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Solid state CP/MAS ^{13}C NMR of the insoluble organic matter of the Orgueil and Murchison meteorites: quantitative study

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Abstract

Solid state CP/MAS ^{13}C nuclear magnetic resonance (NMR) study of the insoluble organic fraction isolated by HF/HCl treatment under an inert atmosphere from the Orgueil and Murchison carbonaceous meteorites is reported. Based on these spectra, eight different types of carbons (aro- and ali-linked CH_3 , CH_2 , aliphatic C-linked to heteroelements, protonated and non-protonated aromatic C, carboxyls and carbonyls) were identified, their relative amounts were determined and theoretical NMR-derived H/C atomic ratios were calculated. Comparison of these H/C ratios with those obtained from elemental analysis revealed that a large part of the carbons of the insoluble fraction of both meteorites are not detected by CP/MAS ^{13}C NMR. Taking into account these undetected carbons, the relative abundance of aromatic carbons (as % of the total carbons) was calculated as between 69 and 78% in Orgueil and 61 and 67% in Murchison and thus shown to be much higher than previously thought. In addition, the NMR data allowed to calculate the ratio of non-protonated and protonated aromatic carbons. Based on previous studies on chemical and thermal degradation, the present NMR data were interpreted as reflecting the occurrence of highly substituted rather small aromatic moieties in these insoluble organic materials. Along with FTIR data, NMR results also pointed to a relatively high branching level in the aliphatic chains, especially for Murchison. According to the above results, the insoluble organic matter in these meteorites did not suffer a marked thermal maturation during the late hydrothermalism of the parent body. Its synthesis involved a statistical combination of all the possible bonds between $-\text{CH}_3$, $-\text{CH}_2$ and $-\text{CH}$ radicals, producing both the aliphatic and the aromatic moieties. This model explains not only the chemical features of the chondritic insoluble organic material but also the typical FTIR signature of the interstellar medium. Therefore, organic material found in the interstellar medium and that incorporated in the most primitive objects of the solar system seem to share a common organosynthesis. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Orgueil Meteorite; Murchison Meteorite; NMR spectra; organic compounds; aromatic hydrocarbons

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1. Introduction

Star formation and subsequent evolution of planetary systems occur in dense molecular clouds, formed of interstellar dust grains gathered from the diffuse interstellar medium. Radio and infrared (IR) observations reveal the presence of organic molecules in the gas phase and dust grains, respectively. Remarkable features of these grains are absorption bands near $3.4\text{ }\mu\text{m}$ (2940 cm^{-1}) towards bright IR objects seen through large column densities of interstellar dust. Comparisons of insoluble organic matter from carbonaceous chondrites with the diffuse interstellar medium have shown that aliphatic hydrocarbon chains are responsible for these bands. Such hydrocarbons carry the $-\text{CH}_2$ and $-\text{CH}_3$ functional groups in the abundance ratio $\text{CH}_3/\text{CH}_2 \approx 0.6$ [1]. On a galactic scale, the intensity of the $3.4\text{ }\mu\text{m}$ band increases along with the Si-O absorption, suggesting these two components are associated as grains with a silicate core and a refractory organic mantle [2]. A better knowledge of the structure and composition of organic matter in chondritic meteorites is thus required to (i) estimate to what extent interstellar organic matter was preserved during the formation of the solar system and (ii) decipher the possible synthetic pathways of this matter in space.

The soluble fraction extracted from chondrites seems to have no counterpart in space when compared to the organic molecules detected in the interstellar medium as grains or in the gas phase. Indeed, most families identified in extracts of carbonaceous chondrites are not observed in space: e.g. although extensively searched, amino acids have not been detected in cold interstellar clouds. The origin of the soluble fraction has been ascribed to organic reactions occurring at (or near to) the surface of the carbonaceous parent bodies during hydrothermal events. Accordingly, the origin of the so-called prebiotic soluble organic molecules is linked to the hydrolysis of a parent precursor – possibly of interstellar origin. This assumption was supported by recent results on Murchison hydrous pyrolysis and supercritical fluid extraction pointing to a relationship between the soluble and insoluble fractions [3]. Therefore,

characterizing the chemical structure of the insoluble fraction in chondrites is a prerequisite to understand if there is a relationship between soluble and insoluble organic matter. Such a characterization is the aim of the present work.

The organic carbon of carbonaceous chondrites is distributed amongst a soluble fraction and an insoluble macromolecular fraction. This macromolecular fraction is usually considered to be free of terrestrial contamination compared to the soluble one [4,5]. Although less abundant, the organic soluble fraction has been extensively studied and its composition is relatively well-known [6–8]. In contrast, the chemical structure of the predominant insoluble fraction (70–90% of the total organic carbon of meteorites, [6–9]) is far from being as well understood. Numerous methods were used for its analysis; thermal and chemical degradation were the most common [3,4,6,10–19]. However, spectroscopic methods such as FTIR [14,20–24] and solid state ^{13}C nuclear magnetic resonance (NMR) show the great advantage of being non-destructive. Solid state ^{13}C NMR using cross-polarization sequence and magic angle spinning (CP/MAS) was previously used by Cronin et al. [25] to study the insoluble fraction of Orgueil and Murchison chondrites.

