

On the origins of organic matter in carbonaceous chondrites

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Abstract

Carbonaceous chondrites, a sub-class of meteorites contain organic matter. This organic matter is a very complex mixture of various kinds of organic molecules together with a highly unsaturated polymer called kerogen. The origins of this organic matter remain a subject of active research. In the work described here, we focused our attention on volatile hydrocarbons. Ratios of heavy to light stable isotopes of carbon and hydrogen are known for this class of molecules. Comparisons between these values and the corresponding values obtained for samples resulting from Fischer-Tropsch-Type synthesis provide information about the origin of volatile hydrocarbons. The presolar origin is certainly a plausible scenario but the FTT synthesis remains a possibility.

INTRODUCTION

Meteorites are fascinating objects. They come from extraterrestrial space. They bring us messages about the Solar System as it was 4.6 billion years ago but, in some respect, we find ourselves in a position similar to Champollion's when faced with the Rosetta stone. We know that these messages contain information but we must find the key to the codes. We know that the messages are encoded in the languages of the planetologist, the chemist, the astrophysicist, the mineralogist, and we therefore know that only a joint effort on the part of specialists in these different disciplines can lead to the correct reading of the messages.

We will insist on the role of the organic chemist in such a joint effort. Indeed, the organic chemist has a role to play because organic molecules - organic matter - is present in various classes of meteorites. We are mainly interested in one particular class, - carbonaceous chondrites - but we will touch upon other extraterrestrial objects which contain organic matter, elemental carbon or carbides.

In 1987, we published a review article on Organic Matter in Carbonaceous Chondrites (ref. 1). One year later Cronin et al (ref. 2) also published a review article on the same subject, while the previous period was covered by the review article of Hayatsu et al (ref. 3), published in 1981.

A comparison of these three papers is interesting because it shows how the field is rapidly evolving and how our ability to read the messages is increasing in a very spectacular way.

In this paper, we will focus our attention on the recent literature.

We also will present original results, some of them have been obtained in collaboration with Doctors F. Pineau and M. Javoy of the Université de Paris 7, and Doctors J.R. Cronin and G.U Yuen of the Arizona University State (Tempe).

PRELIMINARY COMMENTS ON METEORITES, THEIR CLASSIFICATION, AND THEIR ORIGINS

By definition, a meteorite is an object of extraterrestrial origin found on Earth. In some cases the fall is observed, but in many cases the object is discovered either by chance or, more

and more frequently, as the result of a systematic search. The case of Antarctica is very illustrative of a systematic search leading to the discovery of 12,000 meteorites in approximately 20 years (ref. 4).

Meteorites are classified into four classes : chondrites, achondrites, stony-irons and irons. Each of these classes is divided into sub-classes. One of these sub-classes containing the so-called carbonaceous chondrites is itself divided into CI, CM, CO, CV type and the newly defined CK type (ref. 5).

These classifications are based essentially on petrological and mineralogical arguments.

Groups within a classification scheme conventionally contain 5 or more members. Frequently, a new meteorite does not fit the criteria which would enable it to be precisely classified. The Lewis Cliff 85332 meteorite (ref. 7) and the Yamato-82168 (ref. 8) are examples of new kinds of carbonaceous chondrites.

Ordinary chondrites, a sub-class of chondrites, are the most abundant meteorites (ref. 6) and this result is fully confirmed by the systematic search done in the Roosevelt Country Basin, where 154 meteorites were recently discovered. Of the 68 meteorites sufficiently characterized, 66 are ordinary chondrites (ref. 9). It is generally considered that between 70 and 80 % of the modern falls are ordinary chondrites.

Some ordinary chondrites contain more than 1% of carbon, including possibly organic matter (ref. 10), but until now the major part of the studies performed on the organic matter in meteorites has concerned the carbonaceous chondrite sub-class (essentially the CI and CM types). The great majority of meteorites are fragments of larger extraterrestrial objects commonly called parent bodies and identified as asteroids but some meteorites are ejecta from the Moon, while others are ejecta from Mars. Some of them are perhaps comet fragments, and recently Brophy (ref. 11) made the audacious hypothesis that some meteorites could be the debris of other planetary systems (extrasolar origin).

