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ESR BEHAVIOUR AS A POSSIBLE GEOTHERMAL INDICATOR FOR ANCIENT SEDIMENTS

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ESR measurements at X-band (9.5 GHz) frequency, before and after laboratory pyrolysis, have been carried out on a selection of ancient sedimentary rocks (the Gunflint chert, the Nonesuch, the Zvonce, the Antrim, the Irati and the Green River shales) in an attempt to establish the maximum paleotemperatures to which the deposits have been exposed during their geochemical histories. The changes in ESR behaviour on heating suggest mild thermal histories of the sediments in question, except of the Gunflint chert.

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Knowledge of geothermal histories of ancient rocks is of geological, paleontological and geochemical importance since this is closely linked with our concept related to the climates, physical and chemical features of prehistoric continents and oceans. In the work here reported, ESR measurements, before and after laboratory pyrolysis, of six ancient sedimentary rocks have been carried out in an attempt to establish the maximum paleotemperature reached by these deposits. As far as we are aware, this is the first time that such an ESR investigation has been published for sediments of this type.

ESR measurements were performed on finely ground powders which were transferred to ESR quartz tubes. Spectra were recorded at ambient temperature on a Varian Associates E-115 spectrometer, employing 100 kHz modulation and a nominal frequency of 9.5 GHz. The *g*-values and line widths (Table I) were determined relative to a peroxylamine disulphonate standard, having a *g*-value of 2.0055 $\pm$ 0.0001. The spin concentrations (Table I) were determined by the sample interchange method; polyscrystalline DPPH diluted with KBr was employed as the intensity standard. The error in the values for the concentration of spins in the ESR lines of the sediments, shown in chronologic sequence in Table I, was estimated to be 50%. Samples (0.1 - 0.2 g) were also pyrolysed to the desired temperature for 48 hours. The ESR spectra of the rocks studied 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.

ESR spectra of unheated sedimentary specimens examined were similar to the spectrum of the Zvonce shale shown in Fig. 1. In general, the spectra consist of a single, relatively symmetrical line devoid of any fine structure. The *g*-values and spectral line widths of the sediments studied are

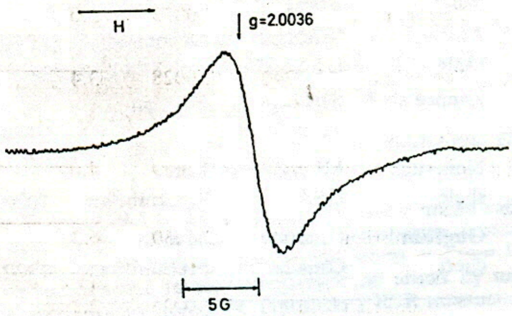

Fig. 1. ESR spectrum of the Zvonce shale.

closely similar to those reported for petroleum asphaltenes (2.0027-2.0036, $\Delta H_{pp} = 3\text{-}9$ G)[1]. Petroleum like organic matter is known to be present in the rocks examined[2] and it seems, likely, that the ESR spectra recorded originate from the free radicals same as those found in petroleum asphaltenes which are believed to be condensed, aromatic ring structures[1]. Geological and geochemical considerations strongly suggest that the organic materials were hardly thermally altered prior to lithification, at the time of original sedimentation[3-5] indicating that these free radicals were presumably mostly produced by some low temperature mechanism during the relatively short period of active metamorphism (or earlier?). It is worth noting in passing that it was not possible to obtain a detectable signal for corresponding organic free radicals (i. e. $< 10^{11}$ spins per gramme was present) on direct ESR examination of samples of the Soudan shale (North East Minnesota, 2700 million years old) and the Fig Tree shale (East South Africa, 3200 million years old), though trapped electrons in silicic environment were observed.

The ESR signals of the Green River and Irati shales become narrower on heating at temperatures above ~200°. Pyrolysis of the Antrim shale at temperatures above ~70° causes a complete disappearance of the ESR signal and a new, narrower one (2.0012, $\Delta H_{pp} = 0.8$ G) appears instead. In both the Zvonce and Nonesuch shales the ESR signals decrease in intensity on carbonization at temperatures above ~300°. The Gunflint chert shows no change in ESR characteristics on laboratory pyrolysis at temperatures up to 600°.

It is worthy of note that the narrowing of ESR line widths simultaneous with the decrease of *g*-values were observed in the earlier studies on kerogen in natural environments[8]. It has been proposed that these ESR changes are related to various paleotemperatures of the sediments studied.

Our estimation of maximum paleotemperatures, given in Table I, for the sediments studied is based on the assumption that if an ancient rock contains stable free radicals at, say, the temperature of T during its geological history, then one would not expect, for certain, changes in ESR behaviour until laboratory pyrolysis temperatures of $2T$ to $3T$ are reached.