Solid state ^{13}C NMR is a powerful tool to determine the nature and environment of carbons in macromolecular materials even when the organic matter is tightly associated with minerals. Indeed, except if the latter are paramagnetics, the only consequence of mineral presence is a lowering of the signal to noise ratio. However, as discussed below, recent studies in solid state ^{13}C NMR spectroscopy revealed some limitations of this method when applied to heterogeneous samples and the use of different sequences is required to derive significant quantitative data on resonant carbons.

Indeed, in the cross-polarization sequence [26] necessary to enhance the signal, magnetization is transferred from the most abundant spins, i.e. the ^1H , towards the analyzed, less abundant spins, i.e. the ^{13}C . During this transfer, termed contact time, ^{13}C magnetization exponentially increases following the T_{CH} time constant. However, simultaneously, the protons are relaxing, hence a decrease

in magnetization according to the spin-lattice relaxation time $T_{1\rho\text{H}}$. The magnetization M (i.e. signal intensity) can thus be expressed as a function of the contact time t_c (Eq. 1):

$$M = M_o(1 - e^{-t_c/T_{\text{CH}}})e^{-t_c/T_{1\rho\text{H}}} \quad (1)$$

[27] with (i) M_o , magnetization in the absence of relaxation effects, directly proportional to the number of resonant carbons and (ii) T_{CH} and $T_{1\rho\text{H}}$ being the cross-relaxation time and the ^1H spin-lattice relaxation time in the rotating frame, respectively. The relaxation times depend on the environment of the carbons (more or less protonated, distances between carbons and protons, molecular motions). Therefore, analysis of complex materials requires to record spectra at different contact times to obtain reliable information.

Magic angle spinning aims at sharpening the NMR peaks. However, for carbons exhibiting a strong anisotropy of their chemical shift, spinning side bands (SSB) occur in addition to the main, isotrope signal. The distance of these bands to the isotrope peak is proportional to the spinning rate. SSB may interfere with other peaks and make difficult spectra interpretation. SSB intensity decreases when the applied magnetic field is lower but the use of low fields results in a marked alteration of spectra resolution and intensity. SSB intensity can also be reduced, without affecting spectra quality, by spinning rate increase. Accordingly, recording spectra of complex materials at high sample spinning rates is especially interesting.

Since the spectra reported by Cronin et al. [25] were obtained using a single contact time of 1 ms and sample spinning rate of 4 kHz, we have performed a complete solid state CP/MAS ^{13}C NMR study of the insoluble organic fraction of Orgueil and Murchison meteorites taking into account the above points. This fraction was isolated via the classical HF/HCl treatment commonly used to isolate kerogens from sedimentary rocks [28]. Prior to this treatment, the soluble and hydrolyzable organic components were removed by extensive extractions and base and acid hydrolyses (the HF/HCl treatment, when performed directly on the crude material, may induce condensation re-

actions leading to insoluble organic matter). So as to avoid oxidative alteration of the organic matter upon isolation, the whole procedure was carried out under an inert atmosphere.

2. Materials and methods

The ground meteorites (Orgueil from Museum National d'Histoire Naturelle, Paris, France, and Murchison from Smithsonian, Washington, DC, USA) were firstly extracted with water (reflux for 60 h), then in a mixture of $\text{CH}_2\text{Cl}_2/\text{MeOH}$, 2/1, v/v (reflux for 2 h) and sonicated (30 min) with the same mixture. After supernatant elimination, the insoluble fraction (i.e. extracted meteorite) was saponified with KOH 7% in MeOH (reflux for 6 h), rinsed with dilute HCl until neutrality and extracted with a mixture of acetone/ CH_2Cl_2 , 1/1, v/v. The insoluble residue (i.e. saponified meteorite) was then submitted to three hydrolyses in HCl 6 N (reflux for 6 h followed by neutralization and stirring at 80°C successively for 6 h and overnight) and, finally, treated in a HF/HCl, 2/1, v/v mixture at 80°C for 24 h. After the HCl hydrolyses and the HF/HCl treatment, the insoluble material was washed with water until neutrality, extracted with CH_2Cl_2 and thoroughly dried before analyses.

Elemental analysis (Wolf Laboratories) showed that Orgueil insoluble material contains 67.5% of C and 4.07% of H and that Murchison C and H contents are 50 and 2.92%, respectively.

Solid state ^{13}C NMR spectra were obtained at 100.62 MHz (Bruker MSL400 spectrometer) using a double bearing probe, high power decoupling, cross-polarization with 5 s recycle time and magic angle spinning at 4 kHz (rotor diameter 7 mm). For variable contact time experiments, t_c ranged from 10 μs to 10 ms. In the inversion recovery cross-polarization (IRCP) sequence, t_c of 1 ms and inversion delays of 25 and 100 μs were used. The spectra were the results of 4900 and 11 500 scans for Orgueil and Murchison, respectively, in the variable t_c experiments and 6480 scans in the IRCP sequence. Free induction decays were analyzed with the Bruker WIN-NMR program and spectra were simulated using the

WIN-FIT program [29]. Spectra were also recorded using a VACPMAS sequence with a spinning rate of 15 kHz (rotor diameter 4 mm) at the same field (Bruker DSX400 spectrometer) with t_c of 1 ms and recycle time of 5 s.

FTIR spectra (Digilab FTS 40 spectrometer) were recorded as KBr pellets (1 mg in 300 mg). The spectra (500 scans) were recorded after pellet desiccation at 50°C for 15 days.

