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EPR study of thermally treated Archean microbial mats analogues and comparison with Archean cherts: towards a possible marker of oxygenic photosynthesis?

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The datation of photosynthesis apparition remains an open question nowadays: did oxygenic photosynthesis appear just before the Great Oxidation Event (GOE) of the atmosphere, 2.3 to 2.4 Gyr ago, or does it originate much earlier? It is therefore of uttermost interest to find markers of oxygenic photosynthesis, applicable to samples of archean age.

In order to handle this problem, *Microcoleus Chtonoplastes* cyanobacteria and *Chloroflexus*-like non-oxygenic photosynthetic bacteria, were studied using Electron Paramagnetic Resonance (EPR) spectroscopy, a high sensitivity technique for the study of organic radicals in mature geological samples (coals, cherts, meteorites...). *M. chtonoplastes* and *Chloroflexus*-like bacteria were sampled in mats from the hypersaline lake "La Salada de Chiprana" (Spain), an analogue to an Archean environment, and were submitted to accelerated ageing through cumulative thermal treatments.

For thermal treatment temperatures higher than 620˚C, a drastic increase in the EPR linewidth of the oxygenic photosynthetic bacteria (*M. chtonoplastes*) occurred, as compared with the anoxygenic photosynthetic one (*Chloroflexus*-like). The EPR study of a thermally treated mixture of the two bacteria evidences that this linewidth increase is driven by catalytic reaction at high temperatures on an element selectively fixed by *M. chtonoplastes*. Based on comparative EDS analyses, Mg is a potential candidate for this catalytic activity but its precise role and the nature of the reaction are still to be determined. The EPR study of organic radicals in chert rocks of ages ranging from 0.42 to 3.5 Gyr, from various localities and that underwent various metamorphisms, revealed a dispersion of the signal width for the most mature samples.

This comparative approach between modern bacterial samples and Precambrian cherts leads to propose the EPR linewidth of mature organic matter in cherts as a potential marker of oxygenic photosynthesis. If confirmed, this marker would support the hypothesis of oxygenic photosynthesis apparition at least 3.5 Gyr ago, long before the GOE.