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Heterogeneous distribution of paramagnetic radicals in insoluble organic matter from the Orgueil and Murchison meteorites

LAURENT BINET,^{1,*} DIDIER GOURIER,¹ SYLVIE DERENNE,² and FRANÇOIS ROBERT³¹Ecole Nationale Supérieure de Chimie de Paris, Laboratoire de Chimie Appliquée de l'Etat Solide, UMR CNRS 7574, 11 rue Pierre et Marie Curie, F-75231 Paris cedex 05, France²Ecole Nationale Supérieure de Chimie de Paris, Laboratoire de Chimie Bioorganique et Organique Physique, UMR CNRS 7573, 11 rue Pierre et Marie Curie, F-75231 Paris cedex 05, France³Museum National d'Histoire Naturelle, Laboratoire de Minéralogie, CNRS FRE 32, 61 rue Buffon, F-75005 Paris, France

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Abstract—An electron paramagnetic resonance (EPR) investigation was performed on the insoluble organic matter from the Orgueil and Murchison meteorites and on terrestrial coals with similar elemental composition. A complementary electron nuclear double resonance (ENDOR) study was also carried out. The measured *g*-factors of the observed paramagnetic radicals in the meteoritic organic matter exhibit a similar correlation with the chemical composition as for the type III (i.e., hydrogen-poor) terrestrial coals. The main result, obtained from EPR saturation and ¹H ENDOR enhancement measurements, showed that the effective local concentration in radicals of about 3 to 4×10^{19} spin.g⁻¹ in the meteoritic organic matter is much higher than the average concentration, hence the occurrence of radical-rich regions accounting for 5% and 20% of the total volume for Murchison and Orgueil, respectively. This heterogeneity of concentration seems to be unique among natural organic macromolecules. It is proposed that these radical-rich regions correspond to pristine parts of the organic matter synthesized in conditions close to those prevailing in the interstellar medium, and which have survived the hydrothermal process on the parent body. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

The primitive carbonaceous chondrites are known to contain substantial amounts of carbon, up to 90% of which consists in an organic macromolecular fraction, insoluble in usual organic solvents (Hayes, 1967; Cronin et al., 1988). This material is often described as “kerogen-like” and compared to the organic matter (OM) of mature terrestrial kerogens (e.g., Hayatsu et al., 1977). The products released upon hydrous pyrolysis from Orgueil and Cold Bokkeveld meteorites were thus shown to be similar to those identified in the volatile fractions of pyrolysates of mature type III kerogens (Sephton et al., 1999). However, the chondritic organic matter is based on small aromatic units, cross-linked by short aliphatic chains rather than large clusters of polyaromatic structures (Gardinier et al., 2000). This reveals that almost no thermal degradation/maturation of the organic precursors occurred at (or near) the surface of the asteroidal parent body.

The origin of this macromolecular material is not yet well understood, and no model is so far able to explain its observed structural diversity along with its H and N bulk isotopic compositions (Alexander et al., 1998; Halbout et al., 1990). The remaining nonmacromolecular carbon, which accounts for up to 15% of total carbon in CI meteorites, consists of soluble organic compounds such as amino acids, aliphatic and aromatic hydrocarbons (Cronin et al., 1988, and references therein). These soluble products may have been produced by hydrolysis taking place during hydrothermal events on parent bodies. In this case, the macromolecular carbon should be regarded as a

left over product of this planetary episode, with no marked thermal degradation with respect to its original structure.

A new way to constrain this model, based on electron paramagnetic resonance (EPR) and electron–nuclear double resonance (ENDOR) spectroscopies, is presented in this paper. EPR, which is a nondestructive technique, has been used to study free radicals in several coals and terrestrial kerogens (see reviews by Whelan and Thompson-Rizer, 1993, and Dickneider et al., 1997), but pioneer work was only done in the 1960s on the organic matter of meteorites (Duchesne et al., 1964; Vinogradov et al., 1964; Schulz and Eloffson, 1965). More recently, paramagnetic defects were also observed in presolar diamonds isolated from the Murchison and Allende meteorites (Braatz et al., 2000). Free organic radicals originate from homolytic cleavages of bonds and are stabilized by the aromatic moieties occurring in these materials. Most of the previous EPR studies were concerned with correlations between EPR parameters and maturation. The most often used parameters are the *g*-factor, spin concentration (number of unpaired electron spins per unit mass), and the power saturation behaviour of the signal. The *g*-factor measures the magnitude of the magnetic moment related to the electron spin and determines the magnetic field at which the EPR spectrum is observed. It is indicative of the chemical structure of the free radicals and their oxygen content. It tends to decrease when maturation increases (Petraakis and Grandy, 1978). The intensity of the EPR signal is proportional to the number of free radicals in the sample and, thus, allows one to determine the spin concentration. The latter is known to increase with increasing sample maturity (Retcofsky et al., 1968; Kwan and Yen, 1979; Bakr et al., 1988), and correlations between spin concentration and burial depth have been recently shown to reliably yield geothermal gradients (Qiu and Wang, 1998). The power saturation measures the response

* Author to whom correspondence should be addressed (binetl@ext.jussieu.fr).

Table 1. Elemental ratios determined by elemental analysis of the insoluble organic matter of Orgueil and Murchison meteorites and of the crude and treated terrestrial coals A1, A2, and A3.

	Orgueil	Murchison	A1		A2		A3
			crude	treated	crude	treated	(treated)
H/C	0.72	0.70	0.93	0.82	0.78	0.75	0.49
O/C	0.18	0.22	0.15	0.20	0.07	0.09	0.04

of the free radicals to changes in the intensity of an applied microwave field, and different saturation behaviours have been reported for coals and kerogens of various maturity (Silbernagel et al., 1984; Dickneider et al., 1995, 1997). ENDOR spectroscopy selectively detects paramagnetic nuclei magnetically coupled to the free radical spins through a change in the EPR intensity of the radicals when the nuclear magnetic resonance (NMR) transitions of these nuclei are saturated. ENDOR has already been used to probe the proton environment of the radicals in terrestrial coals (Uebersfeld, 1984; Wind et al., 1984; Thomann et al., 1984; Schlick and Kevan, 1984), but, to the best of our knowledge, not in the case of the meteoritic OM.

Here we report an EPR and ENDOR study of the macromolecular organic matter of the Orgueil and Murchison meteorites. Although there is a priori no relationship between meteoritic OM and coals, these two materials exhibit similar bulk composition and have often been compared. The EPR and ENDOR parameters obtained for the chondritic organic matter will be compared with those of three selected coals of different ranks. As will be shown in this paper, the EPR signals in the chondritic OM and in the coals share several common features, which make this comparison meaningful. However, they also exhibit subtle differences, revealing the specificity of each type of OM. As the chondritic macromolecular organic matter has been isolated from the crude samples via the classical HF/HCl treatment (Durand and Nicaise, 1980), it was a prerequisite to assess the effect of this acid treatment on the EPR and ENDOR parameters before discussing the comparison (similarity and differences) between terrestrial and extraterrestrial macromolecular organic matters.