3. Results and discussion

3.1. Orgueil meteorite

The spectrum of the insoluble organic matter of the Orgueil meteorite, recorded using high sample spinning rate (15 kHz) and a classical t_c of 1 ms, shows two broad peaks (Fig. 1). The 0–70 ppm peak (maximum at 30 ppm) corresponds to aliphatic carbons. Its width and the shoulder around 50–70 ppm shall reflect the presence of aliphatic carbons linked to heteroatoms. The second signal (maximum at 130 ppm) is due to unsaturated carbons which can be, a priori, in olefinic or aromatic units. However, the occurrence in the FTIR spectrum (Fig. 2) of an intense band at 1600 cm^{-1} reveals that these carbons are mostly aromatic. In addition to the main two peaks,

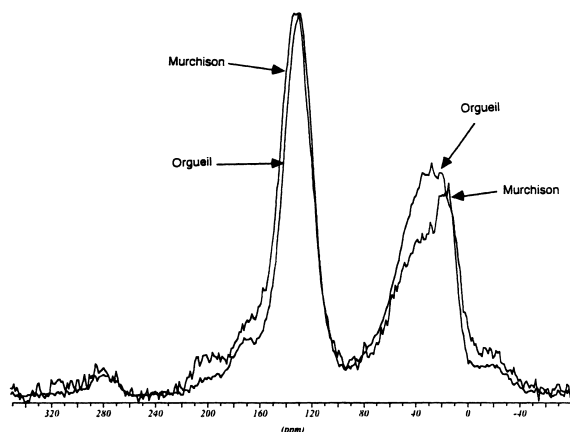


Fig. 1. Solid state ^{13}C NMR spectra of the insoluble organic fraction of the Orgueil and Murchison meteorites recorded with a sample spinning rate of 15 kHz and a contact time of 1 ms.

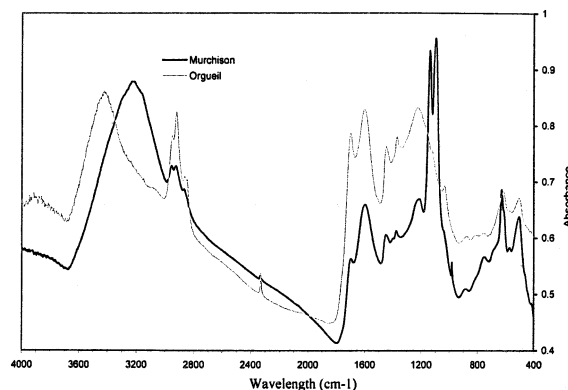


Fig. 2. FTIR spectra of the insoluble organic fraction of the Orgueil and Murchison meteorites.

smaller NMR signals (160–180 ppm and around 200 ppm) should correspond to carbons from carboxyl and carbonyl groups, respectively. Weak SSB of the 130 ppm peak are observed at 280 and -20 ppm. The main types of carbons in the insoluble organic fraction of the Orgueil meteorite were identified from this 15 kHz spectrum. After this qualitative study, a quantitative study was performed using CP/MAS with various t_c . The latter, due to access to NMR facilities, was carried out at a sample spinning rate of 4 kHz.

The spectrum recorded at 4 kHz using the same t_c of 1 ms as above at 15 kHz appears, at first glance, quite different from the latter spectrum (Fig. 3c). This is due to the presence of intense SSB in the 4 kHz spectrum. Five broad peaks can be distinguished. The major one corresponds to aliphatic carbons (the chemical shift of such carbons does not exhibit any anisotropy and thus no SSB is associated with this signal). It maximizes at 30 ppm and comprises a resolved peak at 17 ppm. The peak centered at 130 ppm is the isotrope peak of the aromatic carbons which signal is distributed amongst this peak and SSB at 90, 170 and 210 ppm. A secondary SSB at 50 ppm should also contribute to the aliphatic peak.

Twelve spectra were recorded at different t_c (0.01–10 ms). The peak at 17 ppm only appears at the two longest t_c (Fig. 3) indicating that the contributors to this peak are carbons from methyl groups. Indeed, at the shortest t_c , detected carbons are those exhibiting strong C–H dipolar in-

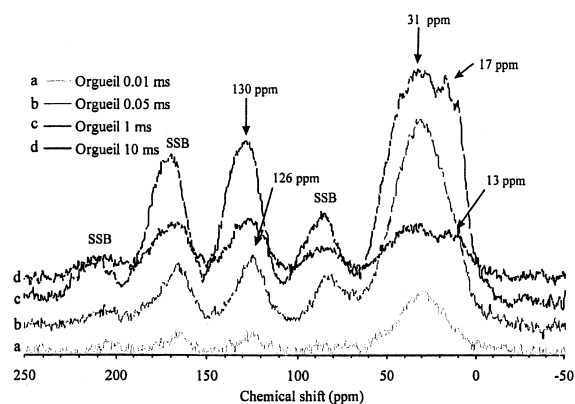


Fig. 3. Solid state ^{13}C NMR spectra of the insoluble organic fraction of the Orgueil meteorite recorded with a sample spinning rate of 4 kHz and variable contact times ranging from 0.01 to 10 ms.

teractions, i.e. protonated carbons. However, in the case of methyl groups, these interactions are averaged by the molecular motions of the fast rotating CH_3 . As a result, these carbons behave similarly to quaternary carbons and only appear at longer t_c . Based on their chemical shift, most of these methyl groups should be linked to aromatic moieties. At the shortest t_c , the aliphatic peak maximizes at 30 ppm, suggesting that methylene groups are the main contributors to the aliphatic signal. The aromatic signal shows a shift of the maximum of the isotrope peak with t_c : from 130 ppm (t_c of 1 ms) to 126 ppm (t_c of 0.01 and 0.05 ms). This shift reflects the occurrence of different types of aromatic carbons and it appears that protonated aromatic carbons occur at 126 ppm.

