NEW EXTRATERRESTRIAL SIGNATURE OF THE INSOLUBLE ORGANIC MATTER OF THE ORGUEIL, MURCHISON AND TAGISH LAKE METEORITES AS REVEALED BY ELECTRON PARAMAGNETIC RESONANCE. L. Binet[1], D. Gourier[1], S. Derenne[1], F. Robert[2], and I. Ciofini[1]. [1]Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, F-75231 Paris cedex 05, France (laurent-binet@enscp.jussieu.fr, gourierd@ext.jussieu.fr, sderenne@ext.jussieu.fr, ciofini@ext.jussieu.fr). [2]Museum National d'Histoire Naturelle, Laboratoire de Minéralogie, CNRS FRE 32, 61 rue Buffon, F-75005 Paris, France (robert@cimrs1.mnhn.fr).

Introduction: Carbonaceous chondrites are known to contain up to 3% of carbon, most of which occuring as macromolecular insoluble organic matter (IOM). This IOM, with complex and largely unknown structure, is considered as a record of interstellar synthesis and may contain precursors of prebiotic molecules which could have been deposited on Earth by meteoritic bombardments. The knowledge of the structure of this IOM is necessary to better understand its genesis and its possible implication in the production of prebiotic molecules. The IOM of the carbonaceous meteorites contains radicals, i.e molecular moieties with unpaired electron spins [1, 2]. Radicals are paramagnetic species and can be studied by Electron Paramagnetic Resonance (EPR). This spectroscopic technique 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. In this contribution we show that the radicals in the IOM possess several specific features which could be the consequence of its chemical history and which make this IOM clearly distinguishable from the terrestrial type III kerogens, to which they are often compared.

Experimental: The IOM of three carbonaceous chondrites, Orgueil, Murchison and Tagish Lake was isolated by the standard HF/HCl treatment. The sample of IOM from Tagish Lake resulting of this treatment is labelled TL1. A fraction of this IOM was also extracted with trichlorobenzene to remove the fullerenes. The resulting IOM is labelled TL2. The radicals contained in this IOM were analysed by EPR with Bruker ESP300e spectrometer operating at 9.4 Ghz. Temperatures in the range 4K-300K were obtained at X-band with an ESR9 helium flow cryostat from Oxford Instruments. The EPR spectra of the meteoritic IOMs were also compared to those of three type III kerogens A1, A2 and A3, ranked in increasing order of maturity. A1 and A2 are Miocene kerogens from the Mahakam Delta (Indonesia) and A3 is a Namurian kerogen from the Solway Basin (Great-Britain).

Results and discussion: For the four meteoritic samples and the three kerogens, the EPR response of the IOM is made of a narrow EPR line (peak-to-peak linewidths in the range 0.4-0.6 mT), corresponding to stable aromatic radicals, superimposed with a broad feature due to ferromagnetic mineral residues (Fig. 1). The latter are known to survive the HF/HCl treatment.

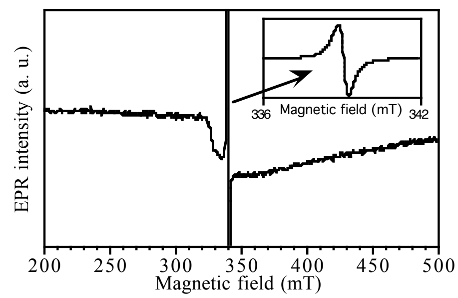

Figure 1: EPR spectrum of the IOM from Orgueil meteorite at 9.4 GHz and T=300 K. The broad line is a ferromagnetic resonance signal from mineral residues. The sharp line (expanded in the inset) is the signal of the organic radicals.

The g-factors (factors scaling the magnetic moments associated with the electron spins) of the radicals is correlated to the content in heteroelements (especially O and N). The small linewidths and the link between g-factors and chemical composition are the only common features between meteoritic radicals and radicals in the kerogens. Clearly, EPR reveals distinctive features for the radicals in the meteorites, which should reflect their extraterrestrial origin.

1- The saturation of the EPR signals shows that the radicals in the meteoritic IOM are heterogeneously spread, unlike the radicals in the kerogens [2]. Although significant differences are noted in average spin concentration amongst the 4 meteoritic samples, strikingly similar values (4.10^{19} spin.g-1) are observed for local spin concentrations (table 1).

