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Electron spin resonance behavior of indigenous organic matter in the silicic rocks on laboratory pyrolysis: the Bitter Springs and Rhynie cherts and petrified wood

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Electron spin resonance behavior of indigeneous organic matter in the Precambrian Bitter Springs and the Devonian Rhynie cherts, and the Permo-Carboniferous petrified wood during laboratory pyrolysis is essentially similar to those observations reported for this matter in the Gunflint chert and for coal macelars (vitrinites and sporinites). The similarity in the spectral features of indigeneous organic matter in the spectral features of indigeneous organic matter in the cherts studied and petrified woods suggests that this organic matter of the Late Precambrian Bitter Springs rock is derived from the plants with the complex tissue structure.

In our initial investigation of a 1.9 Ga old rock, the stromatolitic Gunflint chert (Middle Precambrian, Canada), polyaromatic paramagnetic structures were identified by electron spin resonance (ESR) and were found to be identical to those found in much younger carbonaceous sediments in which their origin is biologically controlled.[1] This study also showed that pyrolytic ESR behavior of organic matter in this rock is essentially similar to those observed for coal macerals.[2] Such experimental approach has formed basis for the extension in scope of our researches to silicic sediments varying in age, geologic type and type of organic matter present.

This communication describes pyrolytic ESR behavior of plant organic matter in: the Late Precambrian Bitter Springs chert and the Lower Devonian Rhynie chert, and the Permo Carboniferous petrified wood. From this study, we expected to see the ESR behavior of plant organic matter of the silicic rock (*in situ* within rock matrix) with elevated temperature, hoping it might help to gain further insight into origin and nature of indigeneous organic matter of Precambrian cherts.

EXPERIMENTAL

The carbonaceous stromatolitic chert of the Bitter Springs Formation (*ca.* 0.9 Ga old, Australia) contains at least thirty species of: algae, bacteria, possible fungi and other microorganisms.[3] The Bitter Springs plant life is comparable to the biota of Middle Precambrian Gunflint Formation, although the Bitter Springs flora is considerably more advanced and includes a number of algae which may be referred to modern blue-green and green algae.[4] The Rhynie chert (ca. 0.4 Ga old, Scotland)[5] is one of earliest records of petrified vascular plants. These plants *Rhynia* and Asteroxylon growing in a peat bog were killed and fixed, apparently very rapidly by boiling water from a volcanic fumarole, and incorporated in a petrified state into a bed of colloidal silica derived from the same source. It is believed that origin, lithology, mode of preservation of organic constituents as well as mild thermal history, is quite similar to those from the Gunflint chert.[6] Grey with black portions and almost completely silicified (petrified) wood (ca. 0.3 Ga old, Croatia) has the internal structure of wood fossil well preserved, so that the general features of vascular plant's anatomy may bee seen.

The extraction and fractination procedure was similar to that used by Premović *et al.*[7] Powdered rock (100 g) was extracted with benzene/methanol (3 : 1 v/v) for 90 hours in a Soxlet apparatus. The extract constitutes the soluble organic fraction of the total sample. The residue remaining in the Soxlet thimble was treated with boiling hydrochloric acid (4 M) to remove most of the carbonates. Carbonate removal was checked by infrared (IR) analysis. The insoluble residue was demineralized further by repeated treatment with boiling hydrofluoric/hydrochloric acid (HF/ /HCl) (22 M and 0.25 M, respectively). This acid mixture removes silicates[7] and the removal was checked by IR, the final residue is indigeneous organic matter. It contained only small traces of inorganic materials, including pyrite, as conxirmed by electron microscopy and microprobe analysis.

The rock were prepared for ESR analysis by first cutting thin chips (ca. 10—50 mg) of several rock specimens. These chips were then treated with boiling HCl (12 M) to remove carbonates and other HCl-soluble inorganic constituents. In order to eliminate the possibility that organic matter studied is present in microfissures and/or pore system (and of relatively recent origin), the chips were extracted with 6 : 1 (v/v) benzene-methanol in a Soxlet apparatus for 24 h.