To specify the chemical shift of the non-protonated aromatic carbons, spectra were recorded using the IRCP sequence: a delay, termed inversion delay, is introduced after the t_c . During this delay, the response of the carbons with strong C–H dipolar interactions, i.e. the protonated ones, decreases or is even inverted. Based on the spectra obtained with the longest inversion delay (Fig. 4c), it appears that the non-protonated aromatic carbons, i.e. the only ones contributing to the aromatic peak under these conditions, occur at 136 ppm along with their SSB at 56, 96, 176 and 216 ppm. The assignment of the non-protonated aromatic carbons (136 ppm) and of the pro-

tonated ones (126 ppm) is consistent with Wilson et al. [30] who noted in coals that the above two types of carbons occur above and below 130 ppm, respectively, but with certain overlap. Concerning the aliphatic peak, the main signal centered at 30 ppm is rapidly inverted thus confirming the protonated nature of the corresponding carbons (CH_2 and CH). The reverse is observed for the 13 ppm peak (chemical shift of CH_3 linked to aliphatic carbons) and to a lesser extent for its shoulder at ca. 21 ppm. The carbons corresponding to this shoulder shall therefore either be non-protonated or exhibit high molecular motions (a chemical shift of 21 ppm is observed in the methyl group of toluene). This low intensity peak is therefore assigned to aromatic-linked carbons. Accordingly, the 17 ppm peak in the spectrum recorded under classical CP/MAS conditions (0 μs inversion delay, Fig. 4a) is a combination of the 13 and 21 ppm signals. The broad signal around 50 ppm (inversion delay of 25 μs , Fig. 4b) corresponds to the secondary SSB of the aromatic peak; however, as shown later on, heteroatom-linked aliphatic carbons also contribute to this signal.

Taken together, the CP sequence with variable t_c (Fig. 3) and the IRCP sequence (Fig. 4) allowed to determine the chemical shifts of five different types of carbons in the insoluble organic fraction of the Orgueil meteorite, aliphatic-linked CH_3 (13

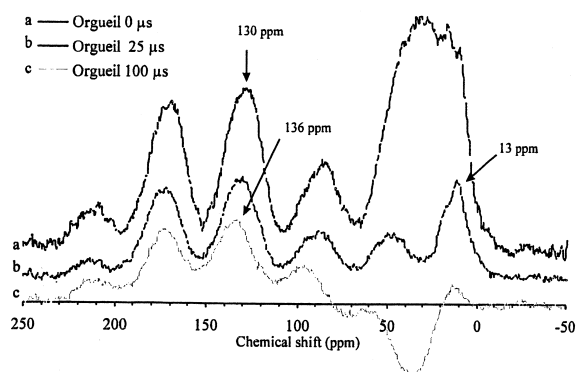


Fig. 4. Solid state ^{13}C NMR spectra of the insoluble organic fraction of the Orgueil meteorite recorded with a sample spinning rate of 4 kHz, a contact time of 1 ms and an IRCP sequence with inversion delays ranging from 0 to 100 μs . Similar results were obtained from the Murchison meteorite.

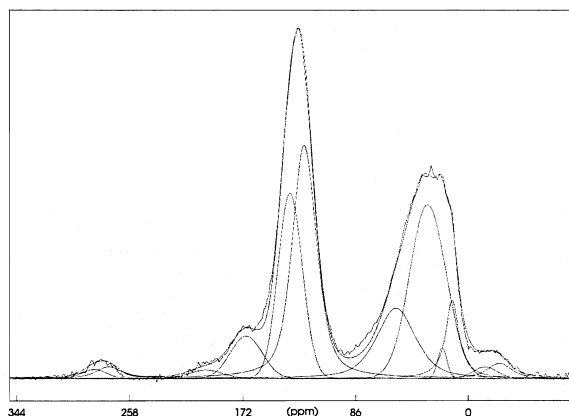


Fig. 5. Deconvolution of the solid state ^{13}C NMR spectrum of the insoluble organic fraction of the Orgueil meteorite recorded with a sample spinning rate of 15 kHz and a contact time of 1 ms.

ppm), aromatic-linked CH_3 (21), methylenes (31), protonated (126) and non-protonated (136) aromatic carbons. The 15 kHz spectrum revealed that two additional types of carbons, carboxyl (167) and carbonyl (200), have also to be considered.

