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Occurrence of abundant diradicaloid moieties in the insoluble organic matter from the Orgueil and Murchison meteorites: A fingerprint of its extraterrestrial origin?

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Abstract—The highly aromatic structure of the macromolecular organic matter (OM) of the Murchison and Orgueil meteorites was recently shown to contain free organic radicals which are concentrated in micro-regions in contrast with terrestrial samples which always show a homogeneous distribution of radicals. An additional signature is revealed, in the present study, by the evolution of the radical concentration with temperature. Whereas in terrestrial samples, this concentration is independent of temperature (Curie magnetism), a significant increase is observed above 150 K in the two meteorites. Based on the electronic structure of organic radicals, calculated by Extended Hückel and Density Functional methods, this behavior was assigned to the occurrence of diradicaloid moieties hosted by aromatic structures of 10 to 15 rings and having a quinoidal structure. They represent 40 and 25% of the total radicals in Orgueil and Murchison, respectively. The search for the cosmochemical interpretation of this unique observation should open a new field of experimental investigations. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

Carbonaceous chondrites are known to contain a substantial amount of carbon (up to 3%), most of which occurring as macromolecular insoluble organic matter (IOM). This IOM is considered as a record of interstellar synthesis and may contain organic molecules with prebiotic utility which could have been deposited on earth by meteoritic bombardments. For these reasons, the chondritic IOM has been of interest to scientists for a considerable time. However, due to limitations on analytical tools, its precise chemical structure is still a matter of debate.

Numerous studies, mainly based on chemical and thermal degradations, pointed to similarities between the chondritic IOM and mature terrestrial coals. However, a clear cut difference is noted between these two materials when the isotope composition, especially the D/H ratio is considered (Robert and Epstein, 1982; Kerridge et al., 1987; Halbout et al., 1990). Moreover, recent investigations using solid state ¹³C nuclear magnetic resonance (NMR) revealed that, contrary to IOM in mature coals which is based on large polyaromatic units, the chondritic IOM mainly comprises rather small, highly substituted polyaromatic units cross-linked by highly branched short aliphatic chains (Gardinier et al., 2000; Cody et al., 2002). This high level of branching also accounts for the typical pattern of the 3.3 μm band observed by infra-red spectroscopy both in chondritic IOM and in the interstellar medium (Ehrenfreund et al., 1991; Gardinier et al., 2000).

The bulk features derived from electron paramagnetic resonance (EPR) spectra of chondritic IOM show strong similarities

with those of terrestrial coals but EPR saturation behaviour and ¹H Electron Nuclear Double Resonance (ENDOR) enhancement measurements revealed in the chondritic IOM the occurrence of radical-rich micro-regions separated by radical-free domains (Binet et al., 2002) whereas, as far as we are aware, radicals are always homogeneously distributed in terrestrial samples (Thomann et al., 1988). The aim of the present work, was thus to examine if, in addition to their distribution, the radicals of the chondritic IOM exhibit typical structures, different from those encountered in terrestrial samples.

It must be noted that, due to the shape of the EPR spectra, i.e., a single structureless line resulting from a narrowing effect by exchange interactions between electron spins of radicals due to their high concentration (10¹⁸ to 10¹⁹ spins.g⁻¹) (Conard, 1984), it is not possible to deduce directly the chemical structure of the radicals which is classically derived from the proton hyperfine structure of the EPR spectra when radicals occur at low concentrations. These interactions, which are the consequence of electron repulsion, induce a long range spin diffusion between radicals, which average to zero the local magnetic fields experienced by the electron spins (Wertz and Bolton, 1972a).

However, indirect information about the nature of paramagnetic species can be obtained from the evolution of the magnetic susceptibility with temperature. The effect of the temperature on the molecular magnetism was thus investigated on the IOM isolated from the Orgueil and Murchison meteorites and compared to that of terrestrial coals. Indeed, to the best of our knowledge, terrestrial coals always exhibit a standard Curie type behaviour (Retcofsky et al., 1981; Conard, 1984; Rothenberger et al., 1993), which means that all the radicals possess a S=1/2 electron spin, despite tentative interpretations of small

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deviations from Curie's law to thermally excited multiplet states (Wieckowski et al., 2000). The interpretation of the temperature effect on the molecular magnetism in the two chondritic IOM was based on semiempirical (Extended Hückel) and ab initio Density Functional Theory (DFT) calculations (Hoffman, 1963; Springborg, 2000a), and any strong deviation from Curie's law was considered as a fingerprint of extraterrestrial IOM.

2. EXPERIMENTAL

Orgueil and Murchison meteorites from Museum d'Histoire Naturelle, Paris, France, and from Smithsonian, Washington DC, USA, respectively, were treated by the standard HF/HCl process for the isolation of the IOM (Durand and Nicaise, 1980). We have checked that this treatment has no effect on preexisting paramagnetic radicals (Binet et al., 2002). The elemental composition of the IOM was analyzed and reported in a previous paper (Gardinier et al., 2000). Before EPR analysis, the samples were loaded into conventional EPR quartz tubes under ambient atmosphere. However, oxygen from air is not expected to influence the EPR in the case of our samples. Oxygen generally induces broad and inhomogeneous EPR lines (Retcofsky et al., 1982). This effect occurs mainly with high rank or heat treated coals (Retcofsky et al., 1982; Conard, 1984), which exhibit major differences in chemical structure with meteoritic IOM and is not observed with natural low-rank coals (Conard, 1984), closer the meteoritic IOM. On the contrary, the EPR signals of our samples appeared to be perfectly stable over more than two years, rather narrow and with perfectly homogeneous lineshapes up to a microwave frequency of 285 GHz (results from multifrequency EPR studies, to be published). Three samples of type III terrestrial coals labelled A₁, A₂, A₃ ranging from the less mature to the most mature were used for comparison of the magnetism of terrestrial kerogens with that of meteoritic IOM. Miocene coals A₁ and A₂ originate from the Mahakam Delta (Indonesia) and the Namurian coal A₃ originates from the Solway basin (Great Britain). All the information concerning these samples have been previously reported (Binet et al., 2002). The EPR measurements were carried out from room temperature to 4K with a Bruker ESP 300e spectrometer operating at 9.4 GHz (X-band). The temperature variations were obtained with a helium flow ESR9 cryostat from Oxford Instruments. The quality factor of the EPR cavity was checked to be constant over the whole explored range of temperature to make sure that changes in EPR intensities are intrinsic to the samples and not related to changes in instrumental characteristics or dielectric losses in the samples. No skin effect, usually occurring with highly conducting samples, was observed, which means that the microwaves fully penetrated the samples and that the entire samples were probed. All the EPR spectra were recorded at a sufficiently low microwave power, $P = 0.2$ mW, to avoid saturation effects (Wertz and Bolton, 1972b). The EPR intensities of the three coals were measured by the usual double integration method. However, in the case of the meteoritic IOM, this method could not be used for the small contribution of the broad ferromagnetic resonance signal superimposed to the IOM signal (Binet et al., 2002) imposed to correct significantly the double integration parameters. This resulted in a significant dispersion of the experimental points, with a standard deviation from the average value about $\pm 5\%$. To avoid this problem, we took into account the perfect Lorentzian shape of the EPR line of meteoritic IOM in the whole temperature range 4 to 300 K. The intensity of the signal was determined by simulation of the EPR lines with the Lorentz function:

$$f(B_0) = -m_1 \frac{(B_0 - hv/g\beta)}{[1 + m_2(B_0 - hv/g\beta)^2]} \quad (1)$$

where B_0 is the amplitude of the scanning magnetic field and $h/g\beta$ is the magnetic field at the center of the resonance line. The other parameters are the g -factor, $g=2.0031$ (Binet et al., 2002), which is very close to the free-spin value $g_e = 2.0023$, the Bohr magneton β and the photon energy hv . The intensity I_s of the spectrum is related to the adjustable parameters m_1 and m_2 of Eqn. 1 by the following expression:

$$I_s = \frac{m_1}{(m_2)^{3/2}} \quad (2)$$

With this simulation method, the dispersion of the EPR intensities was much smaller (standard deviation of $\pm 0.5\%$) than with the double integration method.