Spectra of rock samples were recorded at ambient temperature on a Bruker 200 D ESR spectrometer employing 100 kHz modulation and nominal frequency of 9.5 GHz, with power levels maintained low enough to avoid saturation effects. The ESR spectra of these samples were run both in air and *in vacuo* but because there was no difference in the spectra all the data presented here were obtained from spectra in the air. Linewidths were measured from derivative curves (peak to peak), and signal intensities were calculated by double integration of the first derivatives. In order to calibrate the magnetic field at the sample, a capillary containing a solution of potassium nitrosodisulfonate (Frem's salt) was centred in sample tube prior calibrating. The *g*-value (2.0055 ± 0.0001) and isotropic nitrogen hyperfine coupling splitting ($a_H = 1.309 \pm 0.001$ mT) of this radical are known[8] and were used to calculate the *g*-values of the rock samples studied.

The rock samples (0.1—0.2 g) were pyrolyzed in an electric furnace to the desired temperature (320 K to 1100 K) and holding at this temperature for 2 h. The signal intensities, linewidths and *g*-values were carefully measured at room temperature. The samples treated in an inert atmosphere (oxygen-free nitrogen) seemed not to differ noticeably as far as the ESR properties are concerned from the samples treated in air.

RESULTS AND DISCUSSION

Our analysis indicates that the rock samples are composed of about 98% silicic component (mainly, cryptocrystalline quartz) and contain 0.3—0.8% indigeneous organic matter. Since the rocks were found to contain only traces of soluble organic substances (ca. 10^{-4}%), it is clear that its original biogranic material has suffered complete diagenetic conversion to insoluble organic material and gases-process analogous to coalification. On the other hand, petrologic and geologic evidence suggest that most, presumably all, of the organic materials in these sedimentary rocks are indigeneous and syngenetic.[6]

Unlike the rock studied, the Gunflint chert contains large quantities of paramagnetic aromatic structures (4×10^{16} spins g^{-1}) that resemble those found in coal macerals (vitrinites and sporinites).[1] This indicates that the degree of diagenetic evolution of the Gunflint chert organic matter is quite advanced comparing to those of the rocks in question. In turn, it suggests that silicic matrix of the Gunflint chert did not protect its organic constituents from alteration even under mild thermal condition. The presence of high rank coal-like material in the Gunflint chert were recently confirmed by our recent Fourier transform (FT) IR analysis and nuclear magnetic resonance (NMR) study of indigeneous organic matter in this rock.[9]

Fig. 1 shows the ESR spectra of rock studied before laboratory heating. The signal at g=2.0010±0.0001 is associated with the E' center in quartz and overlaps the signals associated with defects in quartz: signals at g∼2.000 and g∼2.007 are typical spectra of α-induced defects.[10] The quartet signal was clearly observed for