As previously mentioned, the behavior of each type of carbon with varying t_c shall be determined to assess their relative abundances. For long t_c , Eq. 1 can be simplified:

$$M = M_o e^{-t_c/T_{1\rho\text{H}}}$$

Table 1

Chemical shifts, uncorrected and corrected relative abundances of the different carbon types in the insoluble organic fraction of the Orgueil meteorite

Carbon type	δ (ppm)	Relative abundances (%)	Corrected relative abundances ^a (%)	Total (%)
Ali-linked CH_3	12	5.8	3.5–2.5	ali C: uncorrected: 44.4, corrected: 27.1–19
Aro-linked CH_3	20	1.1	0.7–0.3	
CH_2	30	24.8	15.1–10.7	
Ali C-heteroatom	55	12.7	7.8–5.5	
Protonated aromatic C	125	29.7	18.1–12.8	aro C ^b : uncorrected: 49.2, corrected: 69–78.2
Non-protonated aromatic C	136	19.5	50.9–65.4	
Carboxyls	169	5.3	3.2–2.3	
Carbonyls	200	1.1	0.7–0.5	

^aMinimum and maximum corrected relative abundances calculated by assuming that the aliphatic carbons linked to heteroelements (55 ppm) are non-protonated or fully protonated, respectively.

^bThe aromaticity factor, termed f_a , is usually calculated as the ratio of the signal above 100 ppm to the total intensity of the spectrum; it therefore includes both aromatic carbons and $\text{C}=\text{O}$ carbons. Similar calculation leads to f_a values of 0.56 from the uncorrected data and of 0.73–0.81 from the corrected ones.

By plotting $\ln M$ versus t_c , a straight line intercepting the y axis at $\ln M_o$ with a slope of $-1/T_{1\rho\text{H}}$ is obtained. The intensity M of each signal was therefore calculated from the deconvolution of the spectra recorded at long t_c (≥ 1 ms) and M_o was deduced from the corresponding $\ln M = f(t_c)$ plot. Deconvolution was based on all the previously determined types of carbons except the carboxyl ones which could not be differentiated from the 170 ppm SSB. An additional peak at 48 ppm, assigned to aliphatic carbons, had to be considered to obtain a better fit. r^2 values for the linear part of the $\ln M = f(t_c)$ plot ($t_c \geq 1$ ms) range from 0.995 (31 ppm) to 0.848 (210 ppm). The highest values (> 0.99) are observed, as expected, for signals of relatively high abundance and not affected by SSB, like aliphatic CH_2 and CH_3 . For such signals, the relative abundances deduced from their M_o values and those directly calculated on the 4 kHz spectrum recorded with a t_c of 1 ms are similar. So as to avoid problems due to overlapping with SSB, we finally calculated the relative abundances of all the different types of carbons from the deconvolution of the 15 kHz spectrum with this t_c (Fig. 5, Table 1).

The only differences between the two sets of chemical shifts used to deconvolute the 4 and 15 kHz spectra are the 167 ppm peak which can be taken into account in the second case and the

shift of the aliphatic carbons from 48 to 55 ppm. This latter value should be more accurate since the 15 kHz spectrum is not affected by SSB and corresponds to the chemical shift usually observed for aliphatic carbons directly linked to heteroatoms (N or O) via a single bond.

Among the aliphatic carbons, the most abundant type corresponds to CH_2 (Table 1). A substantial contribution of methyl groups is also noted, in agreement with FTIR data which indicate the presence of relatively short chains or branched aliphatic chains. Indeed, the intensity ratio of the CH_2 and CH_3 stretching bands (2920 cm^{-1} and 2960 cm^{-1} , respectively) is relatively low (26–28; Fig. 2) as that of the asymmetric C–H bending bands at 1455 cm^{-1} (CH_2+CH_3) and symmetric C–H bending at 1375 cm^{-1} (CH_3). The aliphatic carbons linked to heteroatoms may contribute to the FTIR band around 1200 cm^{-1} but the latter can also be due to mineral absorptions. When the aromatic carbons are considered, a substantial contribution of protonated carbons is noted, in agreement with FTIR data: only a weak broad shoulder is detected in the $3000\text{--}3100\text{ cm}^{-1}$ range (aromatic C–H stretching vibration) ([27]; Fig. 2).

Based on the relative abundances determined above for the eight types of carbons, a theoretical NMR-derived H/C atomic ratio can be calculated as ranging between 1.13 and 1.0 according as the aliphatic carbons linked to heteroelements are considered to be protonated (CH) or not. These ratios are markedly higher than the actual value obtained from elemental analysis (0.72). This difference can be explained in two ways: overestimation of hydrogens by NMR or underestimation of carbons. In the first case, it should be assumed that some carbons, considered as protonated, are in fact substituted by heteroelements. But (i) aliphatic carbons linked to heteroelements are considered as non-protonated in the calculation yielding a H/C of 1.0 and (ii) the 15 kHz spectrum does not show a significant contribution of aromatic carbons linked to heteroelements (no signal around 150 ppm). Thus, this explanation cannot account alone, by far, for the difference between the H/C ratios derived from elemental analysis and NMR. We must therefore consider that

some carbons of the insoluble material from the Orgueil meteorite are not seen in the NMR spectra. It is well-known that some non-protonated carbons, in the center of large polyaromatic units, cannot be detected by CP/MAS ^{13}C NMR [31]. Experiments on mature coals showed that such carbons cannot be reached by magnetization transfer because they are too far from protons and/or because of paramagnetic microenvironments induced by the presence of organic radicals (the cross-relaxation time T_{CH} varies as the sixth power of the carbon–proton distance and is strongly increased by the presence of such radicals). An incomplete detection of the aromatic carbons in the insoluble fraction isolated from Orgueil is supported by a single pulse ^{13}C NMR experiment reported by Cronin et al. [25]. This spectrum showed a larger aromatic signal when compared to the CP/MAS one but exhibited a too low signal to noise ratio to derive quantitative information.

