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Diradicaloids in the insoluble organic matter from the Tagish Lake meteorite: Comparison with the Orgueil and Murchison meteorites

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Abstract–The radicals in the insoluble organic matter (IOM) from the Tagish Lake meteorite were studied by electron paramagnetic resonance and compared to those existing in the Orgueil and Murchison meteorites. As in the Orgueil and Murchison meteorites, the radicals in the Tagish Lake meteorite are heterogeneously distributed and comprise a substantial amount (~42%) of species with a thermally accessible triplet state and with the same singlet-triplet gap, $\Delta E \approx 0.1$ eV, as in the Orgueil and Murchison meteorites. These species were identified as diradicaloid moieties. The existence of similar diradicaloid moieties in three different carbonaceous chondrites but not in terrestrial IOM strongly suggests that these moieties could be "fingerprints" of the extraterrestrial origin of meteoritic IOM and markers of its synthetic pathway before its inclusion into a parent body.

INTRODUCTION

Carbonaceous chondrites are known to contain a substantial amount of carbon, mostly occurring as macromolecular insoluble organic matter (IOM). Mainly owing to limitations of analytical tools, the precise chemical structure of this IOM is not yet fully known. However, the macromolecular network of the chondritic IOM is known to be based on aromatic moieties linked together by short aliphatic chains and functionalized bridges. These bulk features of the chemical structure of the chondritic IOM are derived from spectroscopic data along with chemical and thermal degradation information (for a review, see Sephton [2002]). Due to this aromatic nature, chondritic IOM has often been compared to terrestrial coals and other natural polyaromatic macromolecules. However, although meteoritic and terrestrial IOM do exhibit similarities, major differences between them have been reported. The primary dissimilarity concerns the stable isotope composition and, especially, the D/H ratio (Robert and Epstein 1982; Kerridge et al. 1987; Halbout et al. 1990). More recently, two additional major differences were revealed through electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) studies on Orgueil and Murchison when compared to coals. First, the effective local concentrations in free organic radicals in chondritic IOM were shown to be much higher than the average concentration, hence, the occurrence of radical-rich regions contrasts with observations for terrestrial samples that always exhibit a homogeneous distribution of the free organic radicals (Binet et al. 2002). Second, the evolution of the radical concentration with temperature shows a significant increase above 150 K in the two meteorites, while terrestrial samples are known to exhibit a Curie magnetism, i.e., radical concentration independent of temperature (Binet et al. 2004). This difference in behavior was assigned to the occurrence of diradicaloids in chondritic IOMs.

To confirm whether these EPR-derived differences can be considered as unequivocal extraterrestrial signatures, we examined another carbonaceous chondrite. Tagish Lake was chosen for this study because it is unusual from several points of view when compared to other carbonaceous chondrites. First of all, the cold environment of the fall site, the rapid collection, and the exceptional conditions of transportation and storage make the Tagish Lake meteorite especially suitable for organic studies. Moreover, this meteorite does not seem to fit in the present meteorite taxonomy. Indeed, the mineralogy, oxygen isotope, and bulk chemical composition of the Tagish Lake meteorite fall between, rather than within, those of the CM and CI meteorites (Brown et al. 2000; Friedrich et al. 2002; Mittlefehldt 2002; Zolensky et al. 2002). The extent of its aqueous alteration leads to a classification as an ungrouped C2 chondrite or as the first example of a CI2 meteorite (Brown et al. 2000; Zolensky et al. 2002; Grady et al. 2002). Based on the comparison of reflectance spectra, Tagish Lake is the first meteorite to be related to the low-albedo, D-type asteroids that populate the outer part of the main asteroid belt (Hiroi et al. 2001). Moreover, Tagish Lake was also shown to be unique in its organic chemistry. Indeed, the soluble fraction is dominated by a few water-soluble organic compounds and is characterized by a virtual lack of amino acids (Pizzarello et al. 2001; Kminek et al. 2002). According to its solid state ^{13}C NMR spectrum (Pizzarello et al. 2001), the macromolecular IOM of Tagish Lake was shown to be much more aromatic than that of Orgueil, Murchison, and Allende. This highly aromatic character was confirmed by pyrolysis-gas chromatography-mass spectrometry, which, in addition, pointed to a more condensed structure with larger aromatic moieties than in Murchison (Gilmour et al. 2001). These differences in chemical structure were supposed to reflect a different pathway for organic synthesis when compared to CI/CM meteorites. (Pizzarello and Huang 2002), and it is assumed that Tagish Lake may be one of the most primitive solar system materials (Brown et al. 2000).

