nostocaceae) and a variety of chemosynthetic bacteria, some of which are mor-phologically comparable to certain extant actino-mycetes and mycobacteria (Barghoorn and Tyler 1965; Cloud 1965). The Gunflint carbonaceous cherts also contain abundant pyrite (Jovanović 1989), suggesting that the bottom waters of the Gun-flint sea were anoxic.

According to Schopf (1972), the surface waters of the Gunflint shallow sea were dominated by oxygen-producing photosynthetic microorganisms (plank-tonic cyanophytes and bacteria). The Gunflint humic substances originated from the debris of these photo-autotrophs. Anaerobic bacteria (e.g., sulfate reducers) were the major agents of the decomposition of pro-teins and polysaccharides in these microbial residues. This is in marked contrast to the formation of humic substances in contemporary aquatic environments, where the principal agents of vascular plant decompo-sition include fungi which are obligate aerobes (Gäumann 1964).

The presence of a high concentration of PPS in kerogen from the Gunflint carbonaceous chert (Table 2) is interpreted in terms of the initial formation of humic substances (with a significant PPS content) which were subsequently transformed into kerogen by molecular rearrangement and aromatization reactions during the rock's 2-Ga catagenetic history. The low atomic H/C ratio (0.50, Table 2) of the Gunflint kerogen is evidence that it has almost certainly undergone extensive dehydrogenation (Hayes et al. 1983).

Insoluble carbon of coal-like material from the Michigamme Formation (Tyler et al. 1957) was re-cently investigated using ^{13}C NMR with magic angle spinning (MAS) and cross-polarization (CP) (Pre-mović et al. 1988a). The results of this work indicate that this carbon contains a very low concentration of relatively small polycyclic aromatic structures. The ESR and ^1H NMR MAS spectra of the Michigamme carbon reveal the absence of PPS (Table 1) and organic protons, respectively. Similar results were obtained for insoluble organic matter in the Sudbury anthraxolite and the Onwatin slate (Table 1).

8.3 The Late Precambrian (1.6–0.6 Ga)

Sedimentologic and stratigraphic analyses indicate that the Nonesuch Formation is primarily a lacustrine deposit (Elmore 1981; Elmore et al. 1989). It is a heterogenous unit, consisting of claystone, car-bonaceous shale, and siltstone (Barghoorn et al. 1965). The Nonesuch carbonaceous shale was deposited under reducing conditions and contains organic mat-ter (up to 2.5% total organic carbon) of algal and bacterial derivation. Algal and possibly fungal or actinomycete remains showing rather poorly pre-served cellular details have been isolated from this shale (Meinschein et al. 1965; Barghoorn et al. 1965; Moore et al. 1969). Differential microbial degradation of algal remains was invoked by Imbus et al. (1988) and Elmore et al. (1989) to explain the existence of two distinct types of kerogen, defined using organic pe-trography in combination with pyrolysis-gas chroma-tography/mass spectrometry. The first kerogen type fluoresces under incident blue light and is essentially aliphatic in character; whereas the other nonfluores-cent variety is either aromatic or aromatic with a significant phenolic component. The latter finding is entirely consistent with the presence of PPS in the Nonesuch kerogen examined in this study.

Carbonaceous cherts from stromatolites of the Bitter Springs Formation formed in a shallow aquatic environment populated by a diverse assemblage of cyanobacteria, bacteria, and green algae (Schopf 1972). Detailed sedimentological work by Southgate (1986) has revealed that these fossiliferous cherts are the results of diagenetic silicification of benthic cyano-bacterial communities which grew in shallow saline lakes or ponds. The mean carbon isotopic compo-sition ($\delta^{13}C = -22.18\%$; n = 48) of kerogen from the Bitter Spring chert (Wedeking et al. 1983) is suggestive of intense photosynthetic activity. A sample of this Bitter Springs kerogen is relatively rich in PPS (Table 2). The Bitter Springs microflora is consider-ably more advanced than that of the Gunflint Iron Formation and includes many species similar to extant fungal organisms (thallophytes). These aerobes may

have played a key role in the formation of nonmarine humic substances in the Bitter Springs microbial mat communities.

9 Precursors of PPS in Selected Paleozoic Carbonaceous Sedimentary Rocks

What does the occurrence of PPS in certain Precambrian kerogens tell us about the biogeochemistry of their host sediments? The answer to this question lies in the comparison of the Precambrian PPS with those of demonstrable biological origin found in Paleozoic sediments (Table 2, Fig. 4).

