EPR AND PRIMITIVE LIFE: DATING AND VISUALIZING THE ORGANIC MATTER IN THE OLDEST ROCKS. L. Binet[1], D. Gourier[1], A. Skrzypczak-Bonduelle[1], O. Delpoux[1] and S. Derenne[2], [1]CNRS UMR 7574, Laboratoire de Chimie de la Matière Condensée de Paris, laurent-binet@enscp.fr, and [2] CNRS UMR 7618 BioEMCo, Laboratoire de Chimie Bioorganique et Organique Physique, Ecole Nationale Supérieure de Chimie de Paris (11 rue Pierre et Marie Curie, F-75231 Paris cedex 05, France).

Introduction: Traces of early life on Earth or of possible life on Mars should occur as carbonaceous matter preserved in very old rocks. However, any fossilized carbonaceous matter, whether biological or abiotic, undergoes a complex evolution over geological times [1]. At the end of this maturation process, the carbonaceous matter has lost most traces of its origin so that biogenicity or abioticity are difficult to assess on a chemical or structural basis. Besides in the case of terrestrial rocks, unavoidable biogenic contamination by endolithic bacteria complicates the problem of proving the biogenicity of ancient terrestrial organic matter [2]. Therefore there is a need for analytical techniques able to: (i) detect minute amounts of carbonaceous matter in mineral samples, (ii) visualize the distribution of the carbonaceous matter inside the samples, (iii) estimate the age of the carbonaceous matter, (iv) determine the origin (biotic or abiotic) of the carbonaceous matter, (v) perform the above mentioned tasks in a non destructive manner, specifically in the case of Martian samples. The aim of this work was to assess the potential of Electron Paramagnetic Resonance (EPR) to address these issues. This non-destructive technique detects radicals (unpaired electrons in dangling bonds) produced by the maturation in the carbonaceous matter [3, 4]. We used cherts (microcrystalline SiO_2), and synthetic silica containing carbonaceous matter as test samples.

Results and Discussion: We performed an EPR study of the carbonaceous matter in cherts of ages ranging from present to 3.5 Byr. The carbonaceous content of the sample can be as low as less 100 ppm in mass in the case of the 3.5 Byr old chert (Warrawoona Group, Australia). We also artificially aged young chert samples or synthetic silica encapsulating Bovine Serum Albumin (BSA) by thermal treatments to simulate the natural maturation over gelogical times. We used the EPR lineshape of the radicals in carbonaceous matter to assess the age of this matter and thus detect possible recent contamination. The EPR lineshape was characterized by a parameter R, which we defined as the deviation from a Lorentzian line and is zero for a purely Lorentzian line, positive for a Voigt lineshape, and negative for a line reaching the baseline more slowly than a Lorentzian line. The latter case (hereafter referred to as supra-Lorentzian) is obtained when the radicals are characterized by a low dimensional (1D or 2D) spatial distribution and interact via dipolar interactions. We showed that the EPR lineshape changes with age from a Voigt lineshape from present times to about 400 Myr, next to a Lorentzian shape for rocks aged up to 1-2 Byr, and finally to a supra-Lorentzian shape for older rocks (Fig. 1). An exactly identical change in the lineshape is observed when artificially aging recent cherts or synthetic silica containing BSA. This demonstrates that the change in EPR lineshape of the radicals in cherts is the result of thermally maturation processes occurring over geological times and common to any fossile carbonaceous matter in siliceous rocks.

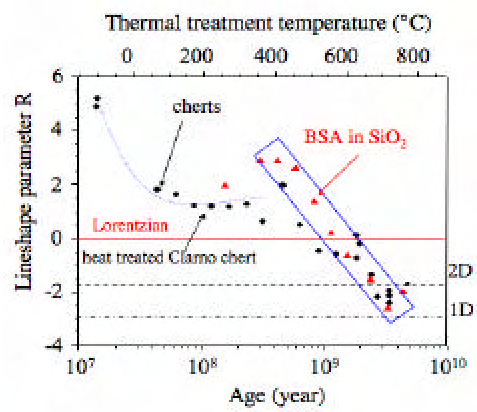

Figure 1: EPR lineshape parameter (0: lorentzian, >0: Voigt, <0: supra-lorentzian) for samples of cherts as a function of age (diamonds), or for artificially aged samples of chert from the Clarno Formation, USA, 45 Myr old (circles) or of BSA in synthetic silica (triangles) as a function of thermal treatment temperature.