The absolute spin concentrations in coals and meteoritic IOM were determined by comparing the EPR intensities of the EPR lines with that of a diphenylpicrylhydrazyl (DPPH) standard known to contain exactly 10^{17} spins. In that case, the simulation method could not be used because the lineshape of the DPPH spectrum is not Lorentzian. Consequently, the EPR intensities were measured by double integration. To minimize differences in EPR intensities due to differences in microwave field at the location of the samples, the latter were inserted at the same position in the cavity with an accuracy < 1 mm. The quality factor of the cavity and the acquisition parameters other than the receiver gain were the same when recording the EPR spectra of the samples and of the DPPH standard, so that differences in EPR intensities after receiver gain correction only reflect differences in spin concentrations. The spin concentration measured at room temperature $N(300K)$ is related to the EPR intensities I_s and I_{DPPH} of the sample and the DPPH standard, respectively, by the following expression:

$$N(300K) = \frac{I_s(300K)}{I_{DPPH}(300K)} \frac{N_{DPPH}}{M} \quad (3)$$

where M is the sample weight and $N_{DPPH} = 10^{17}$ spins. The spin concentrations at other temperatures, $N(T)$, were determined from $N(300K)$ as follows:

$$N(T) = \frac{T \cdot I_s(T)}{I_s(300K) \times 300} N(300K) \quad (4)$$

which takes into account the $1/T$ dependence of the Curie susceptibility.

3. RESULTS

Figure 1 shows the EPR spectra at room temperature of the IOM from Orgueil and Murchison meteorites, and the comparison with theoretical lines calculated with a pure Lorentzian shape (Eqn. 1). The EPR spectra of terrestrial coals, not shown (see Fig. 2 in Binet et al., 2002), exhibit the same shape, except a small gaussian contribution for the less mature samples A₁ and A₂. The temperature dependence of the spin concentrations derived from the EPR intensities of the meteoritic IOM and the three coal samples are shown in Figure 2. To compare the five samples, the spin concentrations $N(T)$ at each temperature T were normalized with respect to the spin concentration at 100K, $N(100K)$. In the case of pure $S=1/2$ radicals, the radical concentration should be independent of temperature if the Curie's law is satisfied, i.e., $N(T)/N(100K)=1$ for all the temperatures. Figure 2 shows that this behavior is observed only between 20K and 120K for all the samples. The spin concentration rapidly decreases below 20K, which is the indication of a spin-pairing phenomenon at low temperatures in both the terrestrial coals and the meteoritic IOM (Fig. 2). The two kinds of samples differ above 120K. While the spin concentration is almost independent of temperature up to room temperature for coals, which is the indication of a Curie magnetism, the spin concentration is multiplied by 1.6 and 2.7 above 120K for Murchison and Orgueil meteorites, respectively. It should be pointed out that coals also exhibit a very small variation of the spin concentration above 120K, however this variation is too weak to be analyzed.

The only way to explain the increase in spin concentration above 120 K is to assume that in addition to the $S=1/2$ radicals, the meteoritic IOM contains diamagnetic moieties ($S=0$) with

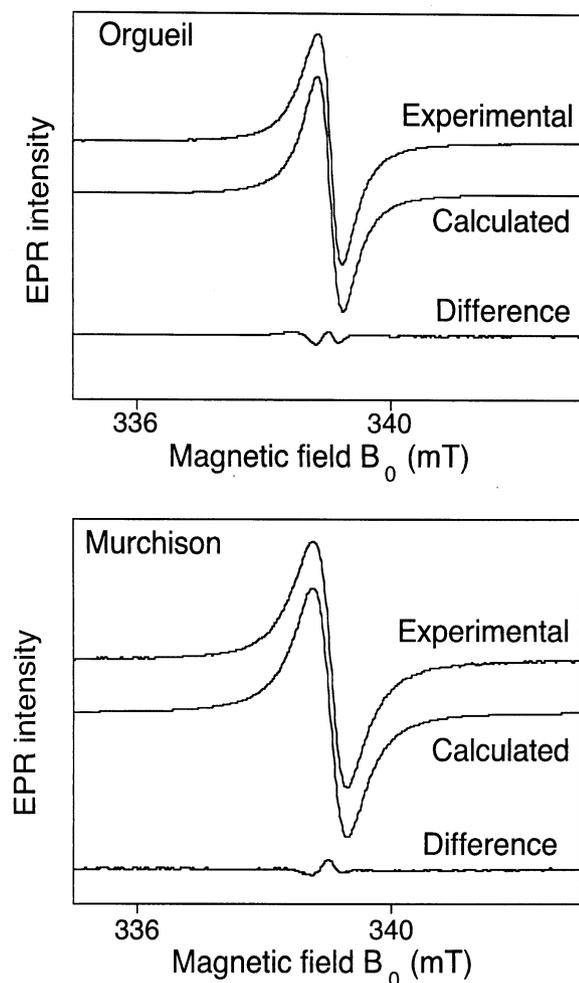


Fig. 1. EPR spectra at room temperature of the insoluble organic matter of the Orgueil and Murchison meteorites. Microwave power 0.2 mW; microwave frequency 9.5131 GHz; modulation amplitude 0.1 mT; time constant 82 ms; scan rate 0.36 mT.s⁻¹. The experimental spectra are compared with pure Lorentzian lineshape functions.

thermally accessible triplet state ($S=1$), hereafter referred to as TATS. Normally a triplet state radical exhibits a two line EPR spectrum resulting from the dipole-dipole interaction between the two electron spins of the radical. However, as stressed above, the exchange line-narrowing phenomenon due to the spin diffusion between radicals eliminates all the structures in the EPR spectra which could help to determine the structure of the mono-radicals and TATS. However, as the temperature dependence of the EPR intensity reflects the variation of magnetic susceptibility upon thermal population of the triplet states at the expense of the singlet state, it is sensitive to the singlet-triplet gap (hereafter referred to as the ST gap), and to the entropy variation induced by this thermal excitation. The former parameter depends intimately on the electronic structure of the TATS moieties, and consequently on its chemical structure.

We thus assume that the meteoritic IOM contains monoradicals ($S=1/2$) and TATS with concentrations N_{mono} and N_{di}^1 , respectively. Moreover TATS may be either in the singlet state

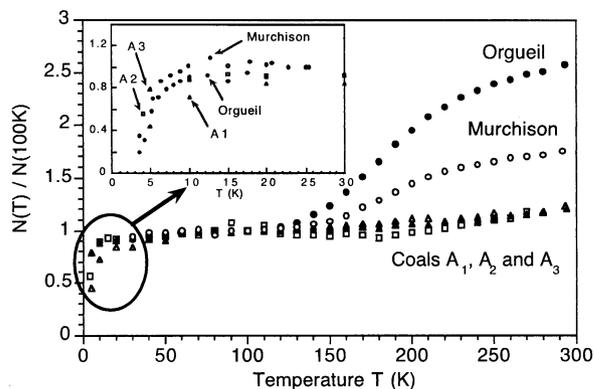


Fig. 2. Temperature dependence of the spin concentration normalized to the value at 100 K for the insoluble organic matter of the Orgueil and Murchison meteorites and the terrestrial coals A₁ (open triangles), A₂ (open squares) and A₃ (black triangles).

