

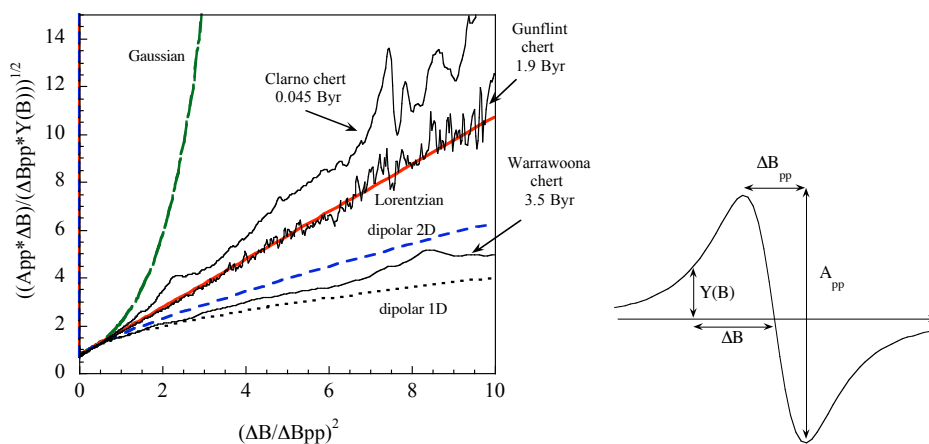
Tracking the oldest traces of life by EPR

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The issue of the origin of life is one of the most debated topics. The earliest living organisms presently remain in form of a highly degraded macromolecular organic matter embeded in sedimentary rocks dating of the Archean (from -2.5 to -3.8 Byr). The identification of the oldest traces of life on Earth, and possibly on Mars, is impeded because of the lack of reliable markers to prove or disprove the biological origin of the organic matter in the archean sedimentary rocks. In this context, the discovery about 20 years ago of carbonaceous microstructures first interpreted as microbial fossiles in cherts (sedimentary quartz) aged of -3.5 Byr from the Warrawoona Group (Western Australia) raised both a sharp interest and a fierce controversy since an alternative explanation as hydrothermal artifacts turned to be also possible. The issue of the origin of the organic matter in archean cherts is made even more complex by the difficulty to attest the actual age of a fossile organic matter, due to the possible contamination over the geological times of the rocks by endolithic organisms, which alter their organic content.

The insoluble and amorphous character of the organic matter in archean cherts make its analysis a very hard task. For such a material, EPR appears to be a valuable analytical tool, for it can be applied to raw rock samples containing minute amounts (*ca.* 100 ppm) of organic matter, with no need to isolate and concentrate this material. We performed an EPR study of the chert from the Warrawoona group (Australia, -3,5 Ga), and also for sake of comparison of cherts of different ages from the formations of Gunflint (Canada, -1,9 Ga), Rhynie (Scotland, -396 Ma) and Clarno (USA, -45 Ma), in which the organic matter has an attested biological origin. All these cherts exhibit an EPR line with no hyperfine structure assigned to organic radicals in the macromolecular organic matter. Additionnal signals due to isolated molecular organic radicals are also found in the cherts from Clarno and Rhynie. The major finding is that the lineshape of the EPR signal of the macromolecular organic matter drastically changes with age, as shown in the figure below.



Left: EPR spectra of the radicals in the macromolecular organic matter of cherts replotted so as to highlight the lineshape. Peaks in the spectrum of th Clarno chert are due to additional molecular radicals. Right: definition of the parameters occurring along the axes on the plot at left.

The lineshape changes from Lorentzian for organic matter of age below *ca* 2 Byr, indicating a three dimensional distribution of the radicals interacting via exchange interactions, to a shape typical of diluted radicals interacting via dipolar interactions and exhibiting a two dimensional distribution, for the organic matter in the Warrawoona chert. This trend was confirmed by the EPR analysis of the radicals in samples of the cherts from Clarno and Rhynie artificially aged by thermal treatments. Additionally, these treatments revealed a four-step ageing process of the organic matter in cherts. During this process, changes in several characteristics (nature, concentration, heteroelement content, EPR linewidth and lineshape) of the radicals could be analysed by EPR. As a conclusion, we showed that EPR can provide original information about changes over geological times in the molecular structure and in the microstructure of the organic matter in cherts, and hence provide a tool for dating this organic matter and detecting possible contaminations.