

Aromatic Free Radicals in the Gunflint Chert

Occurrence of Vascular Plants in the Middle Precambrian

Pavle I. Premović

Department of Chemistry, Faculty of Science, University of Niš, 18000 Niš, Yugoslavia

The Middle Precambrian chert of Gunflint formation contains an exceptionally high amount of bitumen free radicals. The Gunflint chert appears to be the oldest formation in which the presence of these radicals has been found. Their presence in this deposit constitutes evidence for the existence of primitive protovascular plants in the early Proterozoic environment of the Lake Superior Region of Canada.

Organic free radicals in coals and petroleums have been investigated extensively over the years and these studies have helped in understanding the genesis and transformation of natural bitumens. However, other carbonaceous sedimentary rocks also have an appreciable concentration of stable organic free radicals in their native forms; formed, presumably, during diagenesis of fossil organic matter. Thus, organic free radicals can be associated with those reactions by which the organochemical substances in living ancient matter are converted to fossil organic matter. In addition, the organic free radicals offer an excellent means of understanding the structure of fossil organic matter, or at least that part of their structure that has unpaired spins. Surprisingly, organic free radicals in ancient carbonaceous rocks have received little attention. Despite their obvious significance and the fact that the examination of the chemical nature of these organic free radicals and their relationship to the chemical nature of fossil organic matter in ancient carbonaceous rock may show them to be identical to those found in younger carbonaceous rocks, in which the origin is biologically controlled, thus confirming the presence of biological material in particular ancient rocks. Furthermore, we could then, conceivably, relate these organic free radicals to the biota extant during the rock formation.

Electron spin resonance (ESR), a sensitive and non-

destructive method for investigation of paramagnetic species, has been used for the study of organic free radicals in coals [1] and petroleums [2] by several workers. ESR allows detection of many organic free radicals in situ at ppm level in small samples (0.1 g or less) without prior extraction. One great advantage of in situ study lies in the avoidance of external contamination. It also permits examination of organic free radicals in their context with their host and their association with fossil organic matter. We have become interested in the possibility of using ESR spectroscopy to obtain information concerning the nature and origin of organic free radicals in ancient sedimentary rocks which have had a relatively simple geological and chemical history and which are of special interest for paleobiological research. For this reason, we have investigated the organic free radicals in the Gunflint chert (Middle Precambrian, ca. 1.9×10^9 y old, Ontario, Canada) [3] hoping that this might help to elucidate the nature of the ancient living matter present on the Earth. The antiquity of the organic matter in the Gunflint chert and its definite biogenicity lend much interest to various aspects of the Gunflint formation, particularly with reference to problems of the nature of Precambrian life.

Organic Free Radicals in the Gunflint Chert and in Natural Bitumen

The black, fossiliferous chert from the Gunflint formation is composed of about 98% cryptocrystalline quartz and contains about 1% organic matter; it appears to be a chemical sediment of primary origin. The chert was prepared for ESR analysis by first cutting thin chips of several rock specimens and washing carefully with distilled water. They were then treated with boiling 30% hydrochloric acid to remove carbonates and other soluble inorganic constituents. The chips were then etched in 48% hydrofluoric acid and air-dried. Spectra of etched chips were recorded

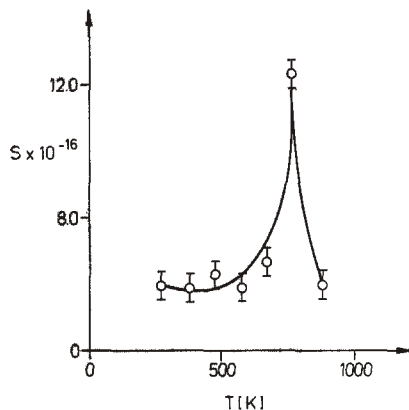


Fig. 1. Variation of spin concentration S (spins g^{-1}) with the pyrolysis temperature T for the bitumen free radicals in the Gunflint chert

at ambient temperature on a Bruker 200D ESR spectrometer employing 100-kHz modulation and a nominal frequency of 9.5 GHz.

A typical ESR spectrum of the Gunflint chert prepared by the procedure described above, is a single, nearly Lorentzian, symmetrical line without hyperfine structure, having a g value 2.0027 ± 0.0001 and linewidth $\Delta H_{p-p} = 0.26 \pm 0.03$ mT. The g value and linewidth of these specimens is similar to those organic free radicals in coals [1] and petroleums [2] which are believed to be rather complex aromatic ring structures.