$S=0$ or in the triplet state $S=1$, with concentrations N_{di}^0 and N_{di}^1 , respectively. The EPR intensity of paramagnetic radicals is proportional to the absorbed microwave power P , given by the following expression (Abragam, 1985):

$$P \propto S(S+1)N/T \quad (5)$$

where N is the concentration of radicals with spin S . Consequently the total EPR intensity of the IOM is:

$$I_s = C_1 \left(\frac{3}{4} N_{mono} + 2N_{di}^1 \right) / T = C_2 N / T \quad (6)$$

where C_1 and C_2 are constants. The quantity

$$N = N_{mono} + \frac{8}{3} N_{di}^1 \quad (7)$$

can be considered as the equivalent spin concentration of $S=1/2$ radicals giving the same EPR intensity as N_{mono} radicals with $S=1/2$ and N_{di}^1 TATS with $S=1$. The actual spin concentration is $N_a = N_{mono} + 2N_{di}^1$. However, taking into account the values of N_{mono} and N_{di}^1 determined below, the equivalent and actual concentrations differ by less than 10% so that we shall keep dealing with the equivalent concentration N in what follows. Table 1 gives the spin concentrations $N(300K)$ deduced from Eqn. 3 for the two meteorites. Despite the fact that the radical concentrations are relatively small ($1.8 \times 10^{18} \text{ g}^{-1}$ and $7 \times 10^{18} \text{ g}^{-1}$ for Murchison and Orgueil, respectively), we have previously shown that the radicals are heterogeneously distributed in the IOM, with highly concentrated micro-regions [$(4.3 \pm 0.6) \times 10^{19} \text{ g}^{-1}$ and $(4.1 \pm 0.6) \times 10^{19} \text{ g}^{-1}$ for Murchison and Orgueil, respectively] separated by radical-free regions

Table 1. Spin concentrations N at 300K in the IOM of Orgueil and Murchison meteorites. N_{rad} is the concentration of radicals, which is the sum of N_{mono} monoradicals and N_{di}^1 diradicaloids.

	$N \text{ (g}^{-1}\text{)}$	N_{di}^1/N_{mono}	$N_{mono} \text{ (g}^{-1}\text{)}$	$N_{di} \text{ (g}^{-1}\text{)}$	$N_{rad} \text{ (g}^{-1}\text{)}$
Orgueil	7×10^{18}	0.68	2.66×10^{18}	1.8×10^{18}	4.5×10^{18}
Murchison	1.8×10^{18}	0.33	10^{18}	0.33×10^{18}	1.3×10^{18}

(Binet et al., 2002). Taking into account the existence of TATS moieties in singlet state $S=0$ at low temperatures, the total concentration of radicals in the IOM is equal to:

$$N_{rad} = N_{mono} + N_{di} = N_{mono} + N_{di}^0 + N_{di}^1 \quad (8)$$

Let us now consider the variation of the spin concentration with temperature, which depends on two energetic quantities, the ST gap $\Delta E = E_1 - E_0$ and the entropy variation $\Delta\sigma = \sigma_1 - \sigma_0$, where E_0 (E_1) and σ_0 (σ_1) are the energies and the entropies, respectively, of the spin state $S=0$ ($S=1$) of the TATS moieties. The concentration N_{di}^1 of TATS moieties in triplet state is related to ΔE , $\Delta\sigma$ and the total concentration N_{di} of TATS by:

$$N_{di}^1 = N_{di} \frac{1}{1 + \exp(-\Delta\sigma/k) \exp(\Delta E/kT)} \quad (9)$$

The spin concentration N , proportional to $I_s T$, is deduced from expressions (6), (7) and (9).

$$N = N_{mono} + \frac{8}{3} N_{di} \frac{1}{1 + \exp(-\Delta\sigma/k) \exp(\Delta E/kT)} \quad (10)$$

Only the spin degeneracy is usually considered to contribute to the entropy variation in the case of diluted free TATS with simple molecular structures, i.e., $\sigma_i = k \ln(2S + 1)$ with $i=0,1$ and $S=0,1$. However, owing to the complexity of the “kerogen-like” meteoritic IOM, other degrees of freedom may contribute to the entropy, such as vibrational entropy for example, so that we choose to keep $\Delta\sigma$ as an adjustable parameter in Eqn. 10, in addition to ΔE and N_{di}/N_{mono} . Figure 3 shows the experimental temperature dependence of the spin concentration N for Murchison and Orgueil meteorites, compared with curves calculated according to Eqn. 10. It was impossible to reproduce the experimental variations by taking into account only the spin degeneracy contribution to the entropy $\Delta\sigma = k \ln 3 \approx 0.76 \text{ cm}^{-1} \text{ K}^{-1}$ (discontinuous line in Fig. 3), even by introducing a distribution of ΔE , which on the contrary flattens the curve, and thus increases the discrepancy with the experimental curve. However a satisfactory fit is obtained if $\Delta\sigma$ is adjusted (full line in Fig. 3). The resulting values of the adjusted parameters N_{di}/N_{mono} , ΔE and $\Delta\sigma$ are given in Tables 1 and 2. At room temperature, Eqn. 10 gives for the total spin concentration:

$$N(300\text{K}) = N_{mono} + \frac{8}{3} N_{di} \times 0.9 \quad (11)$$

with $0.9 \approx [1 + \exp(-\Delta\sigma/k) \exp(\Delta E/kT)]^{-1}$ at 300 K. It is thus possible to determine separately from Eqn. 11 the concentrations N_{mono} and N_{di} of monoradicals and TATS, reported in Table 2. It can be seen that the ratio N_{di}/N_{mono} is relatively high, 0.68 and 0.33 for Orgueil and Murchison, respectively, which means that 40 and 25% of the radicals in these two meteorites are in the form of TATS.

The most interesting result arises from the singlet-triplet gap ΔE and the entropy difference $\Delta\sigma$ (Table 2). Within experimental errors, the two independent simulations give the same values for the two meteorites. In particular the same energy gap $\Delta E = 0.10 \text{ eV}$ is found in the two meteorites. As the ST gap is highly sensitive to the structure of the magnetic molecule, the existence of a unique value of ΔE means that we are dealing

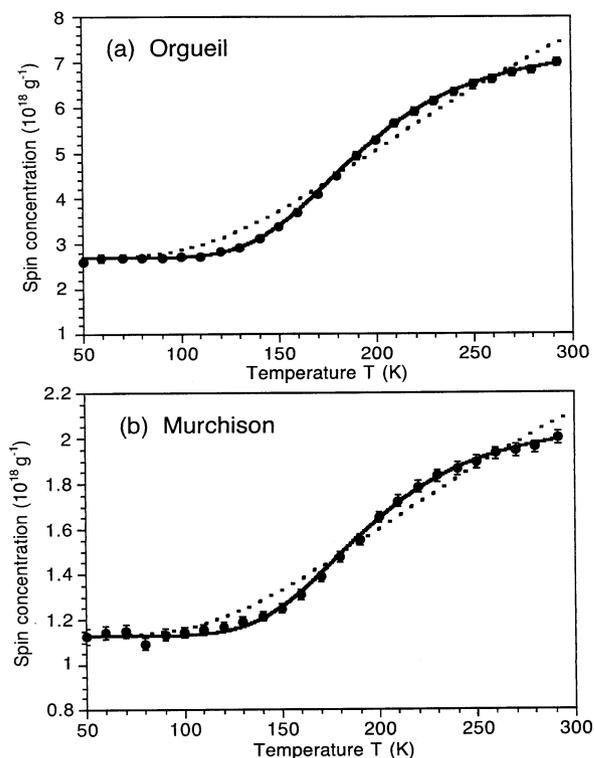


Fig. 3. Temperature dependence of the spin concentration in the organic matter of Orgueil (a) and Murchison (b) meteorites. Points: experimental results; discontinuous line: calculated from Eqn. 10 using only the spin degeneracy contribution $\Delta\sigma = k \ln 3$ to the entropy variation and adjusting the singlet-triplet gap ΔE ; full line: calculated from Eqn. 10 adjusting both $\Delta\sigma$ and ΔE .