The present study aims to determine the EPR features of the IOM isolated from the Tagish Lake meteorite and to compare them with those previously obtained from Orgueil and Murchison.

EXPERIMENTAL

The samples of the meteorites of Tagish Lake, Orgueil, and Murchison were provided by Mike Zolensky from the NASA Johnson Space Center (Houston, USA) with the permission J. Brook (the finder), the Museum National d'Histoire Naturelle (Paris, France), and the Smithsonian Institution (Washington D.C., USA), respectively. Two lithologies were reported for the Tagish Lake meteorites (Zolensky et al. 2002), and our sample most probably contained both of them. The Tagish Lake sample consisted of approximately half of the 10.0 g stone, which was completely surrounded by fusion crust and had been kept frozen since its collection. The IOM was isolated by the conventional HF/HCl treatment (Cronin et al. 1987). The sample of Tagish Lake IOM resulting from this treatment is labeled TL1. A fraction of this sample underwent a subsequent extraction with trichlorobenzene under reflux to remove the fullerenes. The resulting IOM is labeled TL2. The bulk elemental compositions of the residues of the HF/HCl treatments were determined by elemental analysis at Wolf Laboratories (Rueil-Malmaison, France) for Orgueil and Murchison and at Atlantic Microlab, Inc. (Norcross, Georgia, USA) for Tagish Lake. The resulting compositions are $C_{100}H_{72}O_{18}N_3S_2$ for Orgueil, $C_{100}H_{77}O_{22}N_3S_{6.5}$ for Murchison, and $C_{100}H_{46}O_{15}N_{10}$ for TL1. The sulfur content of the Tagish Lake residue TL1 was not determined. The samples still contain inorganic residues amounting to 8.9, 21.8, and 7.2%, respectively. The composition was not determined for TL2, but only a low yield (<1%) is obtained upon fullerene extraction, so this extraction should not affect significantly the elemental composition of the IOM. In addition to data about coals collected in the literature, three samples of type III terrestrial coals labeled A_1, A_2, and A_3, ranging from the less-mature to the most mature, were used for comparison of the EPR of terrestrial coals with that of meteoritic IOM. Miocene coals A_1 and A_2 originate from the Mahakam Delta (Indonesia), and the Namurian coal A_3 originates from the Solway basin (Great Britain). All the information concerning these samples has been reported previously (Binet et al. 2002). The EPR measurements were performed with a Bruker ESP300e continuous-wave spectrometer equipped with a TE_{102} microwave cavity operating at 9.4 GHz and with a helium flow ESR 9 cryostat from Oxford Instruments for temperature variations from 4 K to room temperature. A 100 kHz modulation of the magnetic field was used, with an amplitude smaller than 1/3 of the line width to avoid overmodulation. A receiver time constant smaller than 1/10 of the time through an EPR line was set. The measurement of the electron spin relaxation times T_1 and T_2 was performed by the conventional saturation method, as previously described (Binet et al. 2002). The spin concentrations were determined by comparison of the EPR intensity, calculated by double integration, of the samples with that of a standard diphenylpicrylhydrazyl (DPPH) sample with a known spin concentration. The measurements were performed at sufficiently low microwave power, typically $P \leq 0.2$ mW, to avoid saturation. For the variation of the spin concentration with temperature, the EPR intensity was calculated by simulation of the EPR signal with a Lorentzian function to minimize the dispersion of the data as described in Binet et al. (2004). When comparing the EPR intensities of the samples, and during the temperature variations, the quality factor of the cavity was checked to remain constant to avoid artifacts due to differences or changes in instrumental characteristics or dielectric losses in the samples. The g-factors of the samples were determined from the magnetic field at the center of the resonance lines. The latter was determined as the mean value of the positions of two spectra recorded under slowly increasing and decreasing field sweep, respectively (typically a sweep rate of <0.1 mT s^{-1}), so as to compensate for the small hysteresis of the magnet. The difference between these two positions gives the uncertainty of the g-value. In addition, the resonance fields were corrected from the field shift of the electromagnet by using the EPR line of the DPPH standard with the known g-factor ($g = 2.0037 \pm 0.0002$) inserted at the same height in the cavity as the samples.