Table 1

Local and average spin concentrations in the IOM of Orgueil, Murchison and Tagish Lake meteorites

	Local concentration (10^{19} g^{-1})	Average concentration (10^{19} g^{-1})
Orgueil	4.1±0.6	0.70±0.08
Murchison	4.3±0.7	0.18±0.03
Tagish Lake		
TL1	4.1±0.7	2±0.8
TL2	4.0±0.7	1.6±0.2

2- The major difference between terrestrial and meteoritic IOM concerns the nature of the radicals. The kerogens contain only monoradicals (electronic spin S=1/2). This results in a number of spins independent of temperature for the kerogens as exemplified by A3 in Fig. 2. In the meteoritic IOMs, monoradicals are also found, which exclusively contribute to the spin concentration below 100 K. The specificity of the meteorites is that a significant part of the radicals is in form of diradicaloids i.e. species with a diamagnetic singlet (S=0) ground state and a thermally accesible paramagnetic triplet (S=1) excited state. These diradicaloids are responsible for the increase in spin concentration in the meteoritic IOM when temperature is raised above 100K (Fig. 2).

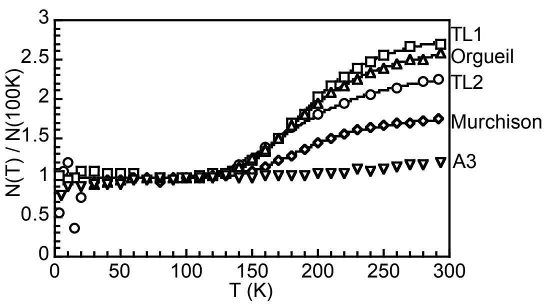

Figure 2: Spin concentration N(T) normalized at the value at 100 K, N(100K), in the IOM of the Orgueil, Murchison and Tagish Lake(TL1 and TL2) meteorites and in the A3 kerogen.

From the simulation of the change in spin concentrations with temperature the singlet-triplet (ST) gaps ΔE, entropy differences Δ□ and the proportion of diradicaloids could be obtained. The diradicaloids in the three meteorites have similar ΔE and Δ□ values, respectively 0.10-0.12 eV and 4.2-4.8 $cm^{-1}.K^{-1}$, except for TL2 (ΔE=0.09 eV and Δ□=3.6 $cm^{-1}.K^{-1}$). This shows that similar species must be considered in the three meteorites. The entropy difference contains a significant vibrational contribution, which indicates that the diradicaloids are probably not isolated molecules but linked to the macromolecular network. The proportions of diradicaloids among the radicals are about 40% for Orgueil and TL1, 35% for TL2 and 25% for Murchison. The existence of diradicaloids supports structural models for the meteoritic IOM based on highly substituded aromatic moieties [3, 4]. In that case, the formation of two radicals in □-position around the same aromatic moiety leading to diradicaloids, is stastically enhanced. We performed electron structure calculations by *Extended Hückel* and *Density Functional Theory* methods on a series of dimethyl substituted aromatic molecules as a function of the size of the aromatic moiety. These calculations show that the formation of a diradicaloid is energetically more favourable than the formation of two separate monoradicals when the aromatic moiety contains less than 30-35 carbon atoms. Besides the variation of the calculated ST gaps with the molecular size show that the diradicaloids in the IOM with ST gaps about 0.1 eV should contain ca 35 aromatic carbon atoms i.e. ca 10-15 rings. The estimated size of the diradicaloids agrees very well with recent NMR [3, 4] and electron microscopy [5] studies suggesting rather small sizes for the aromatic moieties in the meteoritic IOM.

Conclusion: Although bulk features of EPR spectra of meteoritic IOMs are similar to those of terrestrial kerogens, important differences which can be viewed as extraterrestrial signatures are revealed when the nature and distribution of the organic radicals are considered. Indeed, the presence of diradicaloids is along with high D/H ratios a unique feature of meteoritic IOMs. It may either reflect a pristine origin or result from alteration of the IOM caused by various stresses (shocks, high energy irradiation, radioactivity) during the 4.5 Gyr of its lifetime on the parent body. If pristine, these diradicaloids, which are known to be highly reactive, should have been sequestered and should be considered as additional constraints in the models describing the genesis of this IOM especially those involving low temperature reactions.

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