The Zvonce black shale was deposited under reducing conditions in sheltered areas of a Silurian shallow epicontinental sea. This accounts for the observed accumulation of well-preserved graptolite remains and the associated organic matter of bacterial and phytoplanktonic origin (Premović et al. 1986). The depositional environment of the Late Devonian Antrim shale also was highly reducing. Its organic matter is derived mainly from phytoplanktonic and bacterial debris, though fossilized fragments of ancient driftwood (e.g., Callixylon) are also present (Duncan and Swanson 1965). In such anoxic marine depositional environments with relatively high biological (especially bacterial) activity, humic substances form and are subsequently transformed through diagenetic and catagenetic changes into kerogen containing PPS.

The Early Devonian Rhynie chert, one of the earliest records of petrified wood, contains microfossils which may be referred to extant cyanobacteria and green algae. The vascular plants *Rhynia* and *Asteroxylon* growing in a peat bog were killed and fixed, apparently very rapidly, by boiling silica-rich water from a volcanic fumarole (Kidston and Lang 1917–1921). Microscopic examination of the Rhynie chert and the Permian petrified wood indicates that their plant tissues have been extensively attacked by microorganisms, especially fungi, which are likely to have participated in the formation of the humic acid precursors of their kerogen PPS.

The Late Devonian Sosnowiec marine stromatolitic and nonstromatolitic limestones contain abundant bituminous organic matter which is derived from colonial *Eovolvox*-like green algae (Kazmierczak 1975). High contents of PPS ($4-11 \times 10^{18}$ spins g^{-1}, Table 2) of their kerogens are consistent with the marine humic origin of these kerogens.

Both the torbanite (freshwater) and tasmanite (marine) algal kerogens (Table 2) have been examined by ^{13}C NMR CP/MAS, ^{1}H NMR MAS and FTIR spectroscopies (Premović et al. 1986) which showed that these materials have predominantly aliphatic structures with a low total aromatic content. This is consistent with their low PPS concentration ($3-4 \times 10^{17}$ spins g^{-1}, Table 2) and the results of ^{13}C DNP/CP studies (Kitanović 1984).

10 Geothermal History of Precambrian Kerogens Containing PPS

It is of considerable geological interest to know the maximum temperature to which an ancient carbonaceous sedimentary rock may have been exposed during its burial history. This will be particularly so if the kerogen has been thermally altered to such a degree that its carbon isotopic signature is modified (McKirdy and Powell 1974; Schidlowski et al. 1979; Hayes et al. 1983; see also Schidlowski & Aharon and Strauss et al., this Vol.).

Austen et al. (1966) studied the ESR behavior of PPS in a series of bituminous coal macerals (vitrinites, exinites and fusinites) during heating (in nitrogen) from room temperature to about 750 °C. Initial spin concentrations of these macerals were $10-45 \times 10^{18}$ spins g^{-1} for vitrinites and $5-10 \times 10^{18}$ spins g^{-1} for exinites, the ranges reflecting differences in rank. The spin concentrations of vitrinites and exinites were found to increase on laboratory pyrolysis (starting at about 350 °C) to a maximum in the range 500–600 °C, while further increase in the heat-treatment temperature caused an apparent decrease in spin concentration. The changes in spin concentration recorded for vitrinites and exinites are typical of those which have been observed previously with whole coals and other types of organic materials such as cellulose (Milsch et al. 1968). As the pyrolysis temperature increases, the size and number of aromatic ring clusters increase, thus allowing more unpaired electrons to be stabilized. Eventually, a stage is reached where the unpaired electrons become so delocalized that the organic residue (now charred) becomes electrically conducting and spin concentration decreases rapidly. This apparent decrease in unpaired electrons occurs because they become part of the conduction band in a graphite-like structure.

Changes in the ESR characteristics (spin concentration, line-width and g-value) of PPS in bituminous coals and their macerals during laboratory pyrolysis have potential use as a geothermal indicator. Austen et al. (1966) pointed out that if a sedimentary carbonaceous material contains PPS formed at 100 to 200 °C during low-temperature metamorphism, then

its ESR characteristics would not be expected to change during laboratory heating until temperatures of 350–450 °C are reached.