RESULTS

General Features of the EPR Spectra

Figure 1a shows the EPR spectra of samples TL1 and TL2 at room temperature. These spectra are very similar to those of the IOM of the Orgueil and Murchison meteorites (Binet et al. 2002). The spectra exhibit a sharp line, labeled A, corresponding to the radicals in the IOM and a broad feature, labeled B, arising from the mixed magnetic mineral residues that survived the HF/HCl treatment performed to isolate the IOM. Figure 1b shows an expanded view of the signal of the organic radicals. For the two samples, the peak-to-peak line widths are very close, with $\Delta B_{pp} = 0.56 \pm 0.02$ mT for TL1 and $\Delta B_{pp} = 0.54 \pm 0.02$ mT for TL2. However, the g-factors are slightly different, with $g = 2.0032 \pm 1.5 \times 10^{-4}$ for TL1 and $g = 2.0030 \pm 2.5 \times 10^{-4}$ for TL2. The line shape of the spectra of the radicals is purely Lorentzian at all temperatures for both samples, as shown by the good agreement between the experimental spectra and the spectra calculated with a Lorentz function (Fig. 1b):

$$L(B_0) = -\frac{16}{3\pi\sqrt{3}\Delta B_{pp}^3}\frac{(B_0 - h\nu/g\beta)}{\left(1 + \frac{4}{3}[B_0 - h\nu/g\beta]^2/\Delta B_{pp}^2\right)^2} \quad (1)$$

where ν is the microwave frequency, ΔB_{pp} is the peak-to-peak linewidth, β is the electron Bohr magneton, and h is the Planck constant. This means that, as in the case of the Orgueil and Murchison meteorites (Binet et al. 2002), the line-broadening by unresolved hyperfine interactions with protons is averaged out by exchange interactions between radicals. Otherwise, a deviation from a pure Lorentzian line shape with a significant Gaussian contribution would be observed. The major difference between the spectra of TL1 and TL2 concerns signal B and might reveal a change in the size or shape as well as a recrystallization of the mineral particles due to the treatment with a reflux of trichlorobenzene.

Occurrence of Diradicaloids

In a previous paper (Binet et al. 2004), we showed the occurrence of moieties with thermally accessible triplet states in the IOM of Orgueil and Murchison, along with normal monoradicals with spin S = 1/2. These moieties were attributed to diradicaloids. As far as we are aware, diradicaloids were never reported for terrestrial IOM. The presence of such species induces a specific temperature dependence of the number of spins in the IOM. At low temperatures, when only the monoradicals contribute to the EPR intensity, the number of spins is independent of temperature. When the temperature is raised above a given temperature, a significant number of diradicaloids are thermally excited into their paramagnetic triplet (S = 1) state, and consequently, the number of spins rapidly increases.