2. EXPERIMENTAL TECHNIQUES

The insoluble OM of the Orgueil and Murchison meteorites (from Museum National d'Histoire Naturelle, Paris, France and from Smithsonian, Washington, DC, USA, respectively) was isolated from the bulk rock by the standard HF/HCl treatment (Durand and Nicaise, 1980) as previously reported (Gardinier et al., 2000). In short, the ground meteorite is successively extracted with water, $\text{CH}_2\text{Cl}_2/\text{MeOH}$, saponified with KOH, and submitted to hydrolyses with HCl and HF/HCl. The isolated residues still contains insoluble minerals amounting to 8.9 and 21.8 wt.% for Orgueil and Murchison, respectively. They account for 3.3% and 2.3% of the initial mass (ca. 10 g) for Orgueil and Murchison, respectively. These minerals mainly correspond to oxides such as chromite, magnetite, and spinel for Orgueil, along with pentlandite $(\text{Fe,Ni})_9\text{S}_8$ for Murchison. The elemental composition of the OM was determined at Wolf Laboratories (Rueil-Malmaison, France) by a combustion technique under O_2 flow at 1020°C. Carbon and hydrogen contents are determined by thermal conductivity and oxygen by coulometry. Analyses were performed in triplicate and showed variations <1% for C and ca. 5% for H and O which may reflect some heterogeneity of the sample. The results given in Table 1 show that these bulk compositions are similar to those of terrestrial type III

kerogens in the van Krevelen diagram. Three samples of type III terrestrial coals labelled A1, A2, A3, and ranging from the less mature to the most mature, were thus used for comparison with the chondritic OM and to assess the effect of the HF/HCl treatment on native radicals. Coals A1 and A2 are of Miocene age, from the Mahakam Delta (Indonesia) and coal A3, of Namurian age, from the Solway Basin (Great Britain). The T_{max} values from Rock-Eval pyrolysis, indicative of the ranks of the coals, are 420°C for A1, 451°C for A2, and 514°C for A3. Elemental ratios of these coals are given in Table 1. The compositions before treatment were determined for coals A1 and A2, but unfortunately not for A3. One can notice a slight oxidation of the less mature coal A1 during the treatment indicated by a slight decrease of the H/C ratio and an increase of the O/C ratio. The elemental composition of the more mature coal, A2, is not altered by the treatment. It must be noted that this sample is the one that is closest in elemental composition to the organic matter from the Orgueil and Murchison meteorites.

The EPR measurements were carried out at room temperature with a Bruker ESP300e spectrometer operating at 9.4 GHz (X-band) and equipped with a rectangular TE_{102} microwave cavity. The cavity constant relating the incident microwave power P to the microwave magnetic field B_1 was calculated from the saturation behavior of a standard diphenylpicrylhydrazyl (DPPH) sample and was found to be $K = P/B_1^2 \approx 500 \text{ mW.G}^{-2}$. As usual, the EPR signals were lock-in detected with a modulation of the applied magnetic field at a frequency $\nu_m = 100 \text{ kHz}$. 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 (sweep rate $< 0.1 \text{ mT.s}^{-1}$) so as to compensate for the small hysteresis of the magnet. The difference between these two positions gives the uncertainty on 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 known g-factor ($g = 2.0037 \pm 0.0002$) inserted at the same height in the cavity as the samples. The spin concentrations of the samples were measured by comparing the EPR intensities obtained by double integration of the lines, with that of the DPPH standard containing exactly 10^{17} spins. The microwave power $P = 0.2 \text{ mW}$ in these experiments was chosen low enough to avoid saturation of the EPR lines. Actually only the order of magnitude of the overall spin concentrations is obtained, but the relative concentrations in the samples can be reliably compared. The ENDOR measurements were made at room temperature and at 110 K with the same spectrometer as above equipped with a TM_{110} cylindrical cavity. The radiofrequency (rf) field produced by a Wavetek 3000-446 synthesizer was amplified by a 100W ENI 3100L broad-band amplifier. A 12.5-kHz frequency modulation of the radiofrequency carrier (modulation depth 100 kHz) was used for the detection.

3. GENERAL FEATURES OF THE EPR AND ENDOR SIGNALS

The EPR spectra of the insoluble OM of Orgueil and Murchison meteorites are shown in Figure 1. For each sample, the spectrum exhibits two signals: a sharp one, labelled A, due to radicals in the OM, and a very broad feature, labelled B, corresponding to a ferromagnetic resonance signal from the residual mineral matter in the samples, most probably magnetite Fe_3O_4 . As shown in the insets in Figure 1, the A signal for both Orgueil and Murchison meteorites can be simulated by a purely Lorentzian function of the applied magnetic field B_0 , classically given by (Poole, 1983):

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

with ν the microwave frequency, and with the g-factors and the

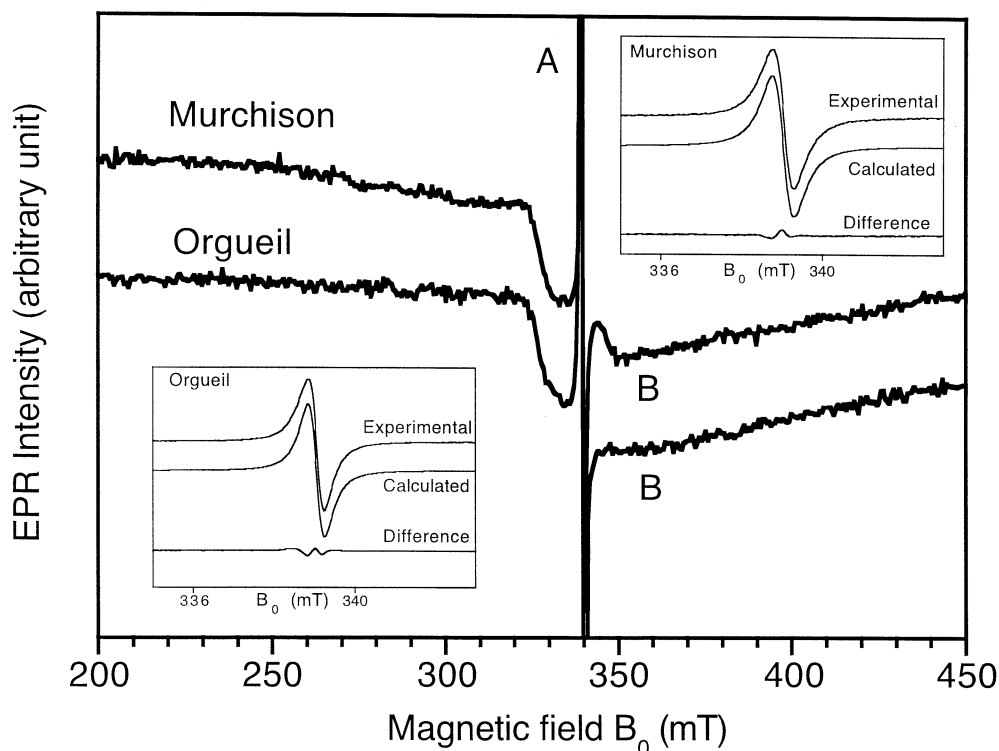


Fig. 1. EPR spectra at room temperature of the organic matter of the Orgueil and Murchison meteorites. Microwave power $P = 30$ mW; microwave frequency $\nu = 9.514$ GHz; modulation amplitude $B_m = 0.5$ mT; time constant $\tau = 1.28$ ms; scan rate $SR = 14$ mT.s $^{-1}$. The insets show an expanded view of the signal of the radicals (A signal) along with the simulations calculated with Eqn. 1 and the corresponding parameters in Table 2. Experimental parameters of the insets: $P = 0.2$ mW, $\nu = 9.5131$ GHz, $B_m = 0.1$ mT, $\tau = 82$ ms, $SR = 0.36$ mT.s $^{-1}$.

peak-to-peak linewidths ΔB_L given in Table 2. Despite the existence of the broad feature B, no baseline correction was necessary for the spectra in the insets in Figure 1. The B signal actually makes no significant contribution to the baseline owing to the very small magnetic field range over which these spectra were recorded.