From time to time the Moon, Mars, the Earth and the other planets in the Solar System collides with impactors of various sizes. The frequency of these impacts was higher at the beginning of the Solar System during the accretion period. As a dramatic example of such an impact it should be borne in mind that the Moon is most probably the direct consequence of the impact on the young Earth of a Mars-sized object (ref. 12). These impacts were, and indeed are still able to eject matter from the colliding objects and this phenomenon is at the origin of the presence of fragments of the Moon, Mars and asteroids on Earth.

A diamond typical of carbonaceous chondrites was discovered recently in a meteorite which was in fact a sample of the lunar regolith (ref. 13). This result fully agrees with what is known from the direct study of the samples of regolith collected on the Moon during the Apollo missions : 1 to 2 % of the lunar regolith is carbonaceous chondrite debris i.e. meteoritic matter. It is interesting to observe that diamond survived the heat and pressure effects associated with the shock of the impactor on the lunar surface. Much more surprising and fascinating if confirmed is the presence of organic matter (and not only elemental carbon) in a martian meteorite (ref. 14). This meteorite - EETA 79001 - was discovered in Antarctica and contains ~ 1,000 ppm of organic material. This result is highly interesting when we remember that the Viking molecular analysis experiments showed that if organic matter is present in the martian soil, it remains below the 1 part per billion level (ref. 15).

However interesting a discussion on organic matter or elemental carbon in lunar and martian meteorites may be, we will focus our attention on carbonaceous chondrites which, themselves, are very probably fragments of asteroids located in the asteroid belt between Mars and Jupiter. The asteroid belt is structured in various regions so defined because the asteroids populating these regions have different reflectance and spectrophotometric properties. One of these regions is characterized by a population maximum in 3 astronomic units (1 AU = 150 million kilometres i.e. the average Earth-Sun distance) containing a majority of C asteroids. Some of these C asteroids are probably the parent bodies of carbonaceous chondrites (ref. 16). The asteroids located in the various regions of the asteroid belt are numerous. An estimate of the total number of asteroids larger than one kilometre in diameter varies between several hundreds of thousands and one million (ref. 17). Around 15,000 main-belt asteroids have been discovered, and we know the circum-solar orbits of 5,000 of them (ref. 17). These asteroids collide from time to time and fragments generated by the collisions may intersect the Earth's trajectory, becoming meteorites if they are recovered and remaining meteors if they are only observed as fireballs, for example. Numerous studies of meteors and meteoritic trajectories lead to the conclusion that, indeed, they come from the asteroid belt (ref. 18). This has

recently been demonstrated for the Murchison, meteorite one of the most famous carbonaceous chondrites. The Murchison meteorite - a CM2 carbonaceous chondrite - fell in Australia on the 28th of September 1969 at 10.58 am (Australian Eastern Standard Time). The fall was observed by various witnesses and the orbit was reconstructed from their descriptions. It appears that the aphelion corresponded to approximately 3 AU, i.e. a point which is located at the concentration maximum of the C-asteroid belt (ref. 19).

The dynamic mechanisms by which meteorites can be delivered to the Earth have been discussed by Wetherill et al. (ref. 18).

The accretion of the parent bodies of carbonaceous chondrites took place in a zone of the early nebula between the silicate-rich inner and the gas-rich outer planet zones. Moreover, due to their size and distance from the Sun, these parent bodies had never reached high temperatures leading to differentiation phenomena. Carbonaceous chondrites can therefore be described as the best testimony of the state of matter in the solar nebula when accretion occurred i.e. 4.5 billion years ago. It is interesting to observe that CI carbonaceous chondrites have an elemental composition which matches the composition of the solar photosphere very well. If we except a few light elements like Li, Be, B, which are destroyed by nuclear reactions in the Sun, the data obtained for CI are within $\pm 9\%$ of the solar values (ref. 12, 20). This does not mean that the matter constituting carbonaceous chondrites had not been modified during the long life-time of the parent bodies or even during the life-time of meteorites as isolated objects in interplanetary space, but it does mean that these modifications took place isochemically.

In the past, the Solar Nebula was described as a very hot (a few thousand degrees) cloud of gas, totally homogenised at the atomic level and therefore also isotopically homogeneous but in 1973, Clayton et al (ref. 21,22) provided the first unambiguous proof that a state of complete homogeneity had never been reached.

During these last twenty years, a lot of new experimental proofs has been added, showing that not only has the solar nebula never been homogeneous, but that it has never been hot in all of its parts (ref. 23).

