

ESR study of the Paradise Creek chert. Polyaromatic paramagnetic structures

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The presence, concentration and nature of organic free radicals in the Late Precambrian Paradise Creek and Early Carboniferous Kieselshiefer cherts were ascertained by electron spin resonance spectrometry (ESR). These radicals have an integrated intensity that shows a non-Curie-Weiss temperature dependence. This ESR line intensity is found to vary smoothly with the microwave power reaching its maximum at *ca.* 10 mW (122 K) and *ca.* 20 mW (room temperature). Careful measurements of *g*-values, line shapes, line widths, and integrated intensities of the observed ESR signals were made before and after laboratory pyrolysis (300 K to 1000 K). These characteristics did not change much on pyrolysis up to at least 800 K. Interpretation of the data is based on earlier works on pure fusinite macerals.

Many electron spin resonance (ESR) studies have been conducted on coal and the signals have been shown to arise from complex aromatic species¹ including charge-transfer compounds.² In addition to coals, other carbonaceous sedimentary rocks have been found to contain appreciable amounts of stable paramagnetic species as a diagenetic product of fossil organic matter.³ We have recently characterized the bitumen free radicals in the Gunflint chert (Middle Precambrian, *ca.* 1.9×10^9 y old, Ontario, Canada)⁴ and implied that their presence in this rock constitutes evidence for the existence of primitive plant organisms in the early Proterozoic of the Lake Superior Region of Canada. It seems that, in general, such studies of organic paramagnetic structures in early sedimentary rocks should serve to augment the morphological fossil records, possibly yielding evidence for the time of origin of major biochemical innovations. Consequently, we examined the Paradise Creek chert (Late Precambrian, *ca.* 1.6×10^9 y old, Australia)⁵ by ESR hoping it might help to gain further insight into the origin and nature of organic matter in this Precambrian sedimentary deposit.

EXPERIMENTAL

The samples studied here were of the fossiliferous black chert collected by S. R. Taylor from silicified stromatolites occurring in the Paradise Creek Formation. This chert is composed predominantly of cryptocrystalline quartz (> 98%) and contains less than 0.5% organic matter.⁶ The Paradise Creek chert exhibits fine, irregular laminations reflecting the presence of algal mats. It is believed that this rock includes both early diagenetic and secondary silica components.⁵

The chert was prepared for ESR analysis by first cutting thin chips (*ca.* 10–50 mg) of several rock specimens. These chips were treated with boiling 36% hydrochloric acid, to remove carbonates and other soluble inorganic constituents, and then etched in 48% hydrofluoric acid. In order to eliminate the possibility that organic matter studied is present in microfissures and/or pore systems, (of relatively recent origin), the chips were extracted with 6 : 1 (v/v) benzene-methanol in a Soxhlet apparatus for 24 h. Spectra of etched chips were recorded at ambient temperature on a Bruker 100 D ESR spectrometer interfaced to an ASPECT 2000 computer, with power levels maintained low enough to avoid saturation effects.

The ESR spectra of a considerable number of etched chips 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 run in the presence of air. For the spectra measured in the temperature range 120 K to 298 K a variable temperature accessory made in our laboratory was used. The temperature were checked by a copper-constantan thermocouple. The Q-value of the cavity increased at lower temperatures, so it was necessary to correct the intensities of the lines for this change in sensitivity. This was done by measuring the change in intensity of the ESR of diphenylpicrylhydrazyl (DPPH) in the same temperature range. DPPH at these temperatures strictly obeys the Curie-Weiss law.⁷ Line width was measured from first derivative curves (peak to peak), and spin concentrations were calculated by double integration of the first derivative using the ASPECT 2000 computer system. The calculations were based upon a comparison with a standard chert sample calibrated with a known amount of DPPH and a Bruker standard char. In order to calibrate the magnetic field at the sample, a capillary containing a solution of potassium nitrosodisulfonate (Fremy's salt) was centred in a sample tube prior to calibrating. The *g*-value (2.0055 ± 0.0001) and isotopic nitrogen hyperfine coupling splitting $a_n = 1.309 \pm 0.001$ mT of this radical are known⁸ and were employed to calculate the *g*-values of the rock studied by the ASPECT system.