with the same type of TATS moieties in the two meteorites. This result is confirmed by the value of the entropy variation $\Delta\sigma$, which amounts to 4.2 and 4.3 $\text{cm}^{-1} \text{ K}^{-1}$ for Orgueil and Murchison meteorites, respectively. This means that in both cases vibrational entropy contributes to about 80% of the total entropy variation. These values for the entropy variation associated to the spin transition are very close, for example, to those found in spin transition metal complexes in the solid state (Zarembowitch and Kahn, 1991). This does not mean that the TATS moieties in the IOM are related to transition metal complexes. It means that these moieties are not isolated molecules, but that they are chemically bonded to the macromolecular network. The vibrational entropy is related to the number of the vibrational modes in given vibrational frequency range, which scales as the number of atoms. Thus if the distribution of these modes on the frequency scale is changed upon the singlet-triplet transition, a large entropy variation can

Table 2. Experimental energy gaps ΔE and entropy differences $\Delta\sigma$ between ground singlet and excited triplet states of the diradicaloids in the Orgueil and Murchison meteorites.

	ΔE (cm^{-1})	$\Delta\sigma$ ($\text{cm}^{-1} \text{ K}^{-1}$)
Orgueil	816 ($\approx 0.101 \text{ eV}$)	4.2
Murchison	841 ($\approx 0.104 \text{ eV}$)	4.3

be expected if the TATS moieties are parts of the macromolecular network. All these features, and the fact that it was not necessary to assume a distribution of ΔE and $\Delta\sigma$ parameters (which would mean a distribution of radical structure) to obtain an excellent fit, indicate that the IOM of the two meteorites contains a well defined type of TATS moieties. This feature has never been observed in terrestrial coals and kerogens, which contain almost exclusively monoradicals with Curie behavior.

4. NATURE AND ORIGIN OF THE THERMALLY ACCESSIBLE TRIPLET STATES

The magnetism of IOM from both terrestrial coals and carbonaceous meteorites shows the presence of paramagnetic organic radicals (with unpaired electron spins) connected by exchange interactions (Conard, 1984; Binet et al., 2002). However these two types of IOM exhibit two important differences: (i) the radicals are inhomogeneously distributed in meteoritic IOM, with highly concentrated regions ($3\text{--}4 \times 10^{19}$ spin.g⁻¹, comparable to mature terrestrial coals), separated by radical-free regions (Binet et al., 2002); (ii) the radicals of Orgueil (Murchison) IOM consist of 40% (25%) of TATS moieties, as revealed in the present study. These two features clearly distinguish the “kerogen-like” meteoritic IOM from terrestrial type III kerogens. We previously proposed that the heterogeneous distribution of radicals reflects the presence of pristine parts of the IOM synthesized in conditions close to those prevailing in the interstellar medium which have survived the hydrothermal process on the parent body (Binet et al., 2002). The issue of the nature and the origin of TATS is more puzzling as their presence may reflect both the structure of the IOM and their mechanism of formation. Despite the fact that the pronounced aromatic nature of the IOM of meteorites is now widely accepted, the size of the aromatic moieties is not definitely determined. Some studies suggested the presence of hydrogen-poor carbon-rich organic domains (Cronin et al., 1987; Kerridge et al., 1987; Cody et al., 1999), with composition intermediate between that of chars and high volatile Illinois bituminous coals in the case of Murchison (Hayatsu et al., 1977). Other works, either involving thermal and chemical degradation techniques (Hayes et al., 1967; Hayatsu et al., 1983; Sephton et al., 1999) point to the presence of highly substituted small aromatic units. The fact that a large part of carbon atoms are not detected by CP/MAS NMR and the presence of a high proportion of non-protonated carbons among aromatics are indeed compatible with the latter hypothesis, but also with the opposite possibility of large aromatic moieties (Gardinier et al., 2000). However, recent observations of the Orgueil and Murchison IOM by high resolution transmission electron microscopy also led to an average diameter of 3 to 4 rings for the polyaromatic units, i.e., comprising 10–15 rings (Derenne et al., 2002). Given the extremely complex structure of the meteoritic IOM, the determination of the molecular structure of the TATS is a real challenge. However, the model must be constrained by several experimental facts: (i) despite similarities in chemical compositions between meteoritic IOM and IOM from mature terrestrial coals, the model must explain why TATS are favored in meteorites and not in coals; (ii) IOM in mature coals is based on large polyaromatic units, while meteoritic IOM contains rather small, highly substituted pol-

aromatic units cross-linked by highly branched short aliphatic chains (Gardinier et al., 2000; Cody et al., 2002; Derenne et al., 2002); (iii) the model for TATS must explain the experimental value of the singlet-triplet gap; (iv) the g-factor $g = 2.0031$ is very close to the free spin value $g_e = 2.0023$ in the two meteorites (Binet et al., 2002).

An a priori possible origin for these TATS could be charge-transfer complexes. Such complexes are sets of two more or less loosely bonded molecules, one acting as an electron donor (D), the other one as an electron acceptor (A). In the ground state (labelled D-A) of these complexes, each molecule is in its non-magnetic ground state. There exists an excited state of these complexes (labelled D⁺-A⁻), in which one electron has been transferred from D to A. In this excited state, each of the two molecules is paramagnetic with spin $S=1/2$, giving rise to a triplet state with $S=1$ for the whole complex. However charge-transfer complexes are very unlikely to account for the TATS in the meteoritic IOM for the following reasons. The great majority of the known complexes have charge-transfer energies, E_{CT} , largely exceeding 1 eV (Foster, 1969a). This charge-transfer energy is the energy required to excite the complex from the D-A ground state to the D⁺-A⁻ excited state, and should be of the same order of magnitude as the singlet-triplet gap ΔE , though it does not exactly correspond to the same transition. To get a charge-transfer energy as low as the experimental S-T gap 0.1 eV, the acceptor must be highly electroattractive (Foster, 1969b) and thus contain a large amount of heteroelements. Indeed, this is inconsistent with the g-factor of the radicals in the meteoritic IOM. The g-shift $\Delta g = g - g_e$ is proportional to the spin-orbit coupling constant λ of the elements bearing the spin density and λ increases with the atomic number (29 cm^{-1} for C, 76 cm^{-1} for N, 151 cm^{-1} for O, 272 cm^{-1} for F, 382 cm^{-1} for S). Though the observed g-factor is an average value over both monoradicals and TATS, a large proportion of heteroelements in the complexes bearing the TATS should lead to g-factors larger than the experimental value $g=2.0031$, at room temperature where TATS contribute up to 40% of the radicals. To give an example if we simply refer to coals, $g > 2.0031$ as soon as $O/C > 0.15$ (Yen and Sprang, 1977). Besides, an increase in the g-factor value should be observed from low temperature where TATS do not contribute to the EPR signal to room temperature, where the TATS' contribution is significant. On the contrary, a slight decrease is observed from 2.0036 to 2.0031, from low to room temperature. A related argument against a significant presence of heteroelements in TATS is that the radicals possess the same g-factor in the two meteorites, although the concentrations of TATS are different (40% in Orgueil and 25% in Murchison). This indicates that both monoradicals and TATS are of similar nature. Consequently, the very small experimental g-shift indicates that the monoradicals and TATS moieties are mainly carbon-based, and if they do contain heteroelements such as O, N or S, the latter do not make a significant part of the atoms bearing the spin density. The second reason against the hypothesis of charge-transfer complexes is that, since E_{CT} and the S-T gap strongly depend on the overlap between the orbitals of D and A, well defined relative positions of D and A are required to get a given value of the S-T gap. This is hardly conceivable in a disordered material such as the meteoritic IOM, where distributions of relative distances and orientations between