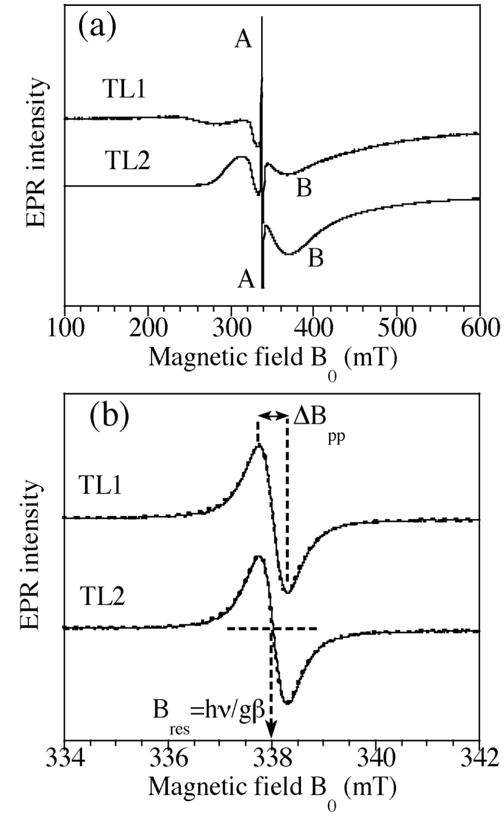

Fig. 1. a) Room temperature EPR spectra of the insoluble organic matter (IOM) of the Tagish Lake meteorite. Signal A corresponds to organic radicals and signal B to magnetic mineral residues; b) room temperature EPR spectra of the organic radicals in the IOM (solid line) and simulation with a Lorentzian line shape (dotted line).

Figure 2 shows the temperature dependence of the normalized number of spins in the two samples of IOM of Tagish Lake meteorites. For comparison, the corresponding data for Orgueil and Murchison meteorites and for coal A_3 are also plotted. The number of spins, N(T), in the two samples of Tagish Lake IOM exhibit the same temperature dependence as in the other two meteorites, with a plateau at low temperature and an increase above ~130 K. The decrease of N(T) below 50 K is observed both in the coals and in the meteorites, with the exception of TL1 (in the case of TL2, this decrease is likely to be due to problems in the temperature monitoring), and is related to a long-range antiferromagnetic ordering and not to the diradicaloids. We showed (Binet et al. 2004) that, in the presence of diradicaloids, the number of spins is given by:

$$N(T) = N_{mono} + \frac{8}{3}N_{di}\frac{1}{1 + \exp(-\Delta\sigma/k)\exp(\Delta E/kT)} \quad (2)$$

where N_{mono} and N_{di} are the number of monoradicals and diradicaloids, respectively, and ΔE and $\Delta\sigma$ are the energy and entropy differences between the singlet (S = 0) ground state and the triplet state of the diradicaloids, respectively. The parameters ΔE and $\Delta\sigma$ and the proportion of the diradicaloids for the two samples of Tagish Lake and for the Orgueil and

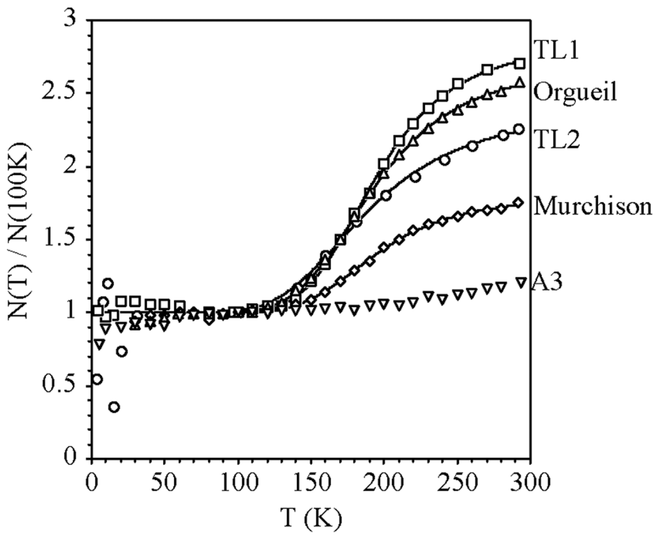

Fig. 2. Spin concentration, N(T), normalized to the value N(100 K) at 100 K versus temperature for the radicals in the meteorites of Tagish Lake, Orgueil, Murchison, and coal A_3.