Based on the H/C value from elemental analysis and on that derived from NMR (H/C=1.0) assuming that the aliphatic C linked to heteroelements (55 ppm) are not protonated, it can be calculated that the fraction of aromatic carbons not seen by CP/MAS, i.e. the non-resonant carbons, represents ca. 39% of the total carbons. Since these 39% correspond to non-protonated aromatic carbons, corrected values were calculated for the relative abundances of the eight types previously recognized (Table 1). The non-protonated aromatic carbons then appear to be ca. three times more abundant than the protonated ones. Moreover, the former are probably still underestimated: the above calculation was based on the difference between the actual H/C ratio from elemental analysis and the NMR-derived ratio calculated assuming that all the aliphatic carbons linked to heteroelements are not protonated. It is unlikely that such an assumption is completely fulfilled. Accordingly the difference used and hence the calculated amount of non-detected (i.e. non-protonated) aromatic carbons corresponds to a minimum value. Indeed, the proportion of non-detected carbons in Orgueil raises from 39 to 57% if the aliphatic carbons linked to heteroelements are considered as protonated

and the relative abundance of protonated and non-protonated aromatic carbons shifts from 18/51 to 13/65. These ratios lead to a total number of aromatic carbons accounting for 69–78% of the total carbons. The actual value should be betwixt and between. However, even the minimum value is much higher than the aromaticity factor previously obtained by Cronin et al. [25] ($fa = 0.47$), although the latter value included the contribution of carbons from C=O groups (note b, Table 1).

3.2. Murchison meteorite

The same NMR experiments as above for Orgueil were performed on the insoluble organic fraction of the Murchison meteorite. Strong similarities are found between Orgueil and Murchison 15 kHz spectra (Fig. 1). However, the aliphatic peak is less intense and symmetrical for Murchison and the aromatic one wider.

The deconvolution of the 15 kHz spectrum (Fig. 6), the variable t_c experiment (Fig. 7) and the IRCP sequence (not shown) allowed to identify the same types of carbons in both meteoritic insoluble organic fractions. However, some small differences in chemical shifts are observed (Tables 1 and 2), probably reflecting slightly different mi-

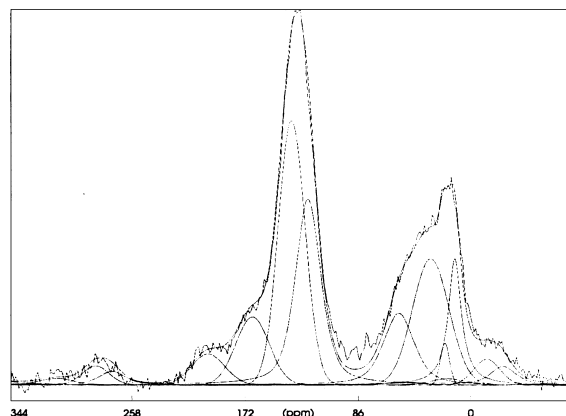


Fig. 6. Deconvolution of the solid state ^{13}C NMR spectrum of the insoluble organic fraction of the Murchison meteorite recorded with a sample spinning rate of 15 kHz and a contact time of 1 ms.

croenvironments. The relative abundances of the different types of carbons were also calculated after deconvolution of the 15 kHz spectrum (Table 2). NMR-derived H/C atomic ratios of 0.93–0.84, calculated as above for Orgueil, are markedly higher than the one from elemental analysis ($\text{H/C} = 0.70$) and it can be calculated that non-detected carbons (non-protonated aromatic) correspond to 20–33% of the total carbons. The corrected relative abundances of the different types of

Table 2

Chemical shifts, uncorrected and corrected relative abundances of the different carbon types in the insoluble organic fraction of the Murchison meteorite

Carbon type	δ (ppm)	Relative abundances (%)	Corrected relative abundances ^a (%)	Total (%)
Ali-linked CH_3	12	8.3	6.6–5.6	ali C: uncorrected: 34.9, corrected: 27.9–23.4
Aro-linked CH_3	20	1.3	1.1–0.9	
CH_2	30	16.0	12.8–10.7	
Ali C-heteroatom	55	9.3	7.4–6.2	
Protonated aromatic C	124	23.2	18.6–15.5	aro C ^b : uncorrected: 51.7, corrected: 61.4–67.6
Non-protonated aromatic C	136	28.5	42.8–52.1	
Carboxyls	166	9.3	7.4–6.2	
Carbonyls	200	4.1	3.3–2.7	

^aMinimum and maximum corrected relative abundances calculated by assuming that the aliphatic carbons linked to heteroelements (55 ppm) are non-protonated or fully protonated, respectively.

^bThe aromaticity factor, termed fa , is usually calculated as the ratio of the signal above 100 ppm to the total intensity of the spectrum; it therefore includes both aromatic carbons and C=O carbons. Similar calculation leads to fa values of 0.65 from the uncorrected data and of 0.72–0.78 from the corrected ones.