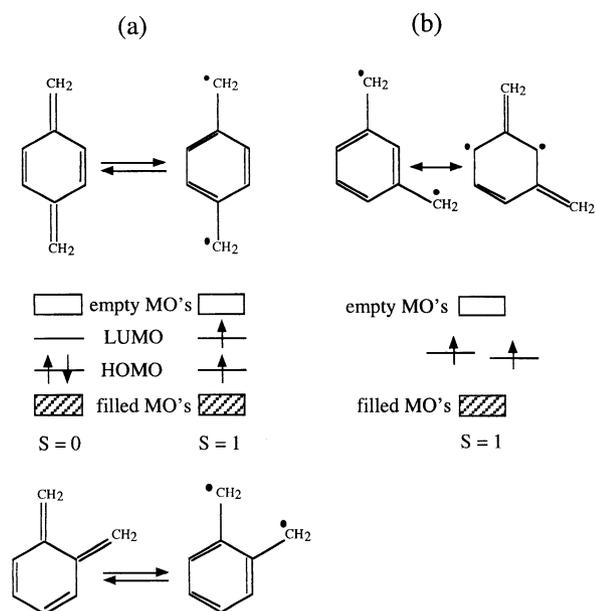


Fig. 4. Example of a diradicaloid (a) and a diradical (b) with the case of benzoquinodimethane.

molecular moieties are expected, which should result in broad distributions of S - T gap. Therefore, the well defined S - T gap must result from intramolecular rather than intermolecular interactions. We are thus faced with TATS moieties which must be mainly carbon-based and which should satisfy the aforementioned constraints. If, at this stage, the possibility of charge-transfer complexes cannot be fully ruled out and if some kind of exotic complex specific to the extraterrestrial IOM were ever responsible for the TATS, we would still be left with the additional problem of the nature of this complex. Indeed, the molecular structure of TATS which is most likely to fulfill these constraints, and which introduces the fewest hypotheses, for they are derived from known features of the IOM, is that of diradicaloids. The concept of diradicaloid is illustrated in Figure 4, with the example of benzoquinodimethanes (Matthew, 1982). In the case of 1,2 and 1,4 isomers (Fig. 4a), the molecules exhibit two forms characterized by their total electron spin state S . The more stable form, referred to as the diradicaloid form, possesses a quinoidal Kekule structure with a non-magnetic ($S=0$) ground state. However the gap between the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) is quite small, so that the molecule exhibits a low-lying excited state in the form of a paramagnetic diradical ($S=1$) with two unpaired electrons mainly localized on the alkyl substituents (Fig. 4a). The 1,3 isomer (Fig. 4b) has two degenerate or nearly degenerate valence orbitals. In this case, the electron repulsion favors the occupation of each orbital with one single electron giving rise to a paramagnetic $S=1$ ground state. This structure is referred to as a diradical and contrary to a diradicaloid, only mesomer forms with two unpaired electrons can be written (Fig. 4b). Such diradicaloid/diradical structures can occur in a variety of condensed aromatic compounds with alkyl substituents, and are thus likely to occur in natural aromatic macromolecules.

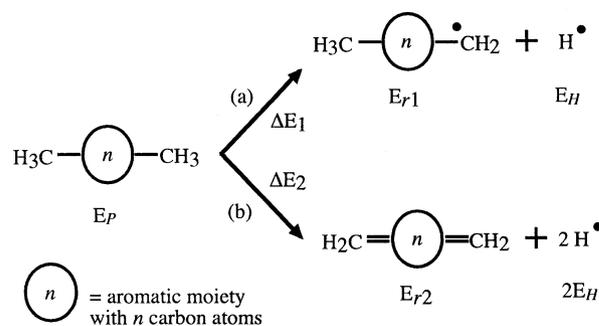


Fig. 5. Reactions of formation of a monoradical [path (a)] and of a diradicaloid [path (b)] from an alkyl doubly substituted aromatic unit. E_P , E_{r1} , E_{r2} and E_H represent the total electronic energies of the pristine molecule, the monoradical, the diradicaloid and the hydrogen atom, respectively. ΔE_1 and ΔE_2 represent the changes in electronic energy corresponding to reactions paths (a) and (b), respectively.

In the following, we show that the occurrence of diradicaloids in the meteoritic IOM agrees with the estimated size of aromatic units, which explains both their stability in meteorites and the S - T gap. Let us consider a condensed aromatic moiety constituted of n aromatic carbon atoms, with a given number of ring protons substituted by alkyl groups (Fig. 5). If one of these alkyl groups loses a hydrogen by homolytic cleavage, then an unpaired electron remains which leads to a mono-radical [Figure 5, reaction path (a)]. If this radical is localized in α -position, the unpaired electron is delocalized over the whole aromatic moiety, which enables a strong stabilization of the radical. If there are a large number of alkyl groups substituting the aromatic hydrogens, which corresponds to the high branching ratio suspected for the meteoritic IOM, there is a high probability that a second alkyl group on the same aromatic moiety loses another hydrogen thus forming a diradical [Figure 5, reaction path (b)]. If the symmetry of these diradicals is sufficiently low (i.e., no rotation axis with order higher than two), all the molecular orbitals are non degenerate and all the electrons are paired for an even number of electrons, giving diradicaloids. In that case the ground state ψ_0 is diamagnetic ($S=0$) as shown in Figure 6. However an electron in the HOMO can be thermally excited into the LUMO giving rise to low-lying excited configuration ψ_1 with two unpaired spins (Fig. 6, left part). A high-lying excited configuration ψ_2 can also be obtained by pairing the two valence electrons in the LUMO. However, electron repulsion mixes these configurations and changes their energies, giving rise to new energy levels characterized by their total electronic spin S (Fig. 6, right part). The ground ψ_0 and second excited ψ_2 configurations are thus shifted downward and upward, respectively. The degeneracy of the first excited configuration ψ_1 is also lifted resulting in a low lying paramagnetic triplet state $S=1$ detectable by EPR and a higher-lying diamagnetic singlet state $S=0$. The energies of these levels can be calculated by a DFT method (see Appendix 1) with takes into account the electron repulsion. The ST gap $\Delta E = E_1 - E_0$ corresponds to the energy difference between the ground state 1^1A and the first excited state 3^1B in Figure 6. Within the Extended Hückel framework (see Appendix 1), which neglects electron repulsion, the ST gap $\Delta E = E_1 - E_0$ is approximated by $\Delta E \approx \Delta E_{HL}$, where ΔE_{HL} is the