TABLE I. *ESR parameters and maximum paleotemperatures of ancient sediments*

Lithology and rock unit	Region	Geologic era	Approximate age in 10^6 years	*g*-value ±0.0003	Line width ±0.1G	Concentration of spins per gramme	Maximum paleotemperatures in °C
Green River shale	Colorado, USA	Eocene	50	2.0036	6.5	1×10^{18}	70–100
Irati shale	Sao Paulo, Brasil	Permian	260	2.0030	5.0	3×10^{16}	70–100
Antrim shale	Michigan, USA	Devonian	340	2.0028	3.4	1×10^{19}	25–35
Zvonce shale	Serbia, Yugoslavia	Silurian	420	2.0029	4.0	4×10^{19}	100–150
Nonesuch shale	Michigan, USA	Late Precambrian	1000	2.0030	6.3	2×10^{16}	100–150
Gunflint chert	Ontario, Canada	Middle Precambrian	1900	2.0026	2.9	3×10^{16}	>200

The paleochemistry of the Gunflint chert presents evidence for the presence of relatively complex organic molecules directly associated with structurally preserved organic remains[6]. Although paleontological studies suggest that this chert has experienced a mild thermal history (brown-to-amber colour of the preserved organic matter, presumably, reflects such a history), the ESR behaviour provides a reasonable basis for believing that a part of organic material had been exposed to an elevated temperature and charred before incorporation in the sediment. It is now difficult to establish whether these carbonized organic constituents are syngenetic with the original sedimentation, and therefore of the same age as the sediment. The fact that the ESR spectral line width of the Gunflint chert is the lowest of all samples investigated would indicate the highest degree of ordering and aromatization of free radical structures in this deposit than those in the other rocks. On the contrary, the decrease of line widths of both the Green River and Irati shales, on laboratory pyrolysis described above, would suggest that such structural transformations of free radical species present in these sediments did not take place during their geologic history. In all three cases, structural rearrangements emerge in the ESR behaviour as the exchange and delocalization narrowing[7].

Treibs[9] first demonstrated that porphyrins exist in bituminous strata and recognized that the preservation of porphyrins is depedent upon mild geothermal conditions. Calculations based on the activation energy required for degradation of porphyrins indicate that these chemical fossils could not have persisted longer than about 100 years in a lithologic enviroment to temperatures of 250°[9] and, therefore, their occurrence in an ancient sediment sets an upper temperature limit to the enviroment during its previous history. The presence of porphyrins in the Nonesuch shale[10], the Zvonce shale[11], the Antrim shale[11], the Irati shale[12] and the Green River shale[13] lends credence to the concept of low temperature origins of these deposits[3–5]. The maximum paleotemperatures estimated from the ESR measurements as above, add certainly support to this concept which offers, on the other hand, some confirmation of the validity of the method of estimation.

The range of maximum paleotemperatures for the Antrim shale would indicate a rather mild thermal history for this bituminous sediment that is not to be expected in view of the age, unless the sediment had been protected from diagenesis in some special fashion. As far as we are aware, the present geological and geochemical evidences neither refute nor confirm such an estimation. In any case, it is apparent from the ESR changes observed that the free radicals in the unheated sample of the Antrim shale have an unexpectedly low thermal activation energy for removal of the unpaired electrons and that the new free radical centres, originating from laboratory pyrolysis described, seem to be scavangers for these electrons. This question will be considered in detail elsewhere.

Various other ESR signals were also detected in certain sediments studied, some of which are characteristic of transition metal ions such as Mn(II), Fe(III), and VO(IV) and some of which were assigned to trapped electrons in the silicic matrix. It is hoped that further ESR studies of such paramagnetic centres in these and other sedimentary rocks would supply valuable informations related to the chemical environment during the depositional stage of sediments in question.

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ИЗВОД

ESR ПОНАШАЊЕ КАО МОГУЋИ ГЕОТЕРМАЛНИ ИНДИКАТОР ЗА СТАРЕ СЕДИМЕНТЕ

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ESR мерења на X-траци (9.5 GHz) учестаности, пре и после лабораторијске пиролизе, обављена су на одабраним древним седиментима (Ганфлинт рожнацу, Нансач шкриљц Звоначком шкриљцу, Антрим шкриљцу, Ирати шкриљцу и Грин Ривер шкриљцу) у покушају да се установе максималне палеотемпературе до којих су наведени депозити били изложени у току своје геохемијске историје. Промене у ESR понашању приликом загревања

посматране су код свих седимената, изузев Ганфлинт рожнаца, и то у области температура од 75 до 450°. Ови резултати указају на благе термалне историје тих седимената. Ганфлинт рожнац се разликовао од других седимената у томе да се ESR карактеристике нису мењале приликом пиролизе на температурама до 600°. Закључено је да је део органске материје у овом депозиту био изложен повишеним температурама (> 200°) и при том угљенисан пре увођења у седимент.

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