Table 1. Energy gaps (ΔE) and entropy differences (Δσ) between ground singlet and excited triplet states for the diradicaloids in Tagish Lake, Orgueil, and Murchison, and the proportion of diradicaloids among the radicals.

	ΔE (eV)	Δσ (cm^{-1} K^{-1})	N_{di} /(N_{mono} + N_{di})
TL1	0.117 ± 0.003	4.8 ± 0.1	42 ± 1%
TL2	0.086 ± 0.004	3.6 ± 0.2	35 ± 1%
Orgueil	0.101 ± 0.003	4.2 ± 0.1	40 ± 1%
Murchison	0.104 ± 0.004	4.3 ± 0.1	24 ± 1%

Table 2. Concentration and heterogeneity of the distribution of the radicals in Tagish Lake, Orgueil, and Murchison.

	Average spin concentration (10^{19} spin g^{-1})	Local spin concentration (10^{19} spin g^{-1})	Heterogeneity[a]
TL1	2.0 ± 0.8	4.0 ± 0.7	2
TL2	1.6 ± 0.2	3.8 ± 0.7	2
Orgueil	0.70 ± 0.08	4.0 ± 0.7	6
Murchison	0.18 ± 0.03	4.3 ± 0.7	24

[a]Defined as the ratio of the local concentration to the mass averaged concentration.

Murchison meteorites are given in Table 1 for comparison. The diradicaloids in Tagish Lake have similar values of ΔE and Δσ, about 0.1 eV and 4.5 cm^{-1} K^{-1}, respectively, as in Orgueil and Murchison. Since these parameters are related to the molecular structure of the diradicaloids, the same types of diradicaloids are present in the three meteorites. Only the proportion of diradicaloids differs among the meteorites, with Tagish Lake TL1, along with Orgueil, being the most enriched in diradicaloids, with 42% of the radicals occurring as diradicaloids. The comparison of TL1 and TL2 reveals significant changes in the g-factor of the radicals, in the singlet-triplet gap, entropy parameter, and abundance of the diradicaloids upon extraction of the IOM by trichlorobenzene. Indeed, a slight decrease in the relative amount of diradicaloids is observed after extraction, along with a decrease in g, ΔE, and Δσ, pointing to an alteration of the remaining diradicaloids. The origin of these changes is not clear, but they show that at least a part of the IOM is sensitive to such a treatment. Notwithstanding, the noticeable amount of diradicaloids remaining after this treatment, which aimed at removing the fullerenes, fully excludes the fullerenes as a possible source of diradicaloids.

Radical Distribution

It has been shown that, in the IOM of the Orgueil and Murchison meteorites, the radicals were heterogeneously distributed (Binet et al. 2002). The heterogeneity was evidenced by correlating the electron spin relaxation times with the mass averaged spin concentration deduced from the EPR intensity. Indeed, the electron spin relaxation times are partly determined by interactions between neighbor spins and are, consequently, rather sensitive to the local concentration. However, when the spins are homogeneously distributed, as is the case for coals (Thomann et al. 1988), local and mass averaged concentrations are identical. Figure 3 shows the product ($T_1 \cdot T_2$) of the spin-lattice (T_1) and spin-spin (T_2) relaxation times for the radicals in two series of coals (black circles and triangles) and in the IOM of the Tagish Lake, Orgueil, and Murchison meteorites. The data for the coals A_1, A_2, and A_3 and for the Orgueil and Murchison meteorites are taken from Binet et al. (2002). The data plotted as triangles are taken from Thomann et al. (1988) and correspond to vitrinite coal macerals. For the latter coals, the relaxation times were deduced from pulsed EPR experiments. The open (black) triangles correspond to $T_1 \cdot T_2$ values in which T_2 was approximated by the phase memory time for the microwave pulse angles $\theta = \pi$ and $\theta \to 0$, respectively, and T_1 was approximated by the values of T_1 from Thomann et al. (1988). The solid lines in Fig. 3 represent exponential extrapolations to high spin concentrations of these two sets of data. A strong decrease of $T_1 \cdot T_2$ is observed for the coals when the spin concentration increases. This behavior can be accounted for within the framework of the Redfield theory for electron-spin relaxation, as described by Slichter (1978). Within this theory, spin relaxation is supposed to be produced by a randomly fluctuating local field, B. Fluctuations can be induced by exchange interactions between radicals and/or motion. The local field may contain contributions from electron dipolar interactions, B_{dip}, and/or from hyperfine interactions with nuclei, B_{hf}, related to each other by $B^2 = B^2_{dip} + B^2_{hf}$. This local fluctuating field acts both on T_1 and T_2, with $T_1 \cdot T_2 \propto B^{-4}$, so that the stronger the local field, the shorter $T_1 \cdot T_2$. In the studied coals, the H/C ratio decreases from 0.91 to 0.61 for the samples from Thommann et al. (1988) and from 0.82 to 0.49