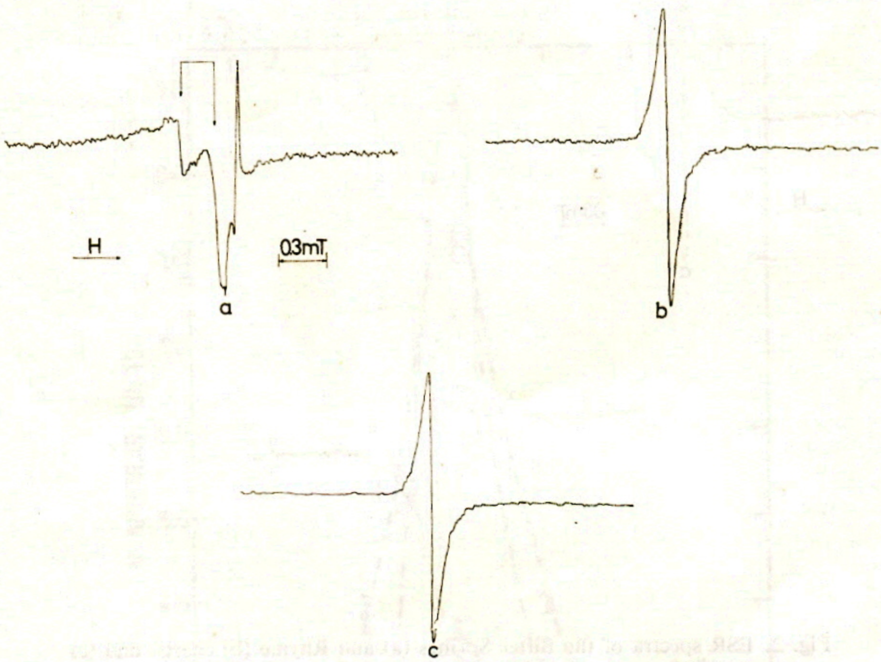


Fig. 1. ESR spectra of the Bitter Springs (a) and Rhynie (b) cherts, and (c) petrified wood: before laboratory pyrolysis.

some samples of both the Rhynie chert and petrified wood though its detection was difficult for the Bitter Springs chert. This signal has $g=2.0029\pm0.0001$ and a proton coupling constant $a_H=2.22\pm0.01$ mT with a relative intensity of nearly 1 : 3 : 3 : 1. Similar quartet spectrum was observed by Ikeya[11] for a number of Phanerozoic petrified woods. He attributed the quartet signal to CH_3 radicals as the decomposition product of wood materiail. The presence of CH_3 radicals in the deposits studied constitutes evidence that the sediments in question have a mild thermal history. The weak triplet signal ($g=2.0029\pm0.0001$ and $a_H=2.17\pm0.01$ mT, with an intensity ratio 1 : 2 : 1) characteristic for CH_2COOH radical was observed for different samples of petrified wood. The presence of CH_2COOH radicals in petrified woods was also reported by Ikeya.[11]

The signal intensity of the quartet was enhanced substantially by laboratory heating reaching its maximum at ca. 600 K, Fig. 2. At this temperature, new (slightly unsymmetrical) single line with $g\sim2.003$ and linewidth $\triangle H_{p-p}=0.6$ mT, Fig. 2, appeared as a result of laboratory pyrolysis. Integrated intensity, I, of this line (linearly proportional to spin concentration) is seen to change moderately up to *ca.* 700 K, Fig. 3. At this temperature the initial ESR signals of the rocks studied vanished, I increases sharply at about 800 K, but both g-value and linewidth (Fig. 4) decrease and, cimultaneously, the lineshape becomes closer to Lorentzian. This ESR signal with $g = 2.0029 \pm 0.0003$ and $\triangle H_{p-p} = 0.20 \pm 0.02$ mT, Fig. 5, is identical to that obtained at *ca.* 800 K by laboratory pyrolysis of indigeneous organic matter in the Gunflint chert.[1] *I* drops substantially on going to 900—1000 K (Fig. 3). This ESR

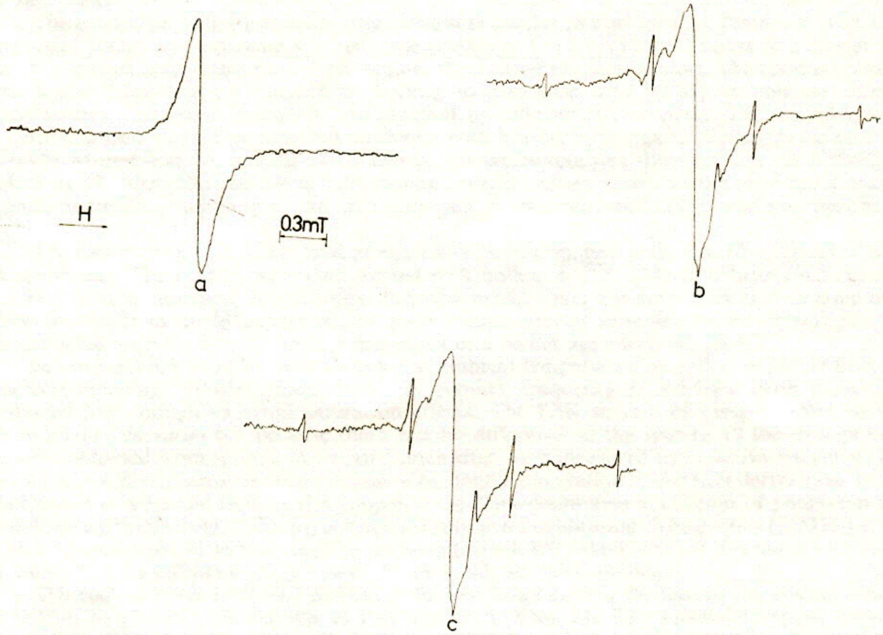


Fig. 2. ESR spectra of the Bitter Springs (a) and Rhynie (b) cherts, and (c) petrified wood: after laboratory pyrolysis at *ca.* 600 K.