The chert samples (0.1 g to 0.2 g) were pyrolyzed by heating to the desired temperature (from 295 to 900 K), and held at this temperature for 2 h. The spin concentration, linewidth and g value were then carefully measured at room temperature. The spin concentration is seen to change dramatically within the temperature range covered (Fig. 1). Up to about 800 K, only moderate changes in spin concentration occur. Spin concentration increases sharply at about 800 K and drops substantially on going to about 900 K (Fig. 2). At this temperature it decreases sharply and, simultaneously, the lineshape becomes closer to Lorentzian. The g value shows no change on laboratory pyrolysis up to 900 K. This temperature ESR behavior on laboratory carbonization is very similar to that found for coals of higher rank and is basically characteristic of vitrinite and sporinite macerals [4].

In order to eliminate the possibility that the free radicals studied are associated with organic matter which is present on the surface of etched chips or in microfissures or pore system (and of relatively recent origin), the chips were powdered and then extracted exhaustively with 7:3 (v/v) benzene-methanol in a Soxhlet apparatus for 24 h. This extraction did not effect

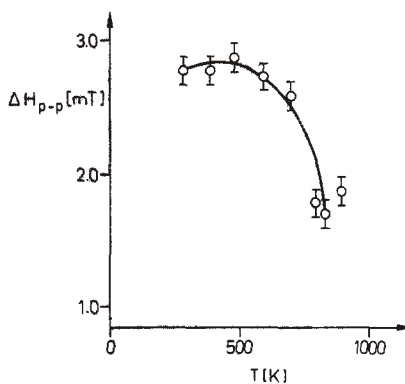


Fig. 2. Variation of the ESR linewidth ΔH_{p-p} with the pyrolysis temperature T for the bitumen free radicals in the Gunflint chert

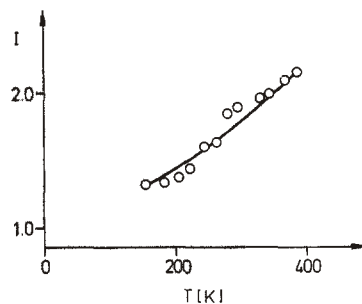


Fig. 3. Temperature dependence of the integrated ESR absorption I (in arbitrary units) for the bitumen free radicals in the Gunflint chert

the concentration of radicals found which indicates that the organic free radicals in the Gunflint chert are associated with insoluble organic amorphous material or morphologically intact insoluble material of (known) biological origin. Obviously, this result also suggests that these radicals are almost certainly indigenous to the chert samples.

One way to understand the nature of spins and their interactions within a complex paramagnetic system is to carry out a basic investigation into the area of spin excitation. For this reason, the signal intensity of organic free radicals in the Gunflint chert sample was measured as a function of temperature in the range from 170 K to 400 K. The results (Fig. 3) indicate that, over the temperature range covered, there is no evidence for a significant decrease in intensity that could be attributed to a component obeying the Curie-Weiss law [5]. For the present, we may take it that nearly all free organic radicals in the Gunflint chert arise from charge-transfer interactions and that the number of simple doublet states independent of their surroundings is very small, if they exist at all. The absence of fine and hyperfine structures, the nar-

row linewidth independent of temperature, as well as a quasi-Lorentzian lineshape at $g \approx 2$, would suggest that we are dealing with Wannier triplet excitons [6]. Such paramagnetic excitations may be associated with organic charge-transfer compounds within the Gunflint chert containing stacks of alternatively donor and acceptor types of aromatic systems.

From the data presented here, it seems most likely that the organic free radicals in the Gunflint chert are the condensed aromatic systems similar to those found in coal asphaltenes and petroleum asphaltenes [5]. In analogy to the genesis of the organic free radicals in coals, the organic free radicals in the Gunflint chert were probably formed in a similar manner by slow pyrolysis during metamorphosis of initial organic matter. If the Gunflint chert has indeed had a relatively mild thermal and chemical history, inevitably, the question of the nature of the precursor(s) of these radicals arises.

Elemental analysis showed that the Gunflint chert contains about 1% of total organic carbon, but our data suggest that the soluble organic substances in this rock is in the 1-ppm range. The trace quantity of soluble organic matter in the sediment samples studied indicates an almost complete diagenetic conversion of the organic matter to gases and insoluble organic material, a process analogous to that observed during coalification. On the other hand, petrologic and geologic evidence suggests that most, and presumably all, of the organic matter in this sedimentary rocks was emplaced prior to lithification, at the time of original sedimentation [3].