Each terrestrial coal, either crude or treated, exhibits a single EPR line as shown in Figure 2. The experimental parameters of the EPR lines are gathered in Table 2 for each sample. For the two coals, A1 and A2, the lineshape significantly deviates from a pure Lorentzian shape and is better simulated by a pseudo-Voigt function:

$$F_V(B_0) = \alpha L(B_0) - (1 - \alpha) \frac{8(B_0 - h\nu/g\beta)}{\sqrt{2\pi}\Delta B_G^3} \exp[-2(B_0 - h\nu/g\beta)^2/\Delta B_G^2] \quad (2)$$

with α the weight of the Lorentzian contribution ($0 \leq \alpha \leq 1$) and ΔB_G the peak-to-peak linewidth of the Gaussian contribution. The purely Lorentzian shape given by Eqn. 1 is the particular case of Eqn. 2 with $\alpha = 1$. For each treated coal, Figure 2 shows the comparison between the pure Lorentzian lineshape (dashed line) and the pseudoVoigt lineshape (dotted line). The simulation parameters for each sample are given in Table 2. For the most mature sample A3, the deviation from a pure Lorentzian shape is hardly perceptible, as shown by the superimposition of the Lorentzian and pseudoVoigt lines in

Figure 2. The Lorentzian or quasi-Lorentzian shape indicates that the EPR lines of both the OM of the meteorites and A3 coal are narrowed by exchange interactions between radicals in the samples. These interactions, resulting from electron repulsion, induce long-range spin diffusion between radicals. As a consequence, the local magnetic fields experienced by the electron spins are averaged to zero and thus no longer cause any line broadening. The exchange interactions also justify that no special care was paid to the wings of the signals when assessing their adequacy with a Lorentzian lineshape, because in case of exchange narrowing the lineshape can not be Lorentzian in the wings (Abragam, 1986). The pseudoVoigt shape for the EPR lines of A1 and A2 indicates that these lines actually result from the overlap of many unresolved EPR transitions (inhomogeneous broadening), showing that exchange narrowing is not so efficient in the two less mature coals.

Figure 3a shows the ENDOR response at room temperature of the three treated coals and of the OM from Orgueil and Murchison. An ENDOR signal is observed only for the two less mature samples, A1 and A2, both for crude and treated coals. Similarly, a weak ENDOR signal is observed for the OM of Orgueil but none for the OM of Murchison. No improvement of the ENDOR response is observed when the spectra are recorded at 110 K. Figure 3b shows a more detailed view of the observed ENDOR signal in the case of A2. The signal is made of a sharp line at the proton frequency $\nu_n = g_n \beta_n B_0$ ($g_n = 5.586$ is the nuclear g-factor and β_n is the nuclear Bohr magneton),

Table 2. EPR and ENDOR parameters of the organic matter of Orgueil and Murchison meteorites and of the terrestrial coals A1, A2, and A3.

	Orgueil		Murchison		A1		A2		A3	
	crude	treated	crude	treated	crude	treated	crude	treated	crude	treated
g-factor	2.00312 ± 0.00005	2.00310 ± 0.00004	2.00333 ± 0.00005	2.003395 ± 0.00005	2.00317 ± 0.00005	2.00323 ± 0.00005	2.00289 ± 0.00005	2.00323 ± 0.00005	2.00289 ± 0.00005	2.00289 ± 0.00007
ΔB_{pp} (mT) ^a	0.38 ± 0.02	0.53 ± 0.02	0.62 ± 0.03	0.55 ± 0.04	0.67 ± 0.03	0.63 ± 0.04	0.42 ± 0.03	0.63 ± 0.04	0.42 ± 0.03	0.44 ± 0.02
Concentration (10 ¹⁸ g ⁻¹)	7.0 ± 0.8	1.8 ± 0.3	6.1 ± 0.9	5.6 ± 0.9	20 ± 3	14 ± 2	34 ± 6	14 ± 2	34 ± 6	34 ± 6
a^b	1	1	0.68	0.63	0.64	0.60	0.84	0.60	0.84	0.84
ΔB_L (mT) ^c	0.41	0.54	0.54	0.47	0.59	0.53	0.39	0.53	0.39	0.40
ΔB_G (mT) ^d	—	—	0.70	0.60	0.75	0.69	0.70	0.69	0.70	0.72
¹ H ENDOR enhancement	0.11	0	0.43	1	0.35	0.52	0	0.52	0	0

^aExperimental peak-to-peak EPR linewidth.

^bWeight of the Lorentzian contribution to the lineshape calculated with Eqn. 2.

^cLinewidth of the Lorentzian contribution in Eqn. 2.

^dLinewidth of the Gaussian contribution in Eqn. 2.

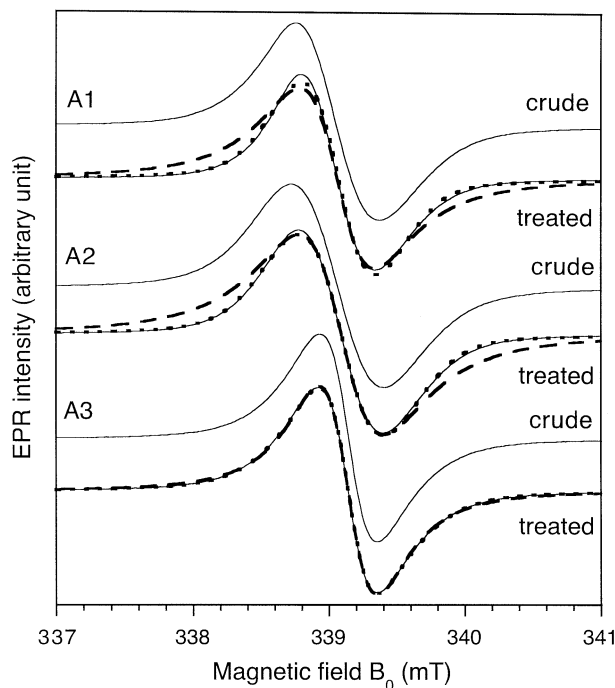


Fig. 2. EPR spectra of the crude and treated terrestrial coals A1, A2, and A3 at room temperature. Microwave power $P = 0.2$ mW; microwave frequency $\nu = 9.514$ GHz; modulation amplitude $B_m = 0.1$ mT; time constant $\tau = 82$ ms; scan rate $SR = 0.36$ mT.s⁻¹. The dashed lines represent the spectra calculated with Eqn. 1, corresponding to a pure Lorentzian lineshape with the linewidths ΔB_L set to the experimental values ΔB_{pp} in Table 2. The dotted lines represent the spectra calculated with Eqn. 2, corresponding to a pseudoVoigt lineshape, and with the parameters given in Table 2.