The rock samples (0.1–0.2 g) were pyrolysed in an electric furnace to the desired temperature (300 K to 1000 K) and held at this temperature for 2 h. The signal intensity, line width 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 samples treated in air.

RESULTS AND DISCUSSION

A typical spectrum of Paradise Creek chert prepared by the procedure described above, is a single, nearly-Lorentzian symmetrical line without hyperfine structure, having a *g*-value of 2.00263 ± 0.00005 and line width $\Delta H_{p-p} = 0.12 \pm 0.1$ mT, Fig. 1. These ESR parameters indicate that we are dealing with organic paramagnetic species. Identical spectrum was observed for the Kielselschiefer. The spectrum, similar to that of natural quartz including E' center ($g_e = 2.0010$)⁹ was also observed.

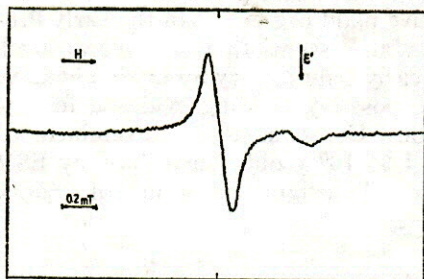


Fig. 1. Room temperature ESR spectrum of paramagnetic aromatic species of the Paradise Creek chert (H is the magnetic field intensity). The spectral parameters were as follows: microwave frequency 9.4216 GHz; microwave power 2 mW; modulated amplitude 0.1 mT; modulated frequency 100 kHz; scan-time rate 0.01 mT/sec.

In order to characterize this singlet species further, the signal intensity of organic paramagnetic structures in the Paradise Creek chert was measured as a function of temperature over the range 120 K to 260 K and the results compared

with those from DPPH. The results are shown in Fig. 2. For the temperature range employed, the signal intensity of chert increases with decreasing temperature at a rate faster than predicated by the Curie-Weiss law. This non-Curie-Weiss temperature dependence indicates the aromatic paramagnetic species responsible for the observed ESR signal may not be an organic monoradical species.¹⁰ Continuing studies are being made to evaluate this idea.

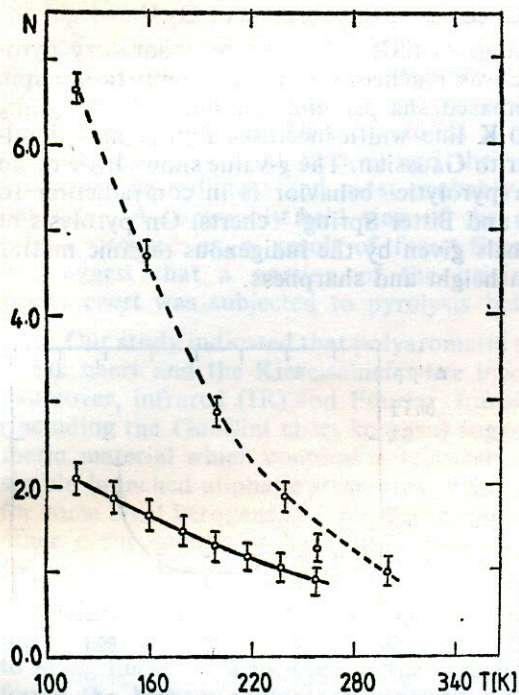


Fig. 2. Relative ESR signal intensity N (normalized to unity at 98 K) in the temperature range 120 K to 300 K: (---) for the Paradise Creek chert and (—) for the DPPH.