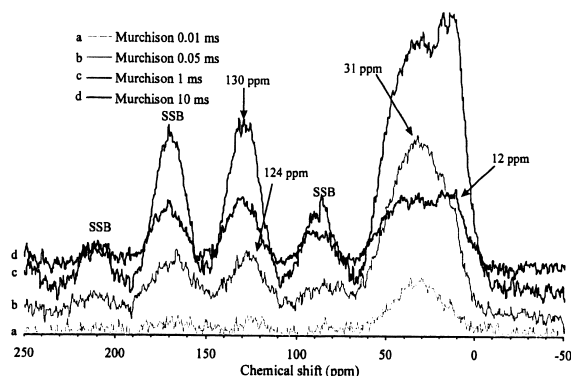


Fig. 7. Solid state ^{13}C NMR spectra of the insoluble organic fraction of the Murchison meteorite recorded with a sample spinning rate of 4 kHz and variable contact times ranging from 0.01 to 10 ms.

carbons taking into account these non-detected carbons are reported in Table 2.

A high proportion of non-protonated aromatic carbons is observed, in agreement with the lack of a band at 3050 cm^{-1} in the FTIR spectrum of Murchison ([24]; Fig. 2). The aromaticity factor reported by Cronin et al. [25] for the insoluble organic matter of Murchison included the contribution of the carbons from $\text{C}=\text{O}$ groups; nevertheless, this value (0.4) was much lower than the aromatic carbon fraction from the present study (61–68% of total carbons). Stepwise combustion and isotopic measurements yielded a relative abundance of 5–18% of aliphatics and ca. 90% of aromatics for Murchison [4] and thus showed more aromatic carbons than the present NMR study. However, some of the carbons (e.g. methyl groups), directly linked to the aromatic units, are probably considered as aromatics upon stepwise combustion, since β -cleavage should be the major process occurring under these conditions, whereas such a drawback is not encountered in NMR studies.

When the aliphatic carbons are considered, a higher relative contribution of the methyl groups and a lower level of CH_2 groups is observed for Murchison relative to Orgueil, thus suggesting a higher branching level for alkyl moieties in the former meteorite. This is fully confirmed by FTIR spectra (Fig. 2): the ratios of the 2920–

2960 cm^{-1} bands and of the $1455\text{--}1375\text{ cm}^{-1}$ bands are much lower in Murchison spectrum.

Comparison between the relative abundance of the carbons in $\text{C}=\text{O}$ groups points to a higher contribution of such functions in Murchison. Since the relative abundance of aliphatic carbons linked to heteroelements is similar in both samples, the higher contribution of carboxyls and carbonyls should account for the difference in the O/C ratio from elemental analysis (0.18 for Orgueil and 0.22 for Murchison).

4. Chemical structure of the insoluble fraction of Orgueil and Murchison

The chemical structure of the insoluble organic fraction of meteorites was previously mostly examined via chemical and thermal degradation and a pronounced aromatic nature is widely accepted for this fraction. The present ^{13}C NMR results confirm this feature and indicate that aromatic carbons are by far the predominant form of carbon in the insoluble fraction of both Orgueil and Murchison. Another important conclusion from the present NMR and FTIR data is the occurrence of a high branching level for the aliphatic moieties especially in the case of Murchison.

The size of the aromatic moieties is still a matter of controversy. Several studies, including that previously using CP/MAS ^{13}C NMR [25], pointed to the occurrence of large polyaromatic units in Orgueil and Murchison insoluble organic fraction. Results from stepwise combustion and isotopic measurements in Murchison were also interpreted as reflecting the presence of highly condensed polyaromatic cores (8–60 rings) [4]. A highly condensed nature was also suggested by Hayatsu et al. [14] who assumed, from results of thermal and chemical degradation, a composition of the insoluble organic fraction of Murchison intermediate between that of chars and high volatile Illinois bituminous coal. (An average size of the polyaromatic units was estimated as 30–34 rings by Derenne et al. [32] for this coal after a model proposed by Dubois Murphy et al. [33].)

The present NMR data and especially (i) the

high number of carbon atoms not detected by CP/MAS even through variable t_c experiments and (ii) the high proportion of non-protonated carbons among the aromatics may reflect the presence of large polyaromatic units. However, these data are also consistent with another type of structure, based on highly substituted rather small aromatic units. Such a structure also exhibits a high level of non-protonated carbons (even when located at the edges of the polyaromatic units) and most of the aromatic carbons are too far from protons to be detected.

Moreover, this highly substituted structure is supported by some previous results obtained via chemical and thermal degradation. For Orgueil insoluble organic matter: ozonolysis yielded benzenetri- to pentacarboxylic acids suggesting an aromatic but not highly condensed structure [6,10] and stepwise pyrolyses yielded C_1 to C_4 alkylbenzenes and naphthalene [13]. The same products along with phenols were obtained from hydrous pyrolysis of Orgueil and Murchison HF/HCl residues by Sephton et al. [3,19] who concluded that this fraction comprises small aromatic units connected by aliphatic and ether bridges. Hayatsu and Anders [7] also proposed for Murchison a structure based on four ring clusters linked by short aliphatic chains ($\leq C_4$), ethers and sulfides. Saponification of the insoluble organic fraction of Murchison which yielded alkylbenzenes, phenols and benzenecarboxylic acids afforded similar conclusions [11]. Depolymerization (with trifluoroacetic acid) and oxidations (with HNO_3 , $Na_2Cr_2O_7$, alkaline CuO and photooxidation) released aromatic hydrocarbons up to fluoranthene and various heteroaromatic compounds [14,15]. Direct volatilization in the mass spectrometer source generated from Murchison several aromatic hydrocarbons including phenanthrene or anthracene [11], 430°C pyrolysis and time of flight mass spectrometry (TOFMS) afforded similar compounds [12,14]. Recently, TOFMS performed on Murchison HF/HCl residue sublimated at 600°C yielded polyaromatic hydrocarbons dominated by benzo-pyrene, perylene or benzo-fluoranthene and extending up to trimethylcoronene thus pointing to the occurrence of aromatic moieties comprising up to seven rings [34].