The spin concentration of anthracites with the carbon contents > 95% C (high rank) does not conform to the behavior of low-temperature sedimentary carbonaceous materials because metamorphism has made them fairly graphitic (van Krevelen 1981). However, the pyrolytic ESR behavior of low-rank anthracites (e.g., Vrška Čuka anthracite, 92.1% C: Kitanović 1984) does change in the manner described for vitrinites and exinites.

Austen et al. (1966) determined spin concentrations in fusinites (ca. $30–74 \times 10^{18}$ spins g^{-1}) and concluded that an initial high number of spin centers was developed early in the coalification process. They also established that the intrinsic ESR signals of fusinites did not change significantly on laboratory pyrolysis up to 750 °C, and argued that temperatures of 400–600 °C were necessary for fusinite formation (e.g., in forest fires: Cope 1980).

The majority of coal researchers agree that temperature is the most important factor in the coalification process. Temperatures lower than about 200 °C would have been required to form anthracite. On the other hand, bituminous coal formation takes place at temperatures of the order of 100–150 °C (Teichmüller and Teichmüller 1979). Thus, it is likely that the temperatures necessary for the genesis of the Vrška Čuka anthracite were about 150 °C (Pantić and Nikolić 1973) Most coals have at no time been exposed to temperatures above 200 °C. According to Retcofsky et al. (1968), carbon radicals in amounts detectable by ESR can be produced in pure hydrocarbons, as well as in natural cellulose derivatives, by slow laboratory pyrolysis (1–2 years) at this temperature.

The Gunflint and Bitter Springs Formations appear to have had mild thermal histories. The petrology and mineralogy of these cherts indicates general absence of metamorphism. The temperature versus ESR behavior of PPS in the Gunflint (Premović 1982) and Bitter Springs (Premović 1986) cherts during laboratory carbonization is similar to that of vitrinites, exinites (Austen et al. 1966), and low-rank anthracites (van Krevelen 1981) such as the Vrška Čuka coal (Kitanović 1984). The Gunflint chert kerogen is characterized by an atomic H/C ratio of 0.50, and a spin concentration of 16×10^{18} spins g^{-1} (Table 2). These features are comparable to those of low-rank anthracites and imply that the maximum temperature to which the Gunflint chert has been exposed during its geological history was about 150 °C. The Gunflint chert was covered by no more than approximately 150 m of Late Precambrian strata (Goodwin 1956). In this case, the sediment has never been buried deeply enough to attain the minimum temperature (ca. 150 °C) required for the formation of low-rank anthracite-like material. However, there is abundant evidence of intensive magmatic (intrusive and extrusive) activity during and after the Middle Precambrian in the Gunflint locality (Goodwin 1956).

The Bitter Springs kerogen has an atomic H/C ratio (0.68, Table 2) and a spin concentration (2×10^{18} spins g^{-1}, Table 2) that are characteristic of bituminous vitrinites (Austen et al. 1966; Wilson et al. 1984). A normal thermal history for the Late Precambrian Bitter Springs Formation is probable since these sediments were overlain by approximately 2500 m strata by the end of the Middle Cambrian (Schopf 1968). At an average geothermal gradient of 4 °C per 100 m, these rocks would have been exposed to temperature of at least 100 °C over an extensive period of time. It is not unreasonable to conclude that these conditions were sufficient to generate the vitrinite-like properties of its kerogen.

Finally, experimental studies by Oehler (1972) documented the structural and chemical changes in cyanobacteria during simulated fossilization in synthetic chert at 100 °C and at 165 °C. The quality of preservation exhibited by these artificial fossils resembles that of naturally silicified cyanobacterial fossils from the Gunflint and Bitter Springs cherts.

For comparison, the Early Devonian Rhynie chert (Premović 1986) and the Late Devonian Sosnowiec stromatolitic limestone (Jovanović 1989) were pyrolyzed at temperatures ranging from 50 to 800 °C. The resultant ESR changes were typical of what has been reported previously for vitrinites and exinites (Austen et al. 1966). On the other hand, the kerogen H/C ratios (ca. 0.9, Table 2) of these two rocks and in the spin concentrations (2 to 4×10^{18} spins g^{-1}, Table 2) are similar to those of exinites in bituminous coals (Austen et al. 1966; Wilson et al. 1984). Thus, it is likely that the Rhynie and Sosnowiec rocks reached temperatures of the order of 100 °C necessary for the formation of exinite-like material.