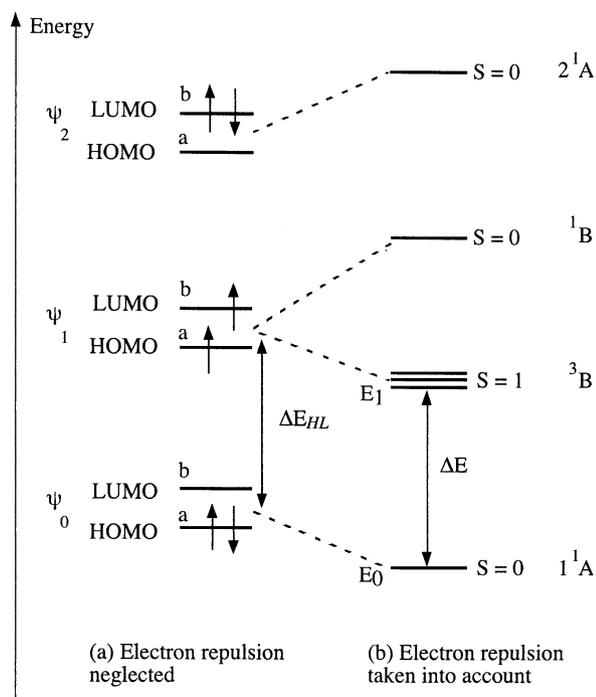


Fig. 6. Simplified electron energy diagram of a diradicaloid. a) Ground, first and second excited configurations (independent electron approximation). The energy difference between the first two configurations gives the HOMO-LUMO gap ΔE_{HL} . b) Effect of electron repulsion giving rise to four energy levels characterized by their total spin values S . The EPR signal arises from the thermal occupation of the first excited state 3B with $S=1$. The experimental singlet-triplet gap ΔE corresponds to the energy difference between the 1^1A ground state and the 3B state.

HOMO-LUMO gap corresponding to the energy difference between the ground ψ_0 and first excited ψ_1 configurations. The large changes in vibrational entropy upon singlet-triplet transition can be qualitatively accounted for by the energy diagram of Figure 6. The singlet-triplet transition involves the excitation of an electron from a bonding orbital (the HOMO) to an antibonding orbital (the LUMO). This can induce slight structural distortions of the diradicaloids, which change the vibrational frequencies, and which can propagate far away from them if they are bonded to the macromolecular network. Since a large number of atoms are involved in these distortions, significant changes in the density of vibrational modes and hence in vibrational entropy may occur, as explained above.

Then two questions have to be answered: (i) To which extent the formation of a diradicaloid is energetically more favorable than two separate monoradicals? (ii) What is the approximate size of the aromatic moiety which would give a ST gap corresponding to the experimental value $\Delta E \approx 0.1$ eV? To address these questions we performed electronic structure calculations on a series of model molecules shown in Figure 7, with different numbers n of carbon atoms in the aromatic moieties. To spare calculation time and minimize the number of structural possibilities, the molecules were chosen as simple as possible. They were chosen as pure hydrocarbons, though in reality the aromatic moieties may contain a slight amount of oxygen probably as quinone functions. Some of these aromatic struc-

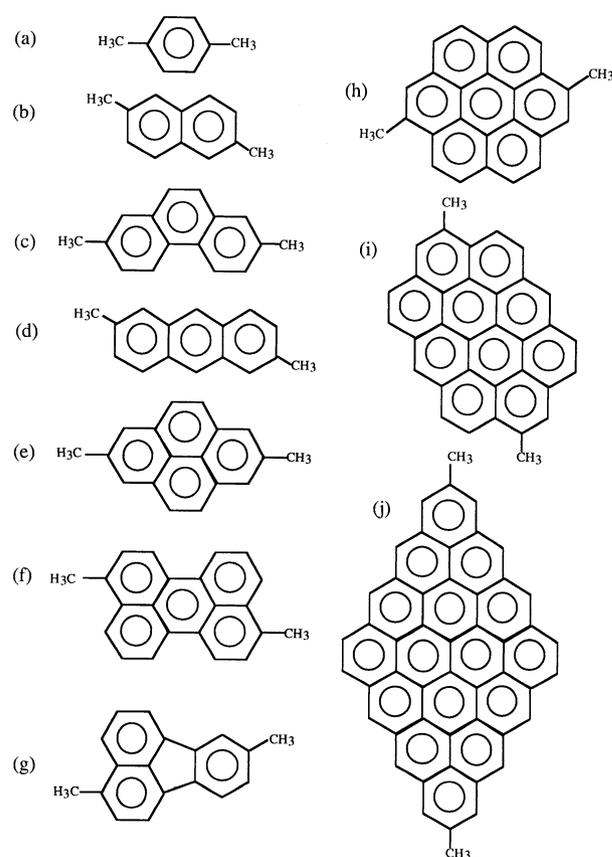


Fig. 7. Molecules used for the calculations of the diradicaloid stabilization energies and singlet-triplet gaps. Monoradicals (diradicaloids) are obtained by replacing one (both) CH_3 by CH_2 .

tures ($n \leq 24$) correspond to fragments detected after pyrolysis of the meteoritic OM of Murchison (Studier et al., 1972; Hayatsu et al., 1977; Hayatsu et al., 1980; de Vries et al., 1993; Sephton et al., 1998). The branching of these aromatic molecules is simulated by two methyl groups. Here again for sake of simplicity, the possibility of more complex alkyl substituents and in a number greater than two was not considered. Anyhow, changing the number and the nature of the alkyl substituents will influence only the low-lying σ -type molecular orbitals and thus should have very little effect on the properties calculated below, which depend mainly on the higher-lying π -type molecular orbitals. The methyl groups can lose a hydrogen atom to form monoradicals and diradicaloids. The energies ΔE_1 and ΔE_2 (Fig. 5) necessary to form a monoradical and a diradicaloid, respectively, are given by:

$$\Delta E_1 = E_{r1} + E_H - E_p \quad (12)$$

and

$$\Delta E_2 = E_{r2} + 2E_H - E_p \quad (13)$$

with E_p , E_{r1} , E_{r2} , $E_H = -13.6$ eV being the electronic energies of the pristine molecule, the monoradical, the diradicaloid and the hydrogen atom, respectively. The stabilization energy of a

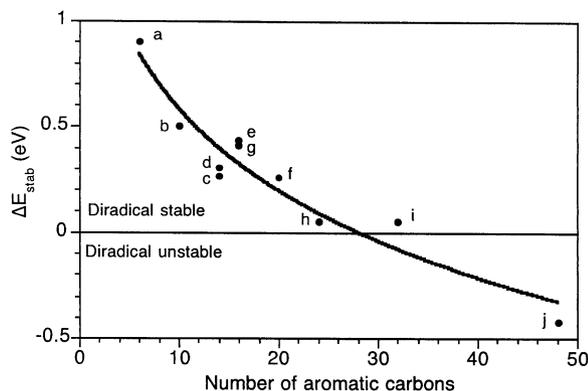


Fig. 8. Stabilization energy ΔE_{stab} defined by Eqn. 14 and calculated by the Extended Hückel method for diradicaloids vs. number of carbon atoms in the aromatic moiety. The continuous lines represent an interpolation. Letters refer to the molecules in Figure 7.

diradicaloid with respect to that of two separate monoradicals is obtained as:

$$\Delta E_{stab} = 2\Delta E_1 - \Delta E_2 \quad (14)$$

Then the formation of a diradicaloid is more favorable than that of two separate monoradicals if $\Delta E_{stab} > 0$. In Figure 8, ΔE_{stab} , calculated by the EH method is plotted versus the number n of aromatic carbon atoms for the molecules of Figure 7. It shows that ΔE_{stab} regularly decreases when n increases. The formation of diradicaloids is thus favorable only for molecules containing less than *ca* 30 aromatic carbon atoms.