The transition from Lorentzian to supra-Lorentzian is presumably due to a modification of the dimensionality of the interactions between radicals, which evolves from 3D to 2D or 1D. These radicals with low dimensional interactions might be the stable radicals, which survived at the boundaries of the aromatic domains within the carbonaceous matter after recombination of bulk radicals by paring off the spins. For ages above 1 Byr, the correlation between the EPR lineshape of the radicals and the age of the carbonaceous matter is monotonous, so that the lineshape can be used as an age marker. For example we used this peculiar lineshape evolution to show that the carbonaceous matter in 3.5 Byr old rocks is contemporary to the rock formation thus excluding any significant recent contamination by endolithic bacteria.

EPR imaging [5] could also be performed to visualize the distribution of the carbonaceous matter within this kind of opaque samples and detect possible ancient bacterial mats. Indeed, as bacteria generally grow as mats they should spread heterogeneously inside rocks. On the opposite, an abiotic chemical production of organic matter should rather lead to a more homogeneous distribution. Figure 2 shows the distribution of the carbonaceous matter arising from ancient cyanobacteria within a sample of chert from the Gunflint Formation, Canada (1.88 Byr), with a resolution of ~0.2 mm.

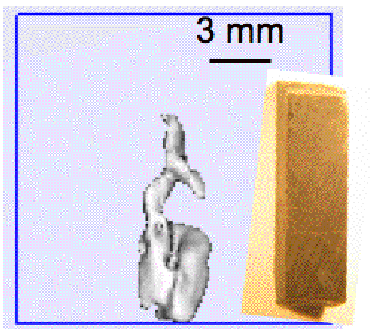

Figure 2: 3D image of the distribution of the carbonaceous matter within a sample of chert from the Gunflint Formation, Canada, 1.88 Byr old obtained by EPR imagning (right: photograph of the sample).

The distribution of the carbonaceous matter in this chert appears to be strongly heterogeneous. This can be compared to the distribution of the carbonaceous matter in a 3.46 Byr old chert from the Warrawona Group, Australia, the origin (biotic or abiotic) of which is still debated. The carbonaceous matter in the Warawoona chert looks much more regularly distributed than in the Gunflint chert, as shown in Fig. 3.

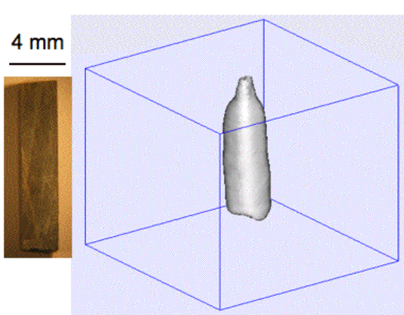

Figure 3: 3D image of the distribution of the carbonaceous matter in a sample of chert from the Warrawoona Group, Australia, 3.46 Byr old, obtained by EPR imaging (left: photograph of the sample).

This suggests either a possible abiotic origin for the carbonaceous matter in the Warawoona chert or, if the origin is biogenic, the occurrence of *post-mortem* processes redistributing homogeneously the carbonaceous matter during the geological history of this chert.

Conclusion: Electron Paramagnetic Resonance could be used to analyze directly small amounts (~10 µg) of carbonaceous matter in siliceous rocks without necessity of extracting and concentrating the carbonaceous matter. This is a major advantage if this technique has to be applied to the analysis of precious Martian samples. The EPR lineshape of the radicals correlates with the maturity of the carbonaceous matter and thus can be used as an age marker for old (>1 Byr) carbonaceous matter. The distribution of the carbonaceous matter inside millimeter size samples can be visualized by EPR imaging with a submillimeter resolution, which may help detecting possible fossile bacterial mats without destroying the sample.

References:

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