The saturation behaviour of the organic paramagnetic species in the Paradise Creek chert is highly temperature dependent. For example, at 122 K these species exhibit saturation effects at a microwave power of 10 mW, Fig. 3a, while saturation

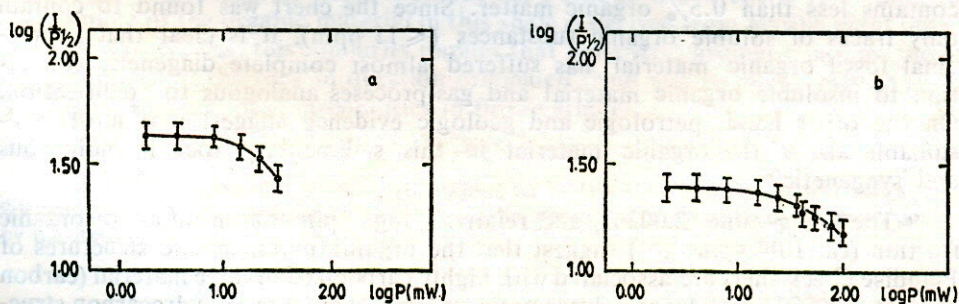


Fig. 3. Plot of $\log(I/P^{1/2})$ against $\log P$ for aromatic paramagnetic structures in the Paradise Creek chert at: (a) 122 K and (b) 298 K.

behaviour at room temperature is not observable until a power level of about 20 mW, Fig. 3b. In these Figures, $\log(I/p^{1/2})$ is plotted against $\log P$ where I is the signal intensity in relative units and P is the magnitude of the microwave power (in mW) incident on the resonant cavity. The initial horizontal line represents no saturation while the downward curve at high power indicates the presence of saturation.¹¹ The saturation behaviour of organic paramagnetic species in the Paradise Creek chert is similar to the saturation behaviour of polyaromatic paramagnetic systems of the S. Africa algal coal,⁹ in the absence of O_2 .¹²

The chert sample showed no change in ESR behaviour on laboratory pyrolysis until a temperature of *ca.* 700 K was reached, and at this temperature spin concentration, 3×10^{16} spins g^{-1} , decreased sharply and it diminished on going to about 900 K, Fig. 4. At about 800 K line width increases Fig. 5, and simultaneously the line shape becomes closer to Gaussian. The g -value shows little or no change on laboratory pyrolysis. This pyrolytic behavior is in contradiction to that found for the Gunflint,⁴ Rhynie and Bitter Spring¹³ cherts. On pyrolysis at temperatures up to *ca.* 800 K the signals given by the indigenous organic matter in these geologic materials increase in height and sharpness.

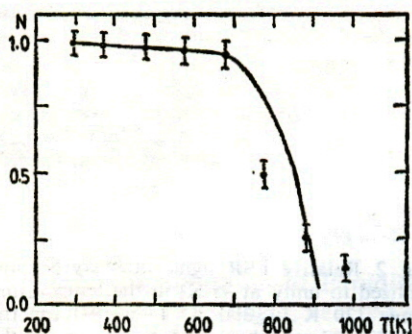


Fig. 4. Variation of the integrated ESR absorption N (normalized to unity at 298 K) with the pyrolysis temperature T .

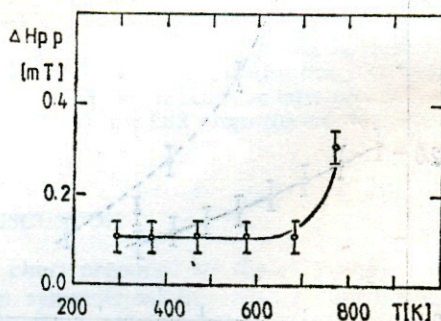


Fig. 5. Variation of the ESR Line width ΔH_{p-p} with pyrolysis temperature T for the Paradise Creek chert.

As we noted above, chemical analysis showed that the Paradise Creek contains less than 0.5% organic matter. Since the chert was found to contain only traces of soluble organic substances (≤ 11 ppm), it is clear that its original fossil organic material has suffered almost complete diagenetic conversion to insoluble organic material and gas-processes analogous to coalification. On the other hand, petrologic and geologic evidence suggest that most, presumably all, of the organic material in this sedimentary rock is indigenous and syngenetic.⁶