The Sosnowiec stromatolitic sample was obtained from a borehole at a present depth of ca. 2400 m (Kazmierczak 1975), leaving no doubt that it has been buried deeply enough to account for the ESR spectrum of its kerogen. In the case of the Rhynie chert, both deep burial (Kidston and Lang 1917–1921) and contact metamorphism contributed to its heating. The silica-rich formation waters of the Old Red Sandstone Formation emanated from hot springs associated with intense volanic activity as indicated by the andesite interbeds in the Rhynie deposit (Gall 1983).
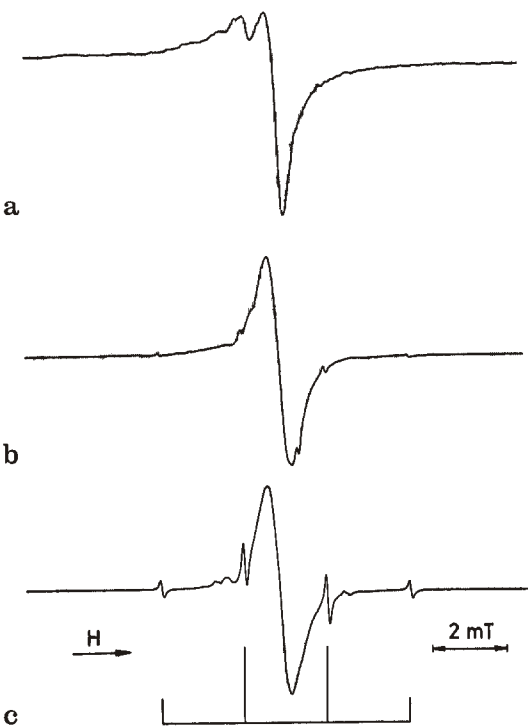
Fig. 8. ESR spectrum of carbon paramagnetic structures in the Paradise Creek chert

Fig. 7a–c. ESR spectra of CH_3 radicals in: **a** Bitter Springs chert. **b** Rhynie chert. **c** Permian silicified wood
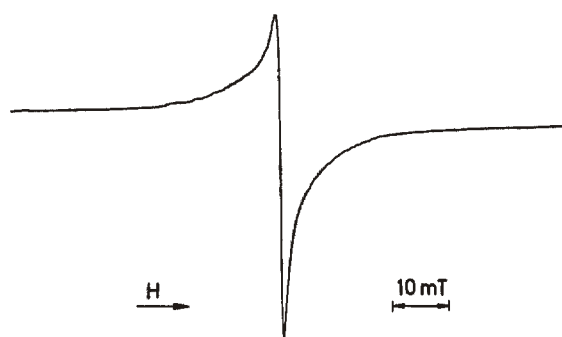
Fig. 9. ESR spectra of insoluble carbonaceous material in the Huntsman stromatolitic limestone

In addition to the ESR signal attributable to kerogen PPS, whole-rock samples of Rhynie chert, Permian petrified wood and, to a lesser degree, the Bitter Springs chert, all show a quartet signal $a_H = 2.22 \pm 0.01$ mT with a relative intensity of nearly 1:3:3:1 (Fig. 7; Premović 1986). A similar quartet spectrum was observed by Ikeya (1982) in several Miocene and Cretaceous petrified woods and attributed to CH_3 radicals among the decomposition products of the woody tissue. Griffiths et al. (1982) detected CH_3 radicals in a Mezozoic chert and suggested that these radicals are trapped in molecular-sized holes in the microcrystalline matrix. In addition, the weak triplet ($g = 2.0029 \pm 0.0001$ and $a_H = 2.17 + 0.01$ mT, with an intensity ratio ca. 1:2:1) characteristic of RCH_2 radicals was observed for different samples of petrified wood. Recently, Ikeya et al. (1986) found that CH_3 radicals appeared after γ-irradiation of granite samples due to the presence of methane trapped in primary or slightly altered quartz. The CH_3 ESR signals is one of the most useful signals in its temperture range for studying the reheating of cherts because of its manifold increase in intensity on heating (Griffiths et al. 1983). Laboratory pyrolysis at 100 °C did not cause a significant change in intensity of the CH_3 signal of unheated Bitter Springs and Rhynie chert samples; and heating at 200 °C produced only a
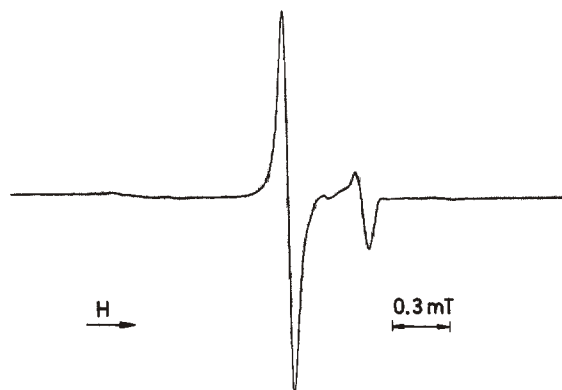
twofold increase in signal intensity. In fact, there was little change in the CH_3 signal until the pyrolysis temperature exceded 200 °C (Jovanović 1989). This finding supports the coalification of the Bitter Springs kerogen at temperatures of the order of 100–150 °C. However, increasing the duration of laboratory heating may shift the maximum signal intensity of the CH_3 radicals towards lower temperatures (Griffiths et al. 1983).