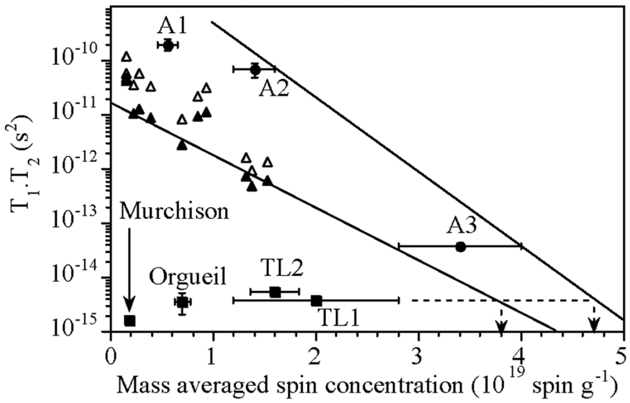

Fig. 3. Product of the electron spin-lattice and spin-spin relaxation time versus mass averaged spin concentration for the radicals in the meteorites of Tagish Lake, Orgueil, and Murchison (squares), coals A_1, A_2, and A_3 (black circles), and vitrinite coal macerals (triangles). For the latter samples, the data are taken from Thomann et al. (1988).

for A_1, A_2, and A_3 when $T_1 \cdot T_2$ decreases from 2×10^{-10} s^2 to 3.8×10^{-14} s^2. This indicates that B_{hf} is not the leading term in the local field, otherwise the opposite correlation would have been observed. The electron dipolar contribution, directly related to the local spin concentration, thus, dominates in the local field so that a higher local concentration will result in a stronger local field and shorter T_1 and T_2.

As seen from Fig. 3, the mass averaged spin concentrations in the meteoritic IOM are spread over a wide range from 1.8×10^{18} spin g^{-1} for Murchison to 2×10^{19} spin g^{-1} for TL1. In contrast, the values of $T_1 \cdot T_2$ are very close and outside the terrestrial domain. Since the meteoritic IOM has H/C ratios in the same range as the coals, differences in relaxation times between meteoritic IOM and the coals is mainly due to differences in radical concentrations. The consequence is that, in the meteoritic IOM, the local spin concentration that actually determines $T_1 \cdot T_2$ is different from the average, and the radical distribution is heterogeneous in Tagish Lake in a similar fashion to that in Murchison and Orgueil (Binet et al. 2002). Translating the points corresponding to the meteoritic IOM to the coal domains, the same local concentration is obtained for the four meteoritic samples despite their differences in mass averaged concentrations (Table 2). This local concentration is ~$(4.0 \pm 0.7) \times 10^{19}$. The heterogeneity, quantified by the ratio of the local to the average concentration (Table 2), is significantly lower for Tagish Lake (~2) when compared with Orgueil (~6) and Murchison (~24). It must be added that, even if the presence of diradicaloids, which concentrate two unpaired electrons in a same moiety, is one cause of the heterogeneity, the majority of the radicals, at least 60%, are monoradicals. Thus, the latter dominantly contribute to the local fields responsible for the spin relaxation. This explains why no significant differences in relaxation times exist despite great differences in diradicaloid proportions in the meteoritic IOM. Consequently, the local concentration values reflect, to a large extent, those of the radicals as a whole.