superimposed with a broader signal centered at the same frequency. A similar signal is observed for A1, the broad line being much weaker. These ENDOR spectra are similar to those previously observed in coals (Uebbersfeld, 1984) where the sharp line is generally attributed to distant protons, interacting with the electron spins through long-range dipole-dipole interaction and the broad line to closer protons interacting through both Fermi contact and dipole-dipole interactions. The ENDOR signal of the OM of Orgueil meteorite exhibits the same, though much weaker, sharp line as in the studied coals. However, due to low signal-to-noise ratio and to baseline distortion, the presence of an ENDOR signal shows that the partial inhomogeneous broadening of the EPR lines of A1 and A2 can be explained by unresolved hyperfine interactions with protons. The Lorentzian EPR lineshape and the absence of ENDOR signal for A3 and for the OM of Murchison meteorite must be related to their high spin concentration (see Table 2). This results in strong exchange interaction between radicals, which is known to narrow the EPR lines (Wertz and Bolton, 1972) and to cause a vanishing of the ENDOR response (Kevan and Kispert, 1976).

4. EFFECT OF THE HF/HCl TREATMENT

Before performing a detailed study of the EPR signals of OM of Orgueil and Murchison meteorites, it is necessary to deter-

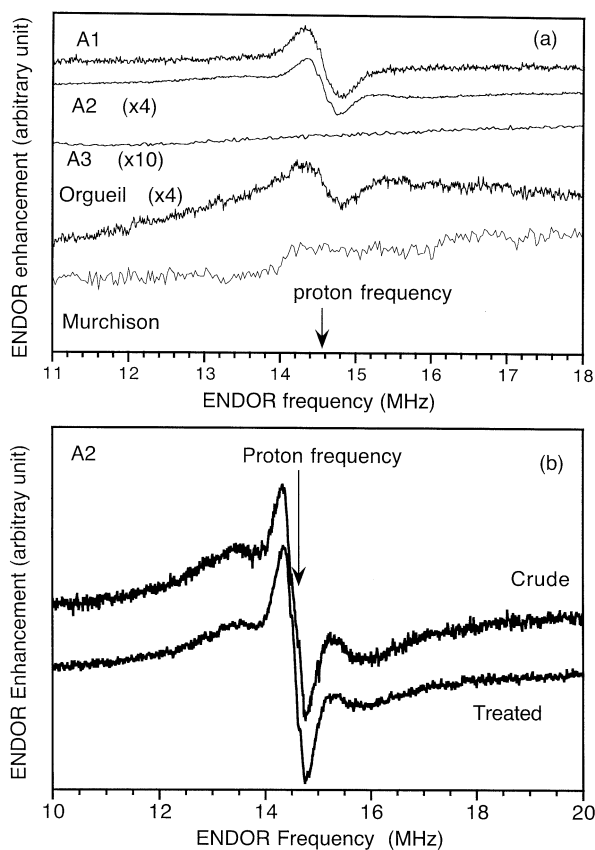


Fig. 3. (a) ENDOR spectra at room temperature of the treated coals A1, A2, and A3 and of the organic matter of Orgueil and Murchison meteorites. (b) ENDOR spectra at room temperature of the crude and treated coal A2. All the spectra are recorded with radiofrequency power $P_{rf} = 100$ W, modulation frequency $\nu_m = 12.5$ kHz, and modulation depth $\nu_d = 100$ kHz. For each sample, the magnetic field was set at the center of the EPR line. Microwave powers: 5 mW (A1), 25 mW (A2, crude), 20 mW (A2, treated), 100 mW (A3), 10 mW (Murchison). Time constants: 1.28 ms (A1, A2 crude, A3, Murchison), 41 ms (A2 treated), 20 ms (Orgueil). Scan rates: $0.13 \text{ MHz}\cdot\text{s}^{-1}$ (A1, A2 treated, Orgueil), $0.52 \text{ MHz}\cdot\text{s}^{-1}$ (A2, crude), $0.72 \text{ MHz}\cdot\text{s}^{-1}$ (A3), $0.69 \text{ MHz}\cdot\text{s}^{-1}$ (Murchison). Scan numbers: 100 (A2 crude), 20 (A2 treated), 5 (A3), 50 (Orgueil), 7 (Murchison).

mine as precisely as possible the effect of the HF/HCl treatment on the OM. For that purpose, the EPR and ENDOR signals of each coal A1, A2, and A3 were compared before and after HF/HCl treatment. Three features can be analyzed from a single EPR line: the lineshape, the g-factor, and the EPR intensity. As shown above, the lineshape in the crude and treated coals results from a balance between unresolved hyperfine interactions and exchange narrowing. Figure 2 compares the EPR signals of the crude coals with that of the same coals treated with HF/HCl. For each coal, the lines of the crude and treated samples are almost superimposable. Actually only a small narrowing of the line is observed after treatment for A1 and A2 (Table 2). It thus appears that the treatment does not alter the lineshape, indicating that there is no drastic change, neither in the strength of the exchange interactions, i.e., the average distance between radicals, nor in the hyperfine inter-

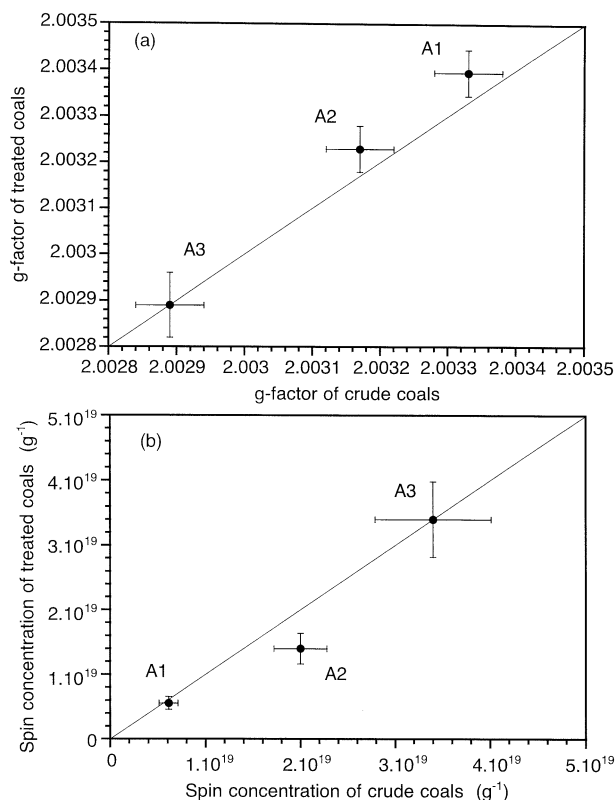


Fig. 4. Comparison of the g-factors (a) and of the spin concentrations (b) of the crude and treated terrestrial coals A1, A2, and A3.

actions, i.e., the number of protons and their distance to the electron spins.