behavior is similar to those observed for coal macerals (basically characteristic of vitrinites and sporinites)[2] and for the Gunflint chert organic matter[1] during laboratory pyrolysis: a critical temperature of about 750—850 K at which both a sudden increase of spin concentration and a decrease in the linewidth occur. These results endorse the original suggestion of Premović[1] that both pyrolytic ESR behavior of indigeneous organic matter in the Gunflint chert and associated paramagnetic aromatic structures constitute further evidence for the existence of primitive plants in the early Protereozoic environment of the Lake Superior region of Canada.

For comparison, we have pyrolysed (from 320 K to 1100 K) a number of Precambrian sedimentary rocks containing ca. 1% of indigenous organic matter, presumably, of plant origin (blue-green algae and/or) bacteria): the Onverwacht chert (Early Precambrian, *ca.* 3.4 Ga old, S. Africa) and overlying Fig Tree shale (Early Precambrian, *ca.* 3.1 Ga old); the Pongola stromatolite (Early Precambrian, *ca.* 3.0 Ga old, S. Africa); the Bulavayan stromatolite (Early Precambrian, *ca.* 2.7 Ga old, Zimbabve); the Soudan shale (Early Precambrian, *ca.* 2.7 Ga old, USA); the Sudbury anthraxolite (Middle Precambrian, *ca.* 1.7 Ga old, Canada); and the Michigamme anthracite (Middle Precambrian, *ca.* 1.7 Ga old, USA); the Nonesuch shale (*c7.* 1.1 Ga old, USA). However, the ESR spectra obtained (before and after laboratory heating) did not reveal the presence of organic paramagnetic species. The limit of detection of the ESR spectrometer employed is about 10^{24} spins g^{-1}.

We have also pyrolysed (from 320 K to 1100 K): the Burgess shale (Cambrian, ca, 0.5 Ga old, Canada); the Bennan Head radiolarian chert (Ordovician, ca. 0.5 Ga old, Scotland); the Sosnovies stromatolite (Early Devonian, ca. 0.4 Ga old, Poland) and the Vranje diatomaceous chert (Miocene, ca. 0.02 Ga old, Serbia) but no ESR signal was detected (before and after laboratory heating) characteristic for coal