DISCUSSION AND CONCLUSION

The radicals in the IOM of the Tagish Lake meteorite exhibit similar features to those observed in the Orgueil and Murchison meteorites. They are heterogeneously distributed with the same local concentration, ~4×10^{19} spin g^{-1}, and they include a significant amount, 42%, of diradicaloids. From the point of view of the radicals, the differences between the three IOMs arise only from the extent of the heterogeneity of distribution (the largest for Murchison and the weakest for Tagish Lake) and from the relative abundance of the diradicaloids (higher in Tagish Lake and Orgueil and lower in Murchison). In a previous paper (Binet et al. 2004), we suggested that the presence of diradicaloids in the IOM of the Orgueil and Murchison meteorites could be an additional extraterrestrial fingerprint of the meteoritic IOM since these species were never reported in terrestrial IOM. The observation of such diradicaloids in the Tagish Lake meteorite strongly supports this idea.

Moreover, the occurrence of large amounts of diradicaloids in the fresh and well-preserved Tagish Lake meteorite excludes any alteration process of the meteoritic IOM on Earth as a possible source of the diradicaloids and, thus, shows that the diradicaloids occurred within the IOM before the meteorite fell to Earth. It is important to notice that the same type of diradicaloids is identified in the three meteorites (aside from the treated sample TL2) despite significant differences between the three IOMs. Indeed, as seen above, the IOMs have different abundances in heteroelements. Moreover, the IOM in Tagish Lake was shown to exhibit a more pronounced aromatic character than that of the previous meteorites (Pizzarello et al. 2001; Gilmour et al. 2001; Cody et al. 2003). The diradicaloids must then be related to some features common to the three IOMs. From what we know, these features are the high substitution (Gardinier et al. 2000; Cody et al. 2003) and the small size of the aromatic moieties, established to 10–15 rings as a whole for Orgueil and Murchison (Derenne et al. 2003) and suspected for Tagish Lake (Cody et al. 2003). This strongly supports our model for the diradicaloids based on small highly substituted aromatic moieties with two carbon atoms in α-position, each bearing an unpaired electron, the wave function of which largely extends over the aromatic moiety (Binet et al. 2004). The close values of the singlet-triplet gap, ΔE, in the three meteorites, despite different abundances in heteroelements, clearly indicate that the latter have no influence on ΔE and that this gap is mostly determined by the size of the aromatic moieties, as supposed in our model. As a consequence, the aromatic moieties in the IOM of Tagish Lake probably have the same size as in Orgueil and Murchison.

The presence of similar diradicaloids, based on aromatic moieties, in meteorites having different degrees of alteration on the parent body and distinguishing themselves both by the mineralogy and the organic carbon systematics indicates that the IOMs in the carbonaceous chondrites shared common steps in their organosynthesis. Since these common steps must have taken place before the accretion of the parent bodies, this strongly reinforces the idea that chondritic IOM is a very primitive material, at least partially synthesized in the interstellar medium or in the proto-solar nebula, as already proposed (Septhon et al. 2000; Flynn et al. 2003). The diradicaloids must then be considered as additional markers of the synthetic process and, as such, should be taken into account in the models or the experiments reproducing the IOM synthesis. The ability of the diradicaloids to survive in a planetary environment under a moderate hydrothermal stress may also have applications in the analysis of the organic matter, if present, within samples from Mars. More precisely, the presence or absence of diradicaloids could help to determine whether the martian organic matter has a well-preserved extraplanetary origin or, on the contrary, whether it was strongly processed under martian conditions.

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