The g-factor is sensitive to the electronic structure of the radicals and to the chemical composition because it is established that in coals the g-factor is related to the abundance of heteroatoms and especially oxygen (Silbernegel et al., 1984). Figure 4a shows the comparison of the g-factors of crude and HF/HCl treated coals. It appears that the values for A1 and A2 samples are slightly larger in treated samples than in crude ones only by about 6×10^{-5} , which is identical to the experimental uncertainty ($\pm 5 \times 10^{-5}$) of the measurements. We can thus conclude that the g-factors are not modified by the HF/HCl treatment, which means that neither the electronic structure nor the oxygen content in the domains spanned by the electron spins are modified by the treatment. As to the concentration of radicals, which is proportional to the EPR intensity, Figure 4b shows that it is not altered by the HF/HCl treatment.

This result is confirmed by ENDOR spectroscopy. Any change of the ENDOR spectrum produced by the HF/HCl treatment would indicate a modification of the hydrogen environment (hydrogen concentration and distance from the electron spin). It is found that the intensity, the lineshape (ratio of the narrow and broad ENDOR lines), and the linewidth are not altered by the treatment. An example is shown in Figure 3b for A2. This indicates that the treatment does not modify the transverse nuclear relaxation time T_{2n} and the ratio between distant and close protons interacting with the electron spins.

All these results demonstrate that the HF/HCl treatment does not induce any detectable effect on the paramagnetic domains

of the coals. Though terrestrial coals and meteoritic OM have different origins, they are both based on aromatic moieties. Therefore it can be safely inferred that the paramagnetic domains are also preserved by the treatment of the Orgueil and Murchison meteorites.

5. COMPARISON OF THE OM FROM ORGUEIL AND MURCHISON METEORITES WITH TERRESTRIAL TYPE III KEROGENS

Up to now, similarity between the OM from Orgueil and Murchison and the terrestrial type III kerogens (i.e., hydrogen-poor) was claimed on the basis of their respective bulk chemical features. The EPR parameters should be more discriminating because they are deeply related to the chemical structure and should consequently allow a more valuable comparison. It is well known that the EPR parameters in coals and kerogens are strongly correlated to the chemical composition and to the degree of catagenesis of these materials (Marchand and Cornard, 1980). Then the question arises to which extent the EPR parameters of the meteoritic OM follow the same correlations.

The *g*-factor of OM in coals is determined by the oxygen content (Silbernagel et al., 1984). Indeed the deviation of the *g*-factor from the free electron value $g_e = 2.002319$ increases with the strength of the spin-orbit coupling. Consequently the *g*-shift is all the more important as the unpaired spin density spends time on oxygen atoms, which have stronger $2p$ spin-orbit coupling ($\xi_O = 151 \text{ cm}^{-1}$) than carbon ($\xi_C = 29 \text{ cm}^{-1}$) (Gordy, 1980). Figure 5 represents the *g*-factors of the studied coals and of the OM from Orgueil and Murchison vs. the O/C ratios. The values are intermediate between the *g*-factors of nonoxygenated aromatic radicals and those of oxygenated radicals such as semiquinones in which the oxygens bears a significant part of the spin density. This indicates a partial delocalization of the spin density on oxygen atoms in the case of both the coals A1, A2, and A3 and the OM from Orgueil and Murchison. The continuous line and the gray area in Figure 5 represent respectively the mean *g*-value and the dispersion of *g*-values given in the literature (Silbernagel et al., 1984) for 31 samples of vitrinite and inertinite coals. The experimental *g*-values of the terrestrial coals fall slightly outside the range spanned by these samples. However, they still exhibit the same trend, i.e., the *g*-factor decreases with the O/C ratio. Anyhow, the most important fact is that the points corresponding to the OM of Orgueil and Murchison are located in the same area as the vitrinite and inertinite coals. This observation along with the fact that OM of Orgueil and Murchison meteorites have very close *g*-factors, although containing much different amounts of sulfur, excludes the influence of other heteroelements, in particular of sulfur. The influence of nitrogen on the *g*-factor can also be ruled out because of its low concentration (N/C = 0.03). Consequently the *g*-factors of radicals in Orgueil and Murchison are mainly determined by the oxygen concentration as in terrestrial coals. Another way of comparing the OM from Orgueil and Murchison with terrestrial coals consists in plotting the experimental data in a *g*-factor (related to O/C) vs. H/C diagram (Figure 6). In this diagram, two domains can be distinguished, corresponding to type I and II kerogens on the one hand and to type III kerogens on the other hand. Moreover, *g*-factors are mainly influenced by the evolution of oxygen

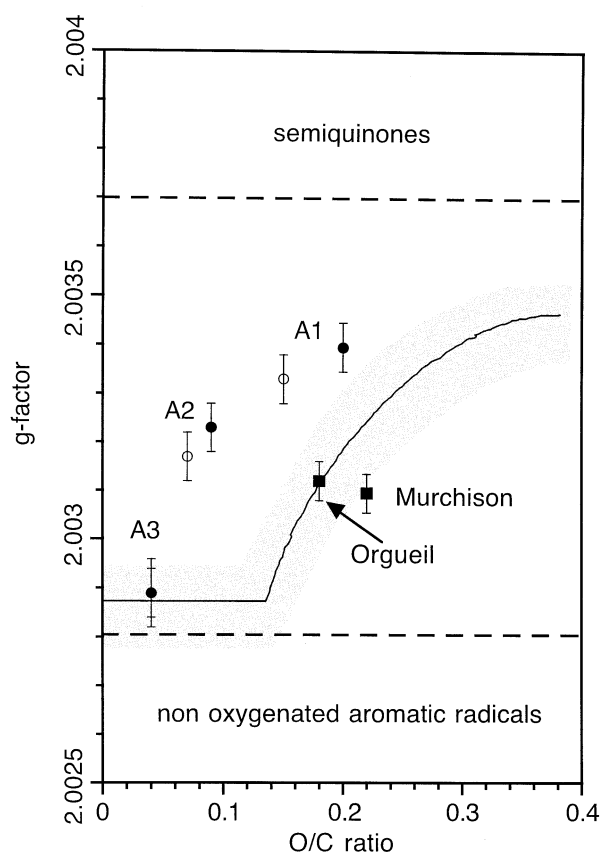


Fig. 5. *g*-factor vs. O/C for the crude (open circles) and treated (black circles) coals A1, A2, and A3 and the organic matter of Orgueil and Murchison meteorites. For the sake of comparison, the gray area represents the range of experimental *g*-factors obtained for 31 samples of vitrinite and inertinite coals from different origins (Silbernagel et al., 1984), and the continuous line represents the mean value.

content. Indeed, during diagenesis, the first stages of kerogen evolution result in a decrease of the *g*-factors. This diagram thus provides evolution paths similar to those observed in a van Krevelen diagram. The plots of the three studied coals fall in the type III domain, and their relative position reflects their relative maturity. Although the origin of the OM of Orgueil and Murchison meteorites is fundamentally different from that of terrestrial coals, the data corresponding to the chondritic OM are located in the type III domain. Moreover, in this domain they are located at the same level as that of coals at the beginning of catagenesis.