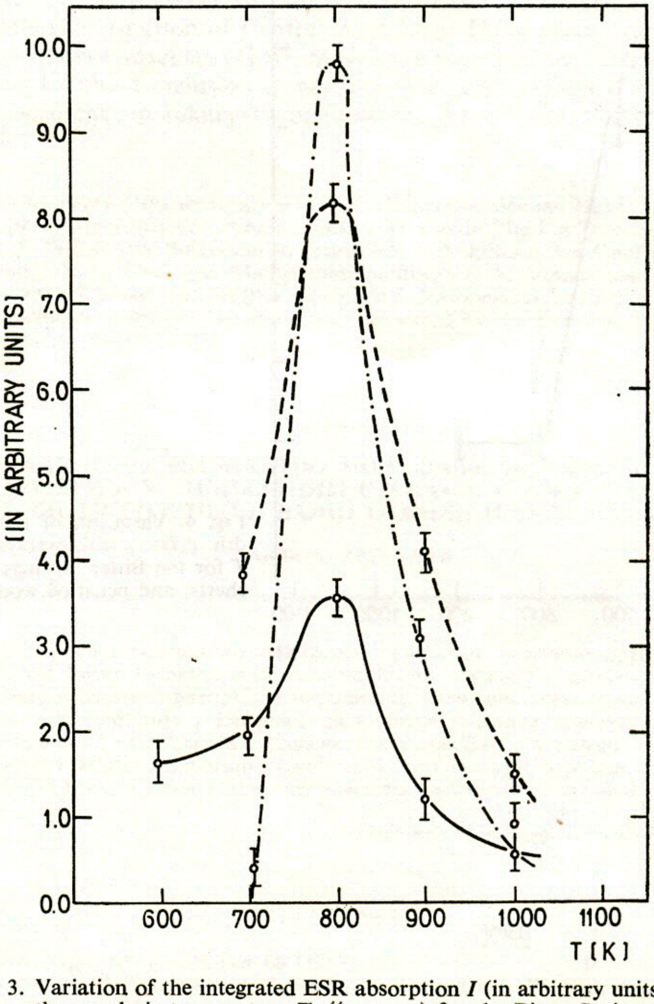


Fig. 3. Variation of the integrated ESR absorption I (in arbitrary units) with the pyrolysis temperature T: ((—.—.—) for the Bitter Springs chert; (— — —) for the Rhynie chert; and (———) for the petrified wood

paramagnetic structures. These rocks contain ca. 1% of indigeneous organic matter derived from algal and/or bacterial organisms. This observation supports our initial notion that indigeneous organic matter in the Gunflint chert are not originated from prokaryotic organisms such as bulue-green algae, bacteria, diatoms (or radiolaria). A determination of the specific organism within plant life would, of course, be of the gratest importance but is exceedingly difficult.

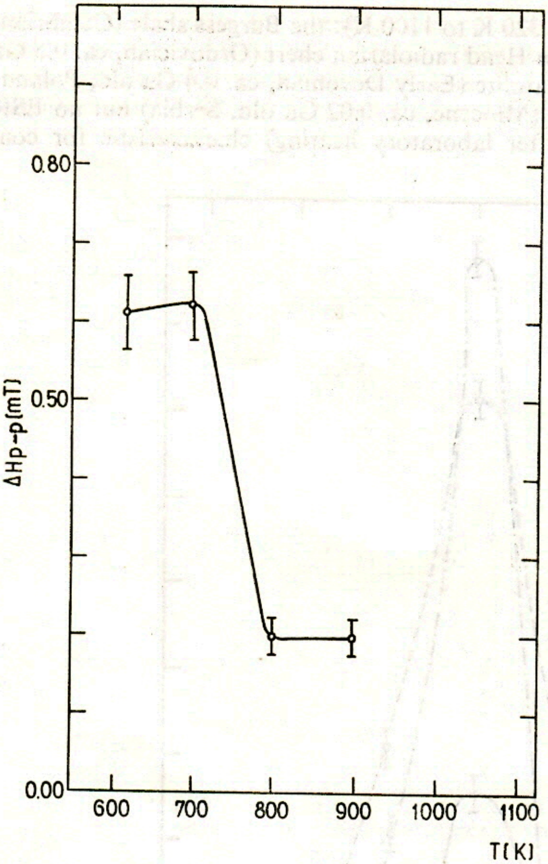
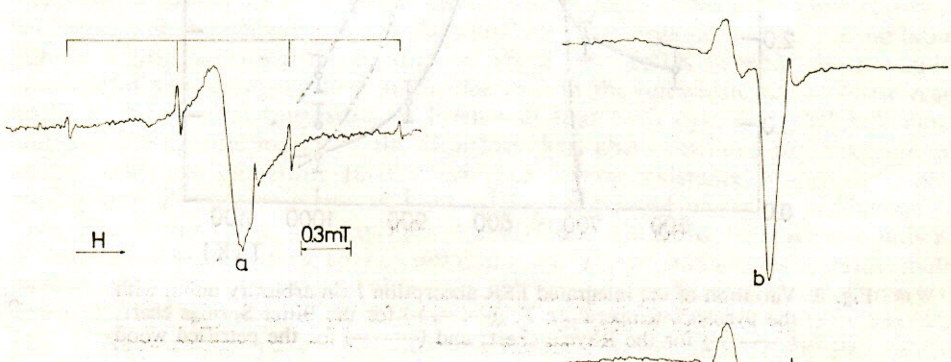


Fig. 4. Variation of the ESR linewidth $\triangle H_{p-p}$ with pyrolysistemperature T for the Bitter Springs and Rhynie cherts, and petrified wood.