The HOMO-LUMO gap ΔE_{HL} (Fig. 6) deduced from EH calculations and the singlet-triplet (ST) gap ΔE deduced from DFT calculations are shown in Figure 9. A positive (negative) ST gap means that the $S=0$ ($S=1$) state is the ground state. For very small molecules, less than *ca* 25 aromatic carbon atoms, the ST gap ΔE is significantly different from the HOMO-LUMO gap ΔE_{HL} calculated by the EH method. The reason is that the EH method does not take into account the electron correlations, which are more important in smaller molecules

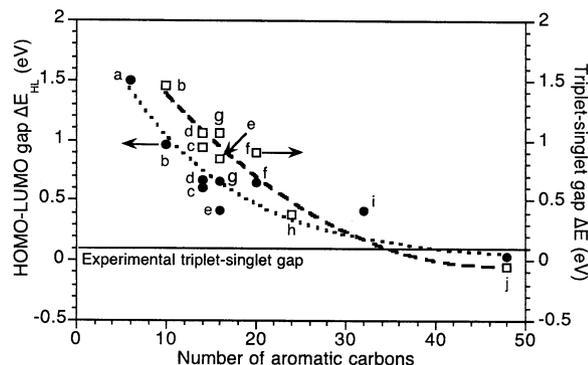


Fig. 9. HOMO-LUMO gap ΔE_{HL} (black circles) calculated by the Extended Hückel method and singlet-triplet gap ΔE (open squares) calculated by DFT for diradicaloids vs. number of carbon atoms in the aromatic moiety. The discontinuous lines represent interpolations. Letters refer to the molecules in Figure 7.

where the average interelectron distances are smaller. For larger molecules (more than 25 aromatic carbon atoms) the ST gap is mainly determined by the HOMO-LUMO gap. It can be noticed that molecules containing about 35–40 aromatic carbon atoms have a ST gap approximately equal to the experimental value $\Delta E \approx 0.1$ eV. For even larger molecules (containing more than *ca* 40 atoms) the ST gap is slightly negative, which means that the $S=1$ state is the ground state, or at least that the diradicaloid state is not stable.

It may appear a slight inconsistency between the maximum size (30 carbon atoms) of the aromatic moiety, allowing the formation of stable diradicaloids and the size, slightly larger (35–40 atoms), giving the correct S - T gap. However these sizes must not be considered from a strict point of view and they are certainly not accurately determined. The approximations in the calculations either in the choice of the model molecules or intrinsic to the calculation methods (see Appendix 1 for details) introduce a certain margin of uncertainty, though not easily assessable, on these sizes. Performing calculations on more realistic molecules, including a slight amount of oxygen and more complex substituents was far beyond the scope of this approach. The maximum size for stable diradicaloids and the size giving the experimental S - T gap could possibly be slightly shifted (upper or lower) with such molecules but shall not be drastically different from the sizes determined from the model molecules for these sizes mainly depend on the aromatic hydrocarbon frame. Consequently the possible diradicaloid moieties in the meteoritic OM are the molecules fulfilling the two following constraints: (i) a ST gap of about 0.1 eV and (ii) an energetically more favorable diradicaloid state. Figures 8 and 9 show that molecules containing *ca* 35 aromatic carbons or approximately 10–15 aromatic rings likely fulfill these conditions.

5. DISCUSSION AND CONCLUSION

The semiempirical (EH) and ab initio (DFT) calculations presented in this paper indicate that the most likely molecular structure responsible for the peculiar molecular magnetism of the IOM from Murchison and Orgueil meteorites can be described as condensed aromatic moieties of approximately 10–15 aromatic rings substituted by alkyl groups. These results are in agreement with the rather small size of the aromatic units recently deduced from the solid state ^{13}C -NMR and electron microscopy studies of the Orgueil and Murchison IOM (Gardinier et al., 2000; Cody et al., 2002; Derenne et al., 2002). They can also account for the similarity of the ^{13}C -NMR spectra recorded with the cross-polarization and single pulse sequences since carbons in the vicinity of radicals will not be detected by any of these two techniques due to a strong decrease in the relaxation times. Such rather small polyaromatic structures favor the formation of diamagnetic diradicaloid states possessing thermally accessible diradical state with ST gap of about 0.1 eV. The highly characteristic and well defined effect of the temperature on the molecular magnetism of the two meteorites show that the latter is dominated by these diradicaloid states, which represent 40 and 25% of the paramagnetic radicals of Orgueil and Murchison meteorites, respectively. In the framework of this model, all the aromatic moieties with more than *ca* 15 aromatic rings should not favor the

formation of diradicaloids, and give only mono-radicals with spin $S=1/2$, characterized by a simple Curie paramagnetism. On the contrary, aromatic moieties with less than *ca* 10 aromatic rings should give stable diradicaloid states. However their ST gap being larger than 0.1 eV, they remain in their non-magnetic state $S=0$ in a very large temperature range, and should contribute to the paramagnetism of the meteoritic IOM only at high temperature. Such diradicaloid cannot be detected at room temperature and below. To the best of our knowledge, the IOM of terrestrial kerogens and coals exhibit only a Curie paramagnetism. This IOM is thus dominated by highly condensed aromatic moieties, and/or the aromatic moieties do not exhibit the configuration of alkyl substituents which allow the formation of diradicaloid states. The presence of diradicaloid moieties with with ST gap of about 0.1 eV in a natural IOM should thus constitute a fingerprint of its extraterrestrial origin, as this type of magnetic behavior has never been observed in terrestrial samples, to the best of our knowledge. This should be confirmed by the study of other carbonaceous meteorites. Moreover, the model should be tested with IOM synthesized in conditions mimicking the natural synthesis of organic matter in space.

It should be stressed that simple diradicaloids such as quinodimethanes (Fig. 3) are known to be highly reactive compounds, so that they cannot be isolated and studied by ordinary methods (Matthew, 1982). The fact that diradicaloid moieties can be stabilized in radical-rich microdomains of the meteoritic IOM shows that these highly reactive molecules are intimately embedded in the dense polymer network of the IOM in such a way that they cannot react with other molecules, so that they indefinitely survive. The reactivity of the diradicaloid compounds have attracted the attention of organic chemists for the synthesis of natural products, e.g., to prepare the framework of steroids (Oppolzer, 1978; Funk and Vollhardt, 1980), or as highly reactive intermediates for polymerization (Hontis et al., 2001).

The question of the cosmochemical significance of diradicaloids in the chondritic IOM must be addressed for the three successive epochs characterizing the formation and evolution of the matter constituting the meteorites. In principle diradicaloids could be formed (i) during the synthesis of the OM, through processes advocated for space organosynthesis such as irradiation of ices, ion-molecule reactions in the gas phase or quenched condensation under thermal disequilibrium; (ii) during the (hydro)thermal episode which could have affected the molecular structure of the OM; or (iii) during the life time of the parent body in the asteroid belt through high pressure peaks caused by mutual shocks between planetesimals, or high energy irradiation by Galactic Cosmic Rays or by the particles which originated from the decay of the radioactive elements for 4.5 Gyr. If hypothesis (ii) seems unlikely because the presence of water has a clear tendency to erase the radicals, the points (i) and (iii) needs to be examined experimentally with a special attention devoted to the processes in which the organic molecules are condensed at temperatures too low to permit the electronic rearrangement of the solid (condensation under thermal disequilibrium).