The low g -value (2.00263) and relatively high spin concentration of organic fraction (*ca.* 10^{18} spins g^{-1}) suggest that the organic paramagnetic structures of Paradise Creek chert are associated with highly carbonized organic material (carbon content $> 90\%$)¹⁴ with large polyaromatic systems, though pure hydrocarbon structures.¹ The fact that the line width of the chert signal is temperature independent, Fig. 5, would suggest that these aromatic structures have a delocalized spin nature

which eliminates fine and hyperfine structures. In these systems, strong elektron exchange occurs leading to a narrowed line (0.12 mT) with a nearly-Lorentzian line shape. The fact that ESR parameters are similar as those reported for fusinites,¹⁵ implies that a similar paramagnetic structural type is present in the Paradise Creek chert. In the case of fusinites, the high resonance stabilization of organic paramagnetic structures is associated with extensive polyaromatic clusters and much experimental evidence has been offered to support this view.^{1,2,11,16,17} It is interesting to compare the ESR properties here for polyaromatic paramagnetic systems of the Paradise Creek rock with those found for the British fusinites by Austen *et al.*¹⁵ These authors studied pure macerals from the British bituminous coals by ESR. They found almost no change in signal strength or line width for the British fusinites below 800 K. They concluded that fusinites achieved their high carbon content (>90% of total carbon) and their spin concentration before incorporation into the sediment and most probably by exposure to moderately high temperatures. A commonly held view of the origin of British fusinites is that pyrolysis occurred as a result of forest fires. In analogy to the British fusinites, we suggest that a portion of the original organic material in the Paradise Creek chert was subjected to pyrolysis before incorporation into the sediment.

Our study indicated that polyaromatic paramagnetic structures in the Paradise Creek chert and the Kieselschiefer are incorporated into their kerogen fraction. Moreover, infrared (IR) and Fourier transform (FTIR) analyses of the kerogens (including the Gunflint chert kerogen) suggest that these are composed of a polymeric material which contains a relatively high proportion of straight-chain and simple branched aliphatic structures.¹⁸ Similar IR and FTIR spectra are observed for some algal kerogens.¹⁹ Lipid²⁰ and cell wall materials²¹ of phytoplanktons and other plant organisms have been proposed as precursors of kerogen aliphatic chains.²²

Paleobiological evidence indicates the occurrence of nannofossils in cherty blebs associated with branched stromatolitic, comprising cubic colonies analogous to living *Eucapsis*, a member of the blue-green algal family *Chroococcaceae*⁵ We found the highest content of aromatic paramagnetic structures associated with the algal mats of Paradise Creek chert implying that these structures may be directly related to fossil plant organisms in this rock.

Some support for the plant precursor(s) is the fact that aromatic paramagnetic structures in the Kieselschiefer chert (*E. Carboniferous*, ca. 345×10^6 y old, Hertz, Germany)²³ are similar to those found in the Paradise Creek chert. According to Hoss¹⁸ most of the organic material in this shale is derived from marine plant organisms. We believe that this similarity implies that polycyclic aromatic paramagnetic ring structures in the rock in question originated from similar plant precursor(s). We aim to explore these possibilities in future studies.

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ИЗВОД

ESR ПРОУЧАВАЊА ПАРАДАЈЗ КРИК РОЖНАЦА. ПОЛИАРОМАТИЧНЕ ПАРАМАГНЕТСКЕ СТРУКТУРЕ

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Присуство, концентрација и природа органских слободних радикала у Парадајз Крик (касни прекамбријум) и Кизелшифер (рани карбон) рожнацима утврђена је електронспинском резонанцијом. Ови радикали имају интегрални интензитет чија температурска зависност не следи Кири-Вајсов закон. Утврђено је да се интензитет ESR линије мења са микроталасном снагом, достижући максимум на око 10 mW (122 K) и на око 10 mW (собна температура). Пажљива мерења *g*-вредности, облика линија, ширине линија и интегралног интензитета посматраних ESR сигнала урађена су пре и после лабораторијске пиролизе (300 K до 1000 K). Мерење ESR карактеристике нису се значајно мењале током пиролизе до око 800 K. Добијени резултати мерења интерпретирани су на основу литературних података за чисте мацерале фузинитског типа.

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