ON THE CONTROVERSIAL BIOGENICITY OF THE ORGANIC MATTER IN THE OLDEST ARCHEAN CHERTS: CAN ELECTRON PARAMAGNETIC RESONANCE PROVIDE CLUES?

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Introduction: The occurrence of objects resembling microbial fossils in the oldest Archean cherts (*ca.* -3.5 Byr) has been claimed as a definitive evidence of the existence of Life at this time [1]. However the biogenicity of the kerogen-like organic matter (OM) contained in these objects is still a matter of controversy [1, 2]. This OM is characterized by a highly refractory nature and only a limited number of analytical tools are available to determine the origin of such macromolecular materials. Moreover, the spectroscopic techniques classically used in organic geochemistry such as solid state ^{13}C nuclear magnetic resonance and Fourier transform infra-red only yield limited information on such highly aromatic macromolecules. In the present study, we used, for the first time on such materials, the electron paramagnetic resonance (EPR) to investigate the origin of this ancient OM through the nature of the organic free radicals it contains. An organic radical in macromolecular carbonaceous matter can be viewed as a single electron in a dangling bond resulting from homolytic cleavage of C-X bonds (X=H, C, N, O,…). The resulting unpaired electron may be stabilized by delocalization over aromatic moieties. EPR is based on the absorption of an electromagnetic radiation in the microwave range by an electron spin submitted to an applied static magnetic field. The absorption spectrum reflects the interactions of the spin with its environment and therefore provides information on the chemical and electronic structure of the surrounding matter. EPR has been scarcely used to analyse OM in geological samples but a recent study on carbonaceous chondrites revealed its potentiality to provide new insights on extraterrestrial macromolecular OM [3, 4]. Due to its high sensitivity, EPR enables to study *in situ* the extremely small amount of OM contained in raw cherts, without the constraint of isolating and concentrating the OM. In the present study, three cherts ranging in age from 45 Myr (Clarno Formation, USA) to 2.1 Byr (Gunflint Formation, Canada) and 3.5 Byr (Warrawoona, Australia) were analysed by EPR. The biological origin of the OM is well documented for the first two cherts but controversial for the Warrawoona chert [1, 2]. This work aims at assessing the ability of the radicals to probe the origin and the ageing stage of the OM in cherts.

Experimental: Samples of the three aforementioned cherts were analysed by EPR with a Bruker ESP300e operating at 9.4 Ghz. Artificial ageings of the samples were achieved by stepwise isochronal (15 min) thermal treatments in air at temperatures ranging from 75 °C to 700°C. An EPR analysis of the samples was performed after each step of the treatment.

Results and discussion: Figure 1a shows a schematic picture of a chert with a SiO_2 matrix embedding inclusions of organic matter. Figures 1b and 1c show EPR spectra of the Warrawoona chert, which illustrate the potentialities of EPR in the study of this kind of material.

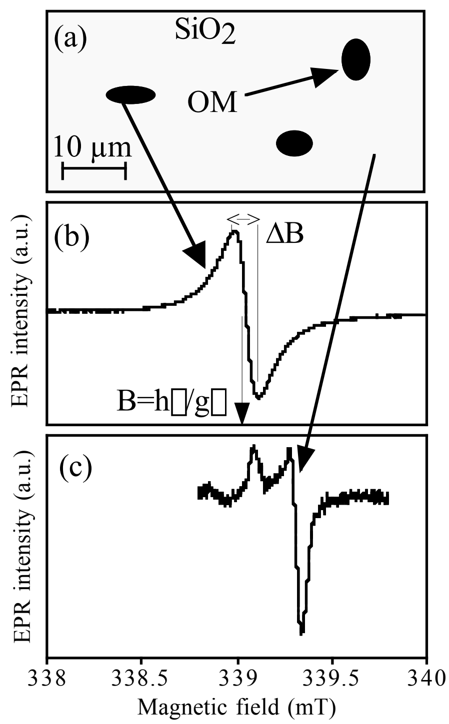

Figure 1: (a) Schematic picture of a chert showing organic matter (black spot) embedded in a SiO_2 matrix. (b) EPR spectrum of the organic radicals in the Warrawoona chert at T=300 K, with microwave power = 20 mW, and in phase with field modulation. (c) EPR spectrum of the E' centers in the SiO_2 matrix at T=300 K, with microwave power = 2 mW, and 90° out-of-phase with field modulation.

According to the acquisition conditions, either the radicals in the organic matter (Fig. 1b) or the E' centers (single electron in a dangling bond on a Si atom around an oxygen vacancy) in the SiO_2 matrix (Fig. 1c) can be selectively detected. *A priori* both kinds of paramagnetic species can be used to probe the history of the sample, but in the present work we will focus on the information provided by the organic radicals.