A second important EPR parameter is the electron spin concentration. Catagenesis involves bond breaking, which leaves unpaired electrons detected by EPR. Many of them recombine with each other but some are stabilized in aromatic radicals. Therefore by contrast with the *g*-factor which characterizes the O/C ratio of the OM, the spin concentration rather reflects the loss of matter and thus the evolution process. The comparison of the spin concentrations in the three studied coals and in the meteoritic OM, which amount to 10^{18} to 10^{19} g^{-1} (Table 2), reinforces the similarity in behavior of terrestrial coals and meteoritic OM.

At this stage of the study, this comparison indicates that the

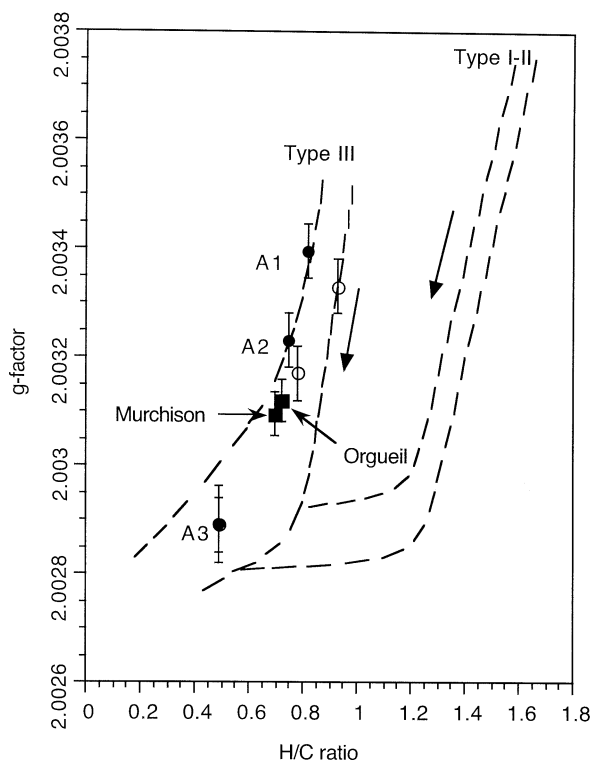


Fig. 6. g -factor vs. H/C for the crude (open circles) and treated (black circles) coals A1, A2, and A3 and the organic matter of Orgueil and Murchison meteorites. The dashed lines delimit the domains corresponding to type I-II and to type III terrestrial coals, respectively (Marchand and Conard, 1980). The arrows show the evolution during catagenesis.

meteoritic OM corresponds to the less mature coal. However, the spin concentrations given in Table 2 are mean values and do not take into account any possible concentration heterogeneities within the samples. Actually, heterogeneities in the electron spin distribution are revealed independently by the saturation behavior of the EPR lines and the ENDOR enhancement, with the consequence that the meteoritic OM contains high local spin concentrations. Figure 7 shows the EPR intensities, obtained by double integration of the EPR lines and normalized to the same spin quantity, vs. the square root of the incident microwave power. For a purely Lorentzian line, the normalized EPR intensity (proportional to the area under the absorption curve) is theoretically given by (Poole, 1983):

$$I = C \sqrt{\frac{P}{1 + \gamma^2 T_1 T_2 P / K}} \quad (3)$$

with C an instrumental constant, $\gamma \approx 1.76 \times 10^9 \text{ rad.s}^{-1} \text{ mT}^{-2}$ the free electron gyromagnetic ratio, T_1 and T_2 the spin-lattice and spin-spin electron relaxation times, respectively, P the microwave power, and K the cavity constant. At low microwave power, $\gamma^2 T_1 T_2 P / K \ll 1$, the intensity is linear in \sqrt{P} . In particular, this is observed for Murchison meteorite when $\sqrt{P} < 7 \text{ mW}^{1/2}$ so that the value of the instrumental constant $C \approx 2.16 \text{ mW}^{-1/2}$ can be obtained from the corresponding data. At high power the intensity reaches a constant value:

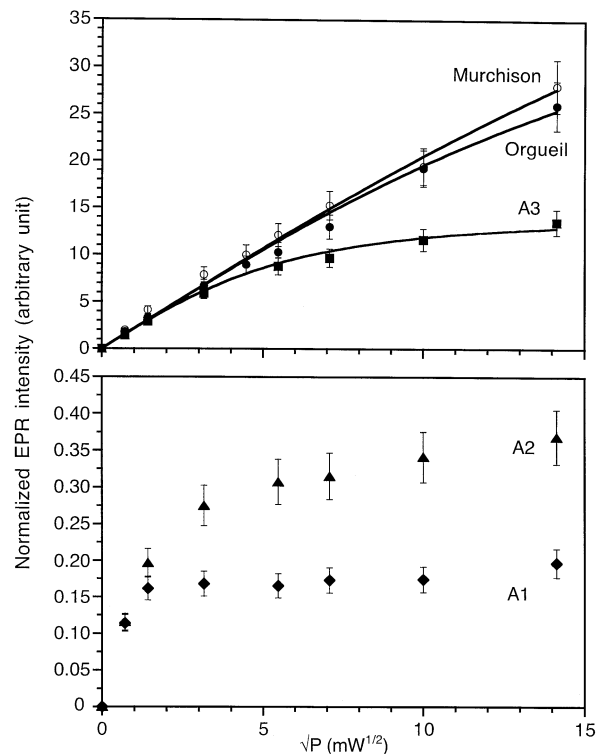


Fig. 7. EPR intensities at room temperature, normalized to the same spin concentration vs. the square root of the microwave power for the treated coals A1, A2, and A3, and the organic matter of the Orgueil and Murchison meteorites. The continuous curves are calculated with Eqn. 3 for Lorentzian lines.

$$I_{max} = C \sqrt{\frac{K}{\gamma^2 T_1 T_2}}, \quad (4)$$

showing that the shorter the spin relaxation times, the higher this value. The plots in Figure 7 for A1, A2, and A3 show that I_{max} increases, i.e., the product $T_1 T_2$ decreases with increasing spin concentration. The decrease of the spin relaxation times with increasing concentration can be accounted for by an enhancement of the exchange interaction, which, as a time-dependent perturbation on the spin states, acts as an efficient spin relaxation mechanism (Wertz and Bolton, 1972). The EPR intensities for the OM of Orgueil and Murchison meteorites in Figure 7 tend to much higher I_{max} values than for the terrestrial coals, indicating shorter T_1 and T_2 values. An estimate of the spin relaxation times can be obtained from the simulation of the experimental intensities with Eqn. 3. We obtain $T_1 T_2 \approx 3.7 \times 10^{-14} \text{ s}^2$ for A3 and $T_1 T_2 \approx 3.6 \times 10^{-15} \text{ s}^2$ for Orgueil. For Murchison, which is almost in the linear domain of Eqn. 3, $T_1 T_2$ should be close to $1.6 \times 10^{-15} \text{ s}^2$, which is the value below which the EPR intensity varies linearly in the whole range of microwave power. The $T_1 T_2$ product cannot be rigorously determined for A1 and A2, because Eqns. 3 and 4 are no longer valid in the case of inhomogeneous broadening. However, as far as only a rough estimate is required, we can use the experimental values of I_{max} and Eqn. 4 to obtain $T_1 T_2 \approx 2 \times 10^{-10} \text{ s}^2$ for A1 and $T_1 T_2 \approx 7 \times 10^{-11} \text{ s}^2$ for A2. If we only compare the geometric means $\sqrt{T_1 T_2}$, they differ by at