It seems likely that the presence of the diradicaloids which is—along with the high D/H ratio—a unique feature of the chondritic origin of the IOM, should be a characteristic signa-

ture of well defined physical conditions. In this respect, the correct interpretation of diradicaloids in meteorites should allow one to point between the various models proposed to account for the origin of the organic matter in the solar system.

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APPENDIX: COMPUTATIONAL DETAILS

Both Extended Hückel (EH) and Density Functional Theory (DFT) calculations were used to help the identification of diradicaloids and explain their origin in the meteoritic IOM. Within the framework of the Density Functional Theory (DFT), the electron energy of a molecule containing P electrons is computed as a function of the electron density $\rho(\vec{r})$. In the Kohn-Sham approach (Kohn and Sham, 1969), the electron density is expanded as a sum of one-electron contributions:

$$\rho(\vec{r}) = \sum_{i=1}^P |\varphi_i(\vec{r})|^2 \quad (15)$$

with the $\varphi_i(\vec{r})$'s being the Kohn-Sham molecular orbitals. The latter are obtained from the basic one-electron equation in canonical form:

$$\left[-\frac{1}{2}\Delta + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V(\vec{r}) + V_{xc}(\vec{r}) \right] \varphi_i = \varepsilon_i \varphi_i \quad (16)$$

The first term in this equation is the kinetic energy operator, the second one represents the Coulomb repulsion between electrons, the third one the interaction with the external potential (including attraction by nuclei) and the last one the exchange-correlation potential. Depending on the implementation either gaussian type orbitals or Slater type orbitals can be used as atomic basis to express the molecular orbitals. All contributions related to exchange and correlation energy are contained in the $V_{xc}(\vec{r})$ potential and, provided that this term is exact, DFT will give the exact energy of the system including electron correlation without any parametrisation, i.e., ab-initio. Unfortunately the exact exchange correlation potential is not known and different approximations have been proposed (Parr and Yang, 1989). Structural optimizations were performed using the gaussian 98 package (Frisch et al., 1998), with the Becke 3 parameters exchange correlation functional (B3LYP) (Becke, 1993) and split valence GTO basis plus 1 polarization function (6–31G*). All optimized structures were characterized by a subsequent frequency calculation. The energy difference between the diamagnetic ground state (with spin $S=0$) and the first excited triplet state (with spin $S=1$), the singlet-triplet energy gap of the diradicaloids, was computed at optimized singlet geometry, using the Single Determinant method of Daul (Daul, 1994). In this method each spin state is described by symmetry adapted linear combination of single determinants, so-called non-redundant single determinant (NRSD). In particular, in our case we computed the singlet-triplet energy gap taking into account, as active magnetic orbitals, only the HOMO, hereafter labelled a , and the LUMO, hereafter labelled b , of the singlet state (Fig. 6). Taking into account only the spin states arising from different occupations of the HOMO and LUMO orbitals, we reduced the problem to that of two electrons in two orbitals of different symmetry. In this case three singlet (two 1A and one 1B) and one triplet 3B states can be generated. The four NRSD arising from the different occupations of the HOMO and LUMO orbitals are written $|a^\alpha a^\beta|$, $|a^\alpha b^\beta|$, $|a^\alpha b^\alpha|$, $|b^\alpha b^\beta|$. Symbols α and β represent spin up and spin down configurations, respectively. The energies of the four states 1A , 1B , 3B and 2^1A are written as (Fig. 6):

$$E(1^1A) = E(|a^\alpha a^\beta\rangle) - \Delta = E_0 \quad (17)$$

$$E(1^1B) = 2E(|a^\alpha b^\beta\rangle) - E(|a^\alpha b^\alpha\rangle) \quad (18)$$

$$E(2^1A) = E(|b^\alpha b^\beta\rangle) + \Delta \quad (19)$$

$$E(3^1B) = E(|a^\alpha b^\alpha\rangle) = E_1 \quad (20)$$

with:

$$\Delta = \frac{E(|a^\alpha b^\alpha\rangle) - E(|a^\alpha b^\beta\rangle)}{E(|a^\alpha a^\beta\rangle) - E(|b^\alpha b^\beta\rangle)} \quad (21)$$

For all systems we have analyzed, the lowest energy singlet results to be the 1^1A state and therefore the singlet-triplet energy gap corresponds to $\Delta E = E_1 - E_0$. The energy of each NRSD has been computed using the ADF package with the Becke exchange (Becke, 1988) and LYP correlation functionals (Lee et al., 1988). The singlet-triplet energy gap has been computed at first order. A double Slater type basis set +2 polarization functions (basis V in ADF2000 nomenclature) was used, keeping as frozen core the 1s orbital of carbon.

The EH method (Hoffman, 1963) is a fast and easy-implementable semiempirical method for electron structure calculations. The P molecular orbitals (MO's) Ψ_i ($i=1, \dots, P$) to be calculated are expanded on a basis of P atomic orbitals (AO's) φ_j ($j=1, \dots, P$):

$$\Psi_i = \sum_{j=1}^P C_{ij} \varphi_j \quad (22)$$

The basis AO's are chosen as the valence orbitals (1s for H, 2s and 2p for C) of the atoms constituting the molecule. Their analytic form is set as Slater-type functions (Springborg, 2000b). These functions contain one parameter, the Slater exponent, which is equal to 1.3 for the 1s AO of hydrogen and to 1.625 for the 2s and 2p AO's of carbon. The energies ε_i of the MO's Ψ_i are given by the roots of the determinant of the secular equation:

$$(H - \varepsilon_r S) \begin{pmatrix} C_{i1} \\ \vdots \\ C_{iP} \end{pmatrix} = 0 \quad (23)$$

where H is the Hamiltonian matrix of an electron in the molecule and

S the overlap matrix with coefficients $S_{ij} = \int \varphi_i^*(\vec{r}) \varphi_j(\vec{r}) d^3\vec{r}$. For the

energies ε_r , the coefficients C_{ij} ($j=1, \dots, P$) in the expansion Eqn. 22 of the corresponding MO's Ψ_i are obtained by solving the linear system given by Eqn. 23. The coefficients H_{ij} of the matrix H in Eqn. 23 are parameterized. The diagonal elements H_{ii} are set as the ionization energies of the AOs ϕ_j . For the 1s AO of hydrogen $H_{ii} = -13.6$ eV, and $H_{ii} = -21.4$ eV and -11.4 eV for the 2s and 2p AO's of carbon, respectively. The off-diagonal elements H_{ij} ($i \neq j$) are calculated with the modified Wolfberg-Helmoltz formula:

$$H_{ij} = K S_{ij} (H_{ii} + H_{jj}) / 2 \quad (24)$$

with $K = 1.75 + \Gamma^2 - 0.75\Gamma^4$ and $\Gamma = (H_{ii} - H_{jj}) / (H_{ii} + H_{jj})$. The total electronic energy of the molecule is given by:

$$E = \sum_{i=1}^P n_i \varepsilon_i \quad (25)$$

where $n_i = 0, 1$ or 2 is the number of electrons in the MO with energy ε_i . The energies of the configurations ψ_0 , ψ_1 and ψ_2 in Figure 6 corresponding to the different possible occupations of the HOMO and the LUMO by two electrons are given by:

$$E(\psi_0) = 2\varepsilon_a \quad (26)$$

$$E(\psi_1) = \varepsilon_a + \varepsilon_b \quad (27)$$

$$E(\psi_2) = 2\varepsilon_b \quad (28)$$

with ε_a and ε_b being the energies of the HOMO and of the LUMO, respectively.