Both the ESR spectrum of kerogen in the Late Precambrian Paradise Creek chert ($g = 2.00263 \pm 0.00005$ and $\Delta Hp-p = 0.12 \pm 0.01$ mT; Fig. 8) and the ESR behavior of its PPS during laboratory heating (Premović et al. 1989) indicate that these structures are similar to those found in fusinites (Austen et al. 1966). Finally, ESR spectra of kerogens from the Huntsman stromatolitic limestone (Fig. 9), the Michigamme anthracite (Fig. 10a) and the Sudbury anthraxolite (Fig. 10b) are characteristic of highly graphitic materials.

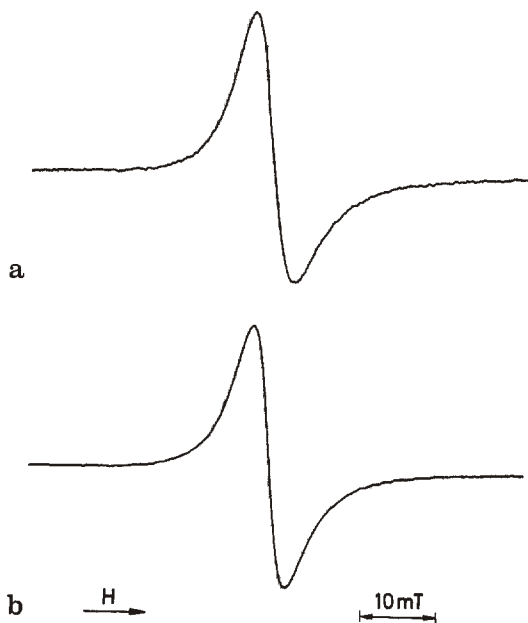The thermal behavior of organic paramagnetic structures in ancient sedimentary rocks is being fur-

Fig. 10a, b. ESR spectra of insoluble carbonaceous material in: **a** Michigamme coaly sediment. **b** Sudbury anthraxolite

ther studied and is likely to prove useful in determining the maximum temperatures to which these sediments have been exposed.

11 Conclusions

The data presented here address the question: Is it feasible to interpret kerogen-hosted PPS in Precambrian carbonaceous sedimentary rocks as evidence of early biological activity? To answer this question the ESR spectra and other geochemical characteristics of the kerogen preserved in selected unmetamorphosed Precambrian sediments were considered. PPS could be detected in only three of the Precambrian kerogens examined: Those isolated from the Gunflint and Bitter Springs cherts and the Nonesuch shale. They are, in fact, among the most intriguing features of these ancient kerogens. All three rocks contain well-preserved, syngenetically emplaced organic microfossils. For comparison, the kerogens and associated PPS of selected Paleozoic and younger carbonaceous sediments of similar origin, lithology, and thermal history were also investigated. From these studies it is proposed that Precambrian kerogens containing PPS (or, more precisely, that part of kerogen structure with unpaired electrons) may be relics of early biochemical processes. The key to future ESR and other chemical studies of Precambrian biological activity lies not in

the analysis of whole (usually highly mature) kerogens, but rather that part comprising intact, organically preserved microfossils. These studies will be particularly effective when properly integrated with existing paleontological and geological information.

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