If 156 is taken as the minimum molecular weight of the aromatic free radicals in the Gunflint chert (corresponding to two stacked benzene rings as the minimum structural element required for charge-transfer complexes) and 4×10^{16} spins g^{-1} is accepted the approximated mean spin concentration (Fig. 1) then the organic material with free-radical character must be ≥ 10 ppm by weight.

Protovascular Plants as a Source of Bitumen Free Radicals in the Gunflint Chert

The presence of aromatic polymers in sedimentary rocks is associated with its derivation from lignins, but the presence of lignins in the Middle Precambrian is rather questionable since lignins are not believed to have evolved (in plants) before the Devonian period. Brooks and Shaw showed that sporopollenin, when heated, gives a specific mixture of aromatic compounds which is almost identical to that produced from most metamorphosed sedimentary kerogens [7]. Potonie and Renhelt showed that aromatic compounds are present in fossil sporopollenin [8]. For

this reason, Brooks [9] postulated fossil sporopollenin as a precursor for the aromatic compounds in the carbonaceous cherts of the Onverwacht formation (Early Precambrian, ca. 3.4×10^9 y old, Transvaal, Southern Africa) and the overlying Fig Tree Formation (Early Precambrian, ca. 3.1×10^9 y old) [10]. Thus one may also infer a fossil sporopollenin precursor for the aromatic free radicals in the Gunflint chert. This need not imply any high degree of heating although in both the Onverwacht and the Gunflint chert the presence of black organic matter would certainly suggest some degree of coalification. Paleobiological evidence seemingly supports sporopollenin as a precursor because of the occurrence of spore-like fossil organisms of diverse and heterogeneous origin in the Gunflint chert [3].

In view of this, we have investigated the ESR spectra of the Onverwacht and Fig Tree chert. However, the ESR spectra obtained did not reveal the presence of bitumen free radicals in these or other carbonaceous rocks: namely, Paradise Creek chert (Late Precambrian, ca. 1.6×10^9 y old, Queensland, Australia) [11]; Brioverian chert (Late Precambrian, ca. 0.7×10^9 y old, Normandy, France) [12]; Rhynie chert (Late Devonian, ca. 0.4×10^9 y old, Scotland) [11] and Karadjordje chert (Late Triassic, ca. 0.2×10^9 y old, Serbia) [13]. The origin, lithology, mode of preservation of organic constituents and thermal history of these rocks appear to be quite similar [10–13] to those of the Gunflint chert [3]. Thus, our results suggest that the paramagnetic assembly of aromatic structures in the Gunflint chert do not seem to be related to the products of diagenetic degradation of ancient fossil sporopollenin similar to those found in the Onverwacht and Fig Tree chert. Alternatively, there is also the possibility that the sporopollenin precursor of aromatic compounds in the Onverwacht and Fig Tree chert had a different chemical constitution to the sporopollenin progenitor of aromatic free radicals in the Gunflint chert. The presence of bitumen free radicals in the Gunflint chert and their absence in both geologically older and younger cherts emphasizes their uniqueness among the cherts of Precambrian time. Additionally, we have found no ESR signal attributable to bitumen free radicals in the carbonaceous shales of Precambrian time: Fig Tree shale (Early Precambrian, ca. 3.1×10^9 y old, Transvaal, Southern Africa) [10]; Soudan shale (Early Precambrian, ca. 2.7×10^9 y old, Michigan, USA) [14]; Nonesuch shale (Late Precambrian, ca. 1.1×10^9 y old, Michigan, USA) [15]; and in the Michigamme algal coal (Middle Precambrian, $\leq 1.9 \times 10^9$ y old, Michigan, USA) [16].

We have found large quantities of paramagnetic aromatic structures in the organic fraction of the Gun-

flint chert (≥ 1000 ppm or 4×10^{18} spins g^{-1}) that resemble those found in pure macerals, vitrinites and sporinites of geologically young coals (ca. 10^{18} spins g^{-1}) [4]. This focuses attention on the somewhat startling conclusion that during the Middle Precambrian in the depositional environment of the Gunflint formation of the Lake Superior Region, primitive (proto) vascular plants existed. These plants must have been rich in cellular tissues (a vitrinite progenitor) and/or rich sources of spores (a sporinite progenitor). In either of the possibilities (proto)lignins are the precursor of the paramagnetic aromatic species in the Gunflint chert. As far as we aware this is the first direct evidence of the existence of plants during the Middle Precambrian.

The occurrence of primitive plants during the deposition of the Gunflint chert seems further supported by paleobiological evidence. The Gunflint chert contains three-dimensional microfossils as the product of deposition in a silica-rich aqueous environment [3]. Present paleobiological evidence of the Gunflint chert indicates the presence of, at least, eight genera of primitive Gunflint (proto)plants ranging from branched and unbranched filamentous structures from 0.6 to 6.0 μm across (length may be greater than 300 μm) to spheroidal spore-like bodies from about 1.1 to 30.0 μm in diameter, representing a morphologically and physiologically diverse population [3].