THE SOLAR NEBULA AND ITS PARENT INTERSTELLAR CLOUD

The Solar Nebula itself was probably a fragment of an interstellar cloud similar to the cold, dark, dense interstellar clouds that we can see today (ref. 24).

T-Tauri stars (as the young Sun probably was) are known to form in this kind of environment, where gases coexist with dust particles. A lot of organic molecules have been detected in cold dark clouds like the famous cyanopolyacetylenes $H(C_2)_nCN$, formic acid, methanol and many others.

The cold dark clouds have a molecular content which is different from that observed in giant molecular clouds like Sgr B2 or OriKL. In this latter case energy phenomena can lead to higher temperature chemistry and efficient grain evaporation due to the formation of massive stars (ref. 24). The temperature of Orion's hot core is so high as 100-200 K, while the ridge temperature is 50-100 K (ref. 25). The situation is different in a cold cloud where the temperature remains around 10 K with densities ranging up to 10^4 - 10^5 molecules per cubic centimetre. The principal component of such a cloud (like TMC-1 or L 134 N) is obviously H_2 , but it is important to point out how large the excess of H_2 is with respect to all the other molecules except, of course He (which represents 25 % in mass).

Table 1 gives some recent values of $N(\text{species})/N(H_2)$ where N is the number of molecules (ref. 24)

TABLE 1 : Chemical abundances in TMC-1, relative to H_2 (ref. 24)

	$N(\text{species})/N(H_2)$
C_3H_2	1.10^{-8}
CH_3OH	$0.2.10^{-8}$
$HCOOH$	$< 0.02.10^{-8}$
H_2S	$< 0.05.10^{-8}$

The concentration of the HC₉N cyanopolyacetylene is of the order of $0.03 \cdot 10^{-8}$ (ref. 25).

The only "abundant diatomic" molecule is CO with a relative abundance of $3 \cdot 10^{-5}$ in TMC-1 (ref. 25).

The molecules adsorbed in grains are less well-known due to the difficulty in analysing diffuse bands deriving from solids. In his survey of the problem Draine (ref. 26) considers that solid water (absorption band at $3.1 \mu\text{m}$), presumably hydrocarbons (characterized by their $3.4 \mu\text{m}$ band) and silicates (band near $10 \mu\text{m}$) are grains constituents.

Grains play a role in the carbon chemistry which takes place in interstellar clouds, but neither on-grain, nor gas-phase chemistry will be reviewed here in detail (readers interested in this subject will find a lot of information in the review articles by Herbst (ref. 27) and Zinner (ref. 28) and in the book by Duley and Williams (ref. 29)).

The only point we would like to stress here is the deuterium enrichment which characterizes many organic molecules found in interstellar clouds. It is useful to express the D/H ratio of a particular sample relative to a reference sample (standard) in terms of its δD value, defined as :

$$\delta\text{D} = \left[\frac{(\text{D}/\text{H})_{\text{sample}}}{(\text{D}/\text{H})_{\text{standard}}} - 1 \right] \times 1000 \quad (1)$$

The standard generally used is the mean ocean water standard (SMOW) with $(\text{D}/\text{H})_{\text{SMOW}} = 15.576 \times 10^{-5}$. A positive value of δD means that the deuterium content of the sample is higher than the deuterium content of SMOW. Formula analogous to (1) are used for other isotope pairs like $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$.

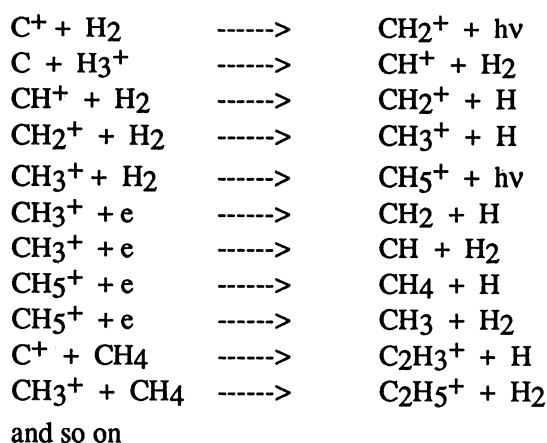
Table 2 gives the δD values for different systems (ref. 28).