In Gunflint and Warrawoona cherts, the EPR of the organic radicals comprises a single narrow line. The signal intensity is proportional to the number of radicals. The field $B = h\nu / g\beta$ (ν: microwave frequency; β: Bohr magneton) at the center of the line gives the g-factor, which scales the magnetic moment induced by the electron spin. The g factor is mainly determined by the concentration in heteroelements and the observed value, g=2.0031, indicates a contribution of 10-15 % of oxygen to these radicals. The linewidths ΔB=0.28 and ΔB=0.12 mT, in Gunflint and Warrawoona cherts respectively result from the competitive effects of the spin concentration, which narrows the line when it increases, and of the unresolved magnetic interactions with protons, which broaden the line. The EPR signals of the organic radicals in Gunflint and Warrawoona cherts are similar to those observed in coals, kerogens and meteoritic insoluble OM. The evolution with temperature of these signals indicate that they do not arise from conduction electrons, and thus that the OM has not yet reached the graphite stage. In the Clarno chert, in addition to the aforementioned narrow line, several signals corresponding to other organic radicals are observed.

To clarify the question of the origin of the OM in the Warrawoona chert, it appeared necessary to look for a link between the organic radicals in these cherts and to compare the ageing process of the OM within. The three cherts were thus heated up to 700 °C as described in the experimental section. For the Clarno chert, three ageing stages, corresponding to domains I, II and III in figure 2a, could be distinguished in the evolution of the EPR signal: (I) T<350 °C, progressive disappearance of the "other organic radicals", leaving only the narrow single line, small increase of the EPR linewidth with a number of radicals approximately constant; (II) 350°C<T<575°C, increase of the number of radicals correlated to loss of oxygenated functions (decrease of the g-factor), strong narrowing of the EPR; (III) T>575°C, decrease of the number of radicals indicating fast inter-radical recombinations. The EPR parameters of the unheated samples of Gunflint and Warrawoona cherts are similar to those obtained with the Clarno chert at 500°C (stage II) and 620°C (stage III) respectively. (Fig. 2b,c). When submitted to the thermal treatment, Gunflint and Warrawoona cherts show similar changes in EPR parameters as those exhibited by the Clarno chert above the former and the latter temperature, respectively. It can be however noticed that the number of radicals in the Warrawoona chert decreases above a lower temperature than in the other two cherts.

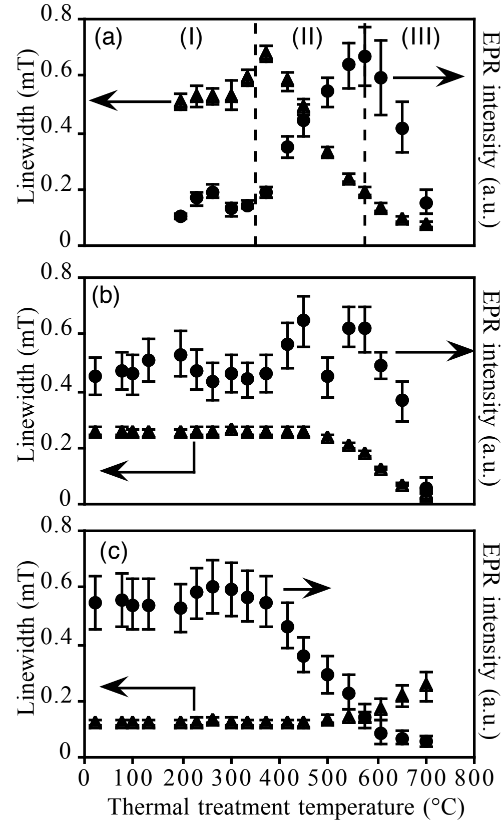

Figure 2: Peak-to-peak EPR linewidths and EPR intensity vs thermal treatment temperature for (a) the Clarno (-45 Myr) chert, (b) the Gunflint (-2.1 Byr) chert, and (c) the Warrawoona (-3.5 Byr) chert.

Conclusion: It thus appears that, regarding the features of the paramagnetic radicals, the OM of the Warrawoona chert exhibits a kerogen-like character. The global behavior of the EPR parameters of the radicals upon thermal treatment shows that the ageing process of this OM is probably ruled by the same mechanisms as for a biogenic OM like that of the Clarno chert. Other paramagnetic species, including organometallic complexes, are currently under study in Warrawoona and Gunflint cherts.

References: [1] Schopf J. W. et al (2002) *Nature*, *416*, 73-76. [2] Brasier M. D. et al. (2002) *Nature, 416*, 76-81 (2002); [3]. Binet L. et al. (2002) *Geochim. Cosmochim. Acta, 66*, 4177-4186. [4] Binet L et al. (2003) this volume.