Indirect support for a lignin precursor of aromatic free radicals in the Gunflint chert seemingly comes from the study of decomposition products of brown algae (*Fucus vesiculosus*) [17] giving definite evidence of the presence of lignin in these algae. This fact suggests the possibility that, at least locally, the algae similar to *Fucus vesiculosus*, rich in conductive tissues, existed in the Middle Precambrian environment of the Lake Superior Region. These algae, undoubtedly, would have been multicellular, thus eukaryotic, photosynthetic, autotrophic and oxygen-consuming. The stable-carbon-isotope studies suggest that the Gunflint organic matter was produced by photosynthesis, by analogy with contemporary photosynthetic products such as wood or with known fossil products of photosynthesis such as coal [18]. We thus infer

the presence of primitive vascular plants in the Middle Precambrian time metabolically similar to modern plants, supporting the view that considers the Gunflint biota as a "bench mark" of Precambrian life in the early Proterozoic [19].

I am deeply grateful to the following for providing the geological samples used in the present study: Prof. V. von Brunn (the Onverwacht chert), Prof. M. Calvin (the Fig Tree, the Soudan, the Gunflint and the Nonesuch rocks), Prof. S.R. Taylor (the Paradise Creek chert), Prof. J.J. Chauvel (the Brioverian chert), Curator P. Aspen (the Rhynie chert) and Dr. R.C. Reed (the Michigamme algal coal). I also thank Dr. L. Castle and M.P. Premović for help. Financial support was from the Republic Science Association of Serbia and Faculty of Science, University of Niš.

1. Ueberfeld, J., Etienne, A., Combrisson, J.: *Nature* 174, 614 (1954); Commoner, B., Townsend, J., Pake, G.E.: *ibid.* 174, 689 (1954); Ingram, D.J.E., et al.: *ibid.* 174, 797 (1954)
2. Gutowski, H.S., et al.: *J. Chem. Phys.* 28, 744 (1958); Yen, T.F., Erdman, J.G., Saraceno, A.J.: *Anal. Chem.* 34, 694 (1962)
3. Barghoorn, E.S., Tyler, S.A.: *Science* 147, 563 (1965)
4. Austin, D.E.G., et al., in: *Coal Science*, p. 344. Washington, D.C.: Am. Chem. Soc. 1966
5. Elofson, R.M., Schultz, K.F.: *Preprints, Am. Chem. Soc., Div. Fuel Chem.* 11, 513 (1967); Yen, T.F., Young, D.K.: *Carbon* 11, 33 (1973); Retcofsky, H.L., et al., in: *Organic Chemistry of Coal*, p. 142. Am. Chem. Soc., Symp. Ser 71 (1978)
6. Soos, Z.G.: *J. Chem. Phys.* 46, 4284 (1967)
7. Brooks, J., Shaw, G.: *Nature* 220, 678 (1968)
8. Potonie, R., Renhelt, K., in: *Sporopollenin*, p. 295 (Brooks, J., et al., eds.). New York: Academic Press 1971
9. Brooks, J., in: [8], p. 351
10. Brooks, J.J., Muir, D., Shaw, G.: *Nature* 244, 215 (1973)
11. Smith, J.W., Schopf, J.W., Kaplan, I.R.: *Geochim. Cosmochim. Acta* 34, 659 (1970)
12. Chauvel, J.J., Schopf, J.W.: *Nature* 275, 640 (1978)
13. Milovanović, D., Karamata, S., Premović, P.I.: unpublished results (1981)
14. Cloud, P.E. Jr., Gruner, J.W., Hagen, H.: *Science* 148, 1713 (1965)
15. Barghoorn, E.S., Menschein, W.G., Schopf, J.W.: *ibid.* 148, 461 (1965)
16. Tyler, S.A., Barghoorn, E.S., Barrett, L.P.: *Geol. Soc. Am. Bull.* 68, 1293 (1957)
17. Reznikov, V.M., Mikhaseva, M.F., Zil'bergleit, M.A.: *Khim. Prirodn. Soedin.* 5, 648 (1978)
18. Craig, H.: *Geochim. Cosmochim. Acta* 3, 53 (1953)
19. Barghoorn, E.S., in: *Paleobotany, Paleocology and Evolution*, p. 1 (Niklas, K.J., ed.). New York: Praeger 1981

Received April 26, 1982