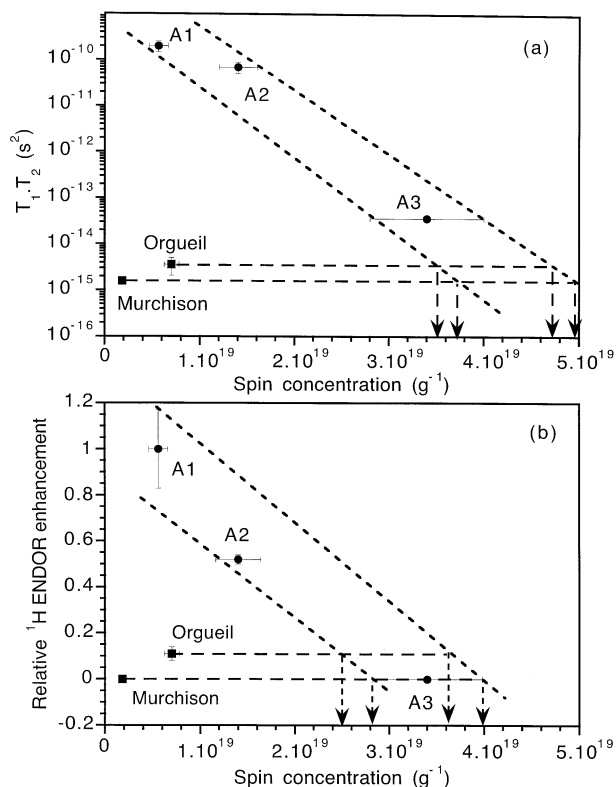


Fig. 8. Values of T_1T_2 product of the electron spin–lattice and electron spin–spin relaxation times (a), and relative ENDOR enhancements (b) vs. spin concentration for the treated coals A1, A2, and A3 and the organic matter of the Orgueil and Murchison meteorites. The dashed lines are guides to show the trend and delimit the range of uncertainty.

least two orders of magnitude between A1 and the OM of Orgueil and Murchison meteorites, whereas the spin concentrations are almost the same. Therefore the relatively short relaxation times for OM of Orgueil and Murchison meteorites, compared with that of the less mature A1 sample, are in favor of stronger exchange interactions between paramagnetic radicals than in the terrestrial coals.

An alternative explanation for these short relaxation times based on magnetic interactions with the mineral residues seems very unlikely. As a matter of fact, the residues are certainly not spread over the sample, but concentrated in small particles exhibiting ferromagnetic resonance. Consequently, most of the organic matter has no contact with the mineral residues. If the mineral residues were to influence the EPR of the radicals, we would have first expected an inhomogeneous broadening of the EPR line of the radicals due to the distribution of static local fields created by the ferromagnetic minerals. This broadening would have resulted in a severe deviation from a Lorentzian lineshape, which is not observed. In other words, the saturation behavior shows that the radicals are not homogeneously distributed in the meteoritic OM, resulting in high local spin concentrations.

This is illustrated in Figure 8a through a logarithmic plot of T_1T_2 vs. experimental spin concentrations, where it clearly appears that T_1T_2 drastically decreases with increasing spin concentration in the terrestrial coals. The envelope in Figure 8a is drawn

for heuristic purposes. The positions of the experimental points of Orgueil and Murchison meteorites, which are clearly outside the coal pathway, can be explained by the fact that $\sqrt{T_1T_2}$ is sensitive to the actual spin concentration experienced by each electron spin and not to the mean concentration. This actual concentration is obtained by translating the points corresponding to the meteoritic OM into the terrestrial OM domain. We thus obtain actual spin concentrations of $(4.1 \pm 0.6) \times 10^{19} \text{ g}^{-1}$ for Orgueil and $(4.3 \pm 0.6) \times 10^{19} \text{ g}^{-1}$ for Murchison, which are now local concentrations. This first evidence of strongly heterogeneous distribution of radicals in meteoritic OM is also qualitatively confirmed by the ENDOR response of these radicals. Figure 8b shows a plot of the relative ENDOR intensities normalized with respect to the spin quantity, vs. the spin concentration. The ENDOR enhancement is known to be highly sensitive to exchange interaction between electron spins. The latter prevents the transfer of spin polarization from electrons to nuclei and reduces the ENDOR intensity (Kevan and Kispert, 1976). In the limit of strong exchange interaction, i.e., high electron spin concentration, no ENDOR response is observed. In Figure 8b, the ENDOR intensities of the coals decrease upon increasing spin concentrations as expected, showing that ENDOR intensities are controlled by electron spin exchange. When the chondritic OMs are considered, their plots in the ENDOR enhancement vs. spin concentration diagram are out of the terrestrial coal domain. Indeed, their spin concentrations are close to that of A1 but their ENDOR intensity is as low as that of A3.

For ENDOR, it thus appears that the chondritic OMs behave as if the local concentrations were $(3.1 \pm 0.6) \times 10^{19} \text{ g}^{-1}$ for Orgueil and higher than $2.8 \times 10^{19} \text{ g}^{-1}$ for Murchison (Figure 8b). These values are very close to those derived from the relaxation time measurements in Figure 8a. These two independent experimental observations clearly indicate that the local concentration of electron spins is much higher in the meteoritic OM than the average concentration, by a factor 4 to 6 for Orgueil and 15 to 20 for Murchison. This shows that large areas of this OM are free from radicals, whereas the latter are concentrated in radical-rich areas, which represent approximately only 20% and 5% of the total volume for Orgueil and Murchison, respectively.

6. DISCUSSION AND CONCLUSIONS

As reported by several authors (Cronin et al., 1988; Gardinier et al., 2000; Cody et al., 2001), a substantial fraction (up to 50%) of the carbon atoms is not detected upon ¹³C cross-polarization/magic-angle spinning (CP/MAS) NMR spectroscopy. It is well established that the presence of organic radicals decreases the relaxation times in NMR and thus impedes the detection of carbon atoms. The occurrence of radicals concentrated in restricted areas in the OM of Orgueil and Murchison likely accounts for this lack of detection. This is further supported by the recent report of the similarity of the NMR spectra of Murchison recorded using the cross-polarization and single-pulse sequences (Cody, oral communication, 2002).