5. Cosmochemical implications

5.1. Chondritic and interstellar signatures of organic polymers

Both meteoritic macromolecules and interstellar organic matter are enriched in deuterium. The enrichment factor of the former is 15–40 ($D/H = 375\text{--}1000 \times 10^{-6}$; [4,5,35,39]) relative to the protosolar hydrogen ($D/H = 25 \times 10^{-6}$; [36]). This enrichment would be a relic of the interstellar chemistry: in cold molecular clouds of the interstellar medium, deuterium enrichment is also observed in the gas phase, for smaller (up to C_5) organic molecules. In interstellar environments, the fractionation is triggered by hydrogen isotopic exchange between ions and molecules in the gas phase, fast even at 10 K [37,38]. The overall isotope exchange rate is mainly controlled by the intensity of the UV flux from the stars surrounding the clouds. Although it is not possible to spectroscopically determine the D/H ratio of interstellar organic macromolecules, if they result from an in situ polymerization of small organic compounds, all these organic species should exhibit D/H ratios similar to those measured in the gas phase.

D/H ratios in interstellar organic species (mean value 2×10^{-2} ; [39]) are much higher than those determined for meteoritic compounds. Therefore, there is a marked isotopic gap between solar system and interstellar organic macromolecules. This gap may reflect an isotopic exchange either between organics and hydrogen in the turbulent protosolar nebula [40], or between organics and water during hydrothermalism on the meteorite parent body [41]. During this exchange, organic matter D/H ratio systematically tends to decrease since the protosolar water D/H ratio is lower than in organics [39]. Accordingly, the organic macromolecules studied here possibly underwent thermal maturation in hydrogen or water. We nevertheless argue in the following that, as far as the chemical structure of the insoluble organic matter is concerned, such a maturation was probably insignificant.

Organic matter maturation yields aromatic moieties with increasing size whereas the present

NMR data and previous thermal and chemical degradation point to the occurrence of rather small and highly substituted aromatic moieties in Orgueil and Murchison. Even if a late isotopic re-equilibration in the solar nebula or during the parent body hydrothermalism cannot be excluded, such an isotopic exchange did not markedly affect the pristine chemical bonds of the meteoritic organic matter. Therefore, as discussed below, the chemical structure of chondritic macromolecules must bear important information on organosynthesis mechanisms in space.

5.2. Global pathways for organosynthesis in space

Previous observations on IR absorption bands around 3.4 μm pointed to pronounced similarities between carbonaceous grains in the diffuse interstellar medium and insoluble meteoritic macromolecules, especially for relative abundances of CH_2 and CH_3 [1,2,21]. This IR interstellar signature has now been found in numerous astrophysical environments and its relation with the column density of SiO suggests that the synthesis of these organic macromolecules in space occurs at the surface of the grains [2]. As previously emphasized [21], two features characterize the interstellar IR spectra: (1) an equivalent intensity of the asymmetric stretching mode absorptions for CH_3 (2960 cm^{-1}) and CH_2 (2920 cm^{-1}) yielding a $[\text{CH}_3/\text{CH}_2]$ ratio of ca. 0.6 and (2) the absence of aromatic stretching mode absorption (3040 cm^{-1}).

The present NMR study also indicates rather high aliphatic CH_3/CH_2 ratios, especially in Murchison (0.52 vs. 0.23 for Orgueil). This high level of branching is a common feature in the interstellar medium as revealed by the typical pattern of the 2960–2920 cm^{-1} bands, markedly different from the pattern of terrestrial organic matter. This should reflect differences in synthetic pathways: it is well-known that terrestrial organic matter results from enzyme-directed biosyntheses. Thus, polymethylenic chains commonly occurring in numerous lipids are biosynthesized via an elongation–decarboxylation mechanism through successive additions of C_2 units. In contrast, in the interstellar medium, reactions probably occur in the gaseous phase at the surface of grains and

involve radical intermediates hence the formation of a number of more stable branched compounds. Therefore, the probability to find long polymethylenic chains in this medium is low hence relatively high CH_3/CH_2 ratios. Moreover, the present NMR and FTIR data revealed that aromatic moieties comprise a relatively low proportion of protonated carbons thus suggesting they are highly substituted. Aromatic moieties in such materials are usually considered to be derived from cyclization and aromatization of some linear chains. However, the more branched the linear chains, the more substituted the aromatic rings. The high branching level in the aliphatic units is therefore fully consistent with the low level of protonation of the aromatic moieties.

The present data, along with previous results from FTIR spectroscopy and thermal and chemical degradation, lead to a chemical structure based on small highly substituted aromatic moieties for Orgueil and Murchison insoluble organic matter and give a basis for a model of organic synthesis in space: the insoluble matter would result from a statistical combination of all possible bonds involving CH_3 , CH_2 and CH radicals, producing both aliphatic and aromatic moieties. This model explains both the chemical feature of these meteoritic macromolecules and the typical FTIR signature of the interstellar medium. Organic material found in the interstellar medium and that incorporated in the most primitive objects of the solar system thus seem to share a common organosynthesis.

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