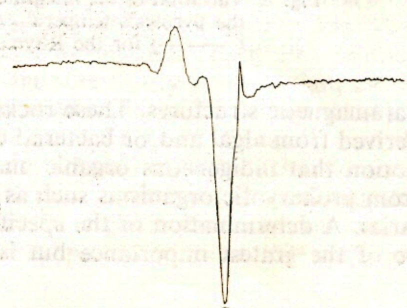


Fig. 5. ESR spectra of the Bitter Springs (a) and Rhynie (b) cherts, and (c) petrified wood: after laboratory pyrolysis at ca. 800 K

Undoubtedly, the most intriguing result is the striking similarity in the ESR spectral features of indigeneous organic matter (before and after laboratory heating) of the cherts in question and petrified woods. This fact suggests that indigeneous organic matter of the Precambrian Bitter Springs chert is derived from the plants with a tissue complexity comparable to those plants found found in the Devonian Rhynie chert and Phanerozoic petrified woods. As far as we are aware, this is the first direct evidence of the presence of plants in the Late Precambrian environment of the Bitter Springs Formation of Central Austrialia. These plants, possibly primitive precursors of modern vascular plants, must have been multicellular and eukaryotic. Direct support for this conclusion comes from the paleobiological studies according to which the occurence of eukaryotic plants in the Bitter Springs assemblage is firmly established.[4]

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ИЗВОД

ЕЛЕКТРОНОСПИНСКО РЕЗОНАНТНО ПОНАШАЊЕ ПРВОБИТНО УГРАЂЕНЕ ОРГАНСКЕ МАТЕРИЈЕ У СИЛИКАТНИМ СТЕНАМА У ТОКУ ЛАБОРАТОРИЈСКЕ ПИРОЛИЗЕ: БИТЕР СПРИНГС И РАЈНИ РОЖНАЦ И СИЛИФИКОВАНО ДРВО

ПАВЛЕ И. ПРЕМОВИЋ

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Електроноспинско резонантно понашање првобитно уграђене органске материје у прекамбријумском Битер Спрингс и девонском Рајни рожнацу и пермо-карбонском силификованом дрвету у току лабораторијске пиролизе је, у основи, слично том понашању карактеристичном за исту материју у Ганфлинт рожнацу и угљеним мацералима (витринити и споринити). Сличност у спектралним особеностима првобитно уграђене органске материје у проучаваним рожнацима и силификованим дрветима указује да је ова материја у каснопрекамбријумском Битер Спрингс рожнацу изведена од биљака са сложеном ткивном структуром.

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REFERENCES

1. P. I. Premović, *Naturwissenschaften* **60** (1982) 479
2. D. E. G. Austen, D. J. E. Ingram, P. H. Given, C. R. Binder, L. W. Hill, *Advance in Chemistry*, Series No. 55 (1966) 344
3. J. W. Schopf, *J. Paleontol.* **42** (1968) 651
4. J. W. Schopf, *Biol. Rev.* **45** (1970) 319
5. R. Kidston, W. H. Lang, *Trans. Roy. Soc. Edinburgh* **51** (1917—1921)
6. J. W. Smith, J. W. Schopf, I. R. Kaplan, *Geochim. Comsochim. Acta* **34** (1971) 659
7. J. D. Saxby, *Chem. Geol.* **6** (1970) 173
8. P. I. Premović, *Geochim. Cosmochim. Acta* **48** (1984) 873
9. R. J. Faber, G. K. Fraenkel, *J. Chem. Phys.* **47** (1967) 2462
10. P. I. Premović, S. R. Stojković, R. J. Pugmire, W. R. Woolfenden, *Precambrian Res.* in press.
11. P. W. McMorria, *Nature* **222** (1968) 870
12. M. Ikeya, Jap. *J. App. Phys.* **71** (1982) I—28.