With respect to the origin of the chondritic OM, several implications can be drawn from the present study. In the g-factor vs. O/C and H/C diagrams (Figs. 5 and 6), the chondritic matter falls in the domain defined by the terrestrial coals. Because the g-factor is known to be related to the oxygen content of free radicals, this suggests that the latter are similar

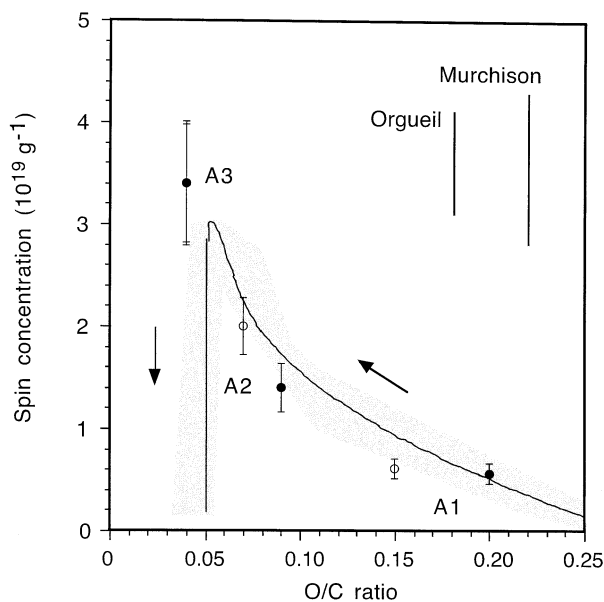


Fig. 9. Spin concentrations vs. O/C for the crude (open circles) and treated (black circles) coals A1, A2, and A3, and the organic matter of the Orgueil and Murchison meteorites. For the latter, the bars represent the range of local spin concentrations as estimated in section 5 of the text. For the sake of comparison, the grayed area represents the range of values obtained for 16 samples of type III kerogens from the Douala Basin (Cameroon) and the continuous line represents the mean value (Marchand and Conard, 1980). The arrows show the evolution during catagenesis.

for coals and chondritic OM of same elemental composition. However, it should not be taken for granted that the oxygen fugacity of the fluids—essentially water—in carbonaceous chondrite planetoids was similar to those in terrestrial sediments. This similarity with terrestrial coals disappears when the spin concentration is considered. Saturation behavior of the EPR and ENDOR enhancement point to high local spin concentrations which can be viewed as radical-rich micro-regions, heterogeneously distributed in the chondritic matter. Such a local heterogeneity of free radicals is, to the best of our knowledge, unique among natural organic macromolecules and can be viewed as an extraterrestrial signature. It should reflect the lack of thermal equilibrium between the different organic radicals which contribute to the bulk composition of the chondritic OM. The bulk chondritic OM thus appears as a mixture between locally concentrated organic radicals and more scattered radical-free molecules. As free radicals are unstable in the presence of water, the locally concentrated organic radicals may correspond to pristine molecules which would have survived the hydrothermalism event, whereas the radical-free regions, more abundant, would have been altered. Another extraterrestrial signature of the meteoritic OM is suggested by the spin concentration in the radical-rich areas vs. the O/C ratio. Figure 9 represents the spin concentration vs. the O/C ratio (equivalent to the *g*-factor), for the terrestrial coals and the meteoritic OM. For the latter, only the local spin concentration determined in section 5 was considered. For the sake of comparison, the gray area represents the range of values corresponding to terrestrial type III kerogens from the Douala Basin in Cameroon (Marchand and Conard, 1980). During the coal-

ification process, indicated by arrows in Figure 9, O/C ratios decrease and radicals are generated up to a maximum concentration of about 3 to 4×10^{19} in the case of kerogens (Marchand and Conard, 1980). Then the recombination of radicals becomes faster than their generation and the spin concentration drastically drops. In this final stage, the radicals condense into large aromatic units leading ultimately to graphite (Marchand and Conard, 1980; Mrozowski, 1988a and b). As shown by Mrozowski (1988a and b), this two-stage evolution is a general behavior of any carbonaceous matter, whether biologic or not, submitted to a heat treatment. Figure 9 shows that the spin concentrations and the O/C ratios of the studied terrestrial coals match the correlation expected for this kind of OM. The meteoritic OM exhibits a local spin concentration close to the maximum value obtained with terrestrial kerogens. This shows that this OM has not reached the final stage of coalification, which is consistent with the small size of the aromatic units constituting this OM (Gardiner et al., 2000). However, Figure 9 shows that the local spin concentration in the meteoritic OM, about 3 to $4 \times 10^{19} \text{ g}^{-1}$ for $\text{O/C} \approx 0.2$, is much higher than that observed for a terrestrial coal with the same O/C ratio. By comparison with the terrestrial coals, such a high concentration would be obtained for $\text{O/C} \approx 0.05$, i.e., 4 times lower. An actual value $\text{O/C} \approx 0.05$ for the radical-rich domains in the meteoritic OM seems unrealistic because their oxygen content $\text{O/C} \approx 0.2$ has been shown to be consistent with the *g*-factor (section 5). This discrepancy between radical concentrations in the meteoritic OM and the terrestrial coals suggests that these radicals originate from different processes.

In the interstellar medium, several processes can be considered to produce the building blocks of the chondritic insoluble OM: ion–molecule reactions in the gas phase, low-temperature gas–grain reactions, gas-phase unimolecular photodissociation, and ultraviolet photolysis (Sandford et al., 2001). These four processes are compatible with the deuterium enrichment observed in the chondritic insoluble organic matter (Robert and Epstein, 1982; Kerridge et al., 1987; Halbout et al., 1990). Apart from unimolecular photodissociation, the other three processes take place at low temperature (10 K) and, therefore, the thermal equilibrium between the reactants is likely not to be achieved. The high local spin concentration reported in this paper may reflect such nonthermal processes, in agreement with recently reported models (Seph-ton and Gilmour, 2000). In addition, these organic radicals produced at low temperature are neither rearranged nor eradicated during the parent body hydrothermalism.

These results are compatible with a model for the formation of chondritic organic matter involving the photolysis of icy interstellar grains. In cold interstellar space, most organic species, formed in the gas phase by ion–molecule reactions, condense onto mantle grains and are then photolyzed by the ambient UV radiations. Some species are also formed by gas–grain surface reactions. Laboratory experiments have shown that these icy grains are chemically processed: molecules are destroyed and new molecules, including radicals and ions, are continuously formed (Agarwal et al., 1985). These radicals remain trapped in their icy matrix. If the organic fraction of the carbonaceous meteorites was originally constituted by such interstellar grains, the thermal stress induced by parent body accretion would have caused ice to melt, liberating the organic products in liquid water. Once in water ($<100^\circ\text{C}$ in carbona-

ceous chondrites), most of the radicals were eliminated through the chemical reactions which have altered the precursors of chondritic OM. During this secondary hydrothermal process, it can be postulated that the equilibration of the organic radicals was kinetically inhibited in some protected regions of the mineralogical matrix or for some specific organic moieties. These regions, having preserved their original high density of radicals, are presently detected through the EPR technique. Such an interpretation will be tested using laboratory analogs of interstellar organic grains, formed by UV irradiation at 10 K.

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