TABLE 2 : Observed D-enrichment (ref. 28)

	D/H ($\times 10^5$)	$\delta\text{D}_{\text{SMOW}} \text{‰}$
SMOW	15.6	0
Interstellar H ₂	0.5 to 2	-968 to -872
Solar Nebula H ₂	2 ± 1	-872 ± 65
Jupiter (CH ₄)	3.6 ± 1.2	-769 ± 77
Interstellar molecules		
HCN	80-680	$4.1 \cdot 10^3$ to $4.3 \cdot 10^4$
HCO ⁺	40-10,000	$1.6 \cdot 10^3$ to $6.4 \cdot 10^5$
HNC	> 50,000	> $3.2 \cdot 10^6$
C ₃ H ₂	2,900	$1.9 \cdot 10^5$

Table 2 includes a δD value for the Solar Nebula. Obviously this value is deduced indirectly (ref. 28). Nevertheless, the relationship between the Solar Nebula and the dark cloud is obvious. Indeed as pointed out previously, a presolar nebula is a fragment of a cold molecular cloud which has become unstable and given rise to the accretion phenomenon. Following the cold cloud fragmentation process, the nebular lifetime was short: only a few million years (ref. 30). The formation of the Sun probably started before the accretion of the giant planets which, itself, predated the formation of the terrestrial planets. This very complex phenomenon was discussed recently by Taylor (ref. 12). During accretion the nebula remained cool, but was also subjected to localized events involving heating, local mixing, high pressure and so on. During all its T-Tauri phase, the young Sun was characterized by strong activity. Solar winds were probably very intense : during some eruptive phases, the mass loss was perhaps as high as 10^{-5} solar mass per year. In this highly dynamic environment, the constituents of the dark cloud gases and dust-particles were obviously modified, but not as much as previously hypothesized. The D-enrichment observed in many interstellar molecules can be explained by gas phase chemical reactions taking place at a very low temperature between ions and neutral molecules. These reactions have been discussed by many authors (see ref. 27, 28, 29 and references cited therein).

The synthesis of hydrocarbons may start from two precursors : C and C⁺.
The following scheme has been proposed (27) :



Such a scheme, founded on gas-phase simulation experiments, cannot be considered as being fully demonstrated.

Nevertheless, the D-enrichment can be explained if we remember that D is essentially present as HD. A reaction like

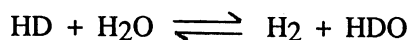


is exoenergetic due to zero point energy differences between the deuterated and non-deuterated species: $\Delta E/k = 140\text{K}$ (ref. 29)

Computer simulations taking into account a large number of possible reactions have been performed by various authors. As an example, we would like to cite the work by Tielens (ref. 31). In his model he took into account 1,530 gas-phase ion-molecule reactions together with 440 grain surface reactions. This kind of simulation leads to calculated enrichment factors which have the correct order of magnitude. We can conclude that even if we do not know all the details of the enrichment processes exactly, we can explain semi-quantitatively why many interstellar organic molecules are D-rich. So we can safely assume that the Solar Nebula contained gaseous D-rich molecules and perhaps also dust particles or grains covered by a mantle of D-rich molecules.

The deuterium content of water in the Solar Nebula can be inferred from the D/H ratio of terrestrial water ($15.5 \cdot 10^{-5}$), which is very similar to the ratio measured in the OH-bearing materials in meteorites (ref. 32).

Such a D-content can be explained by the isotopic exchange reaction (ref. 32)



as already suggested twenty years ago by Geiss et al (ref. 33)

The Solar Nebula, a fragment of a dark cloud submitted to local instabilities, local heating and local high pressure events, was therefore a very inhomogeneous medium with various hydrogen reservoirs of different sizes and different D/H ratios. A large reservoir of molecular dihydrogen with a D/H ratio around $2 \cdot 10^{-5}$ and two smaller D-rich reservoirs. One of these reservoirs contained complex organic molecules with D/H ratios as high as 10^{-2} and the other, made up of water, was characterized by a D/H ratio around $15 \cdot 10^{-5}$.

In the case of carbon, we can also predict isotopic fractionation in the dark cloud during the synthetic steps leading to complex molecules. Direct observations of the $^{13}\text{C}/^{12}\text{C}$ ratio for various interstellar molecules and simulation experiments lead to the conclusion that, as can easily be predicted, the isotopic fractionation is much lower for carbon than for hydrogen but nevertheless remains significant (ref. 28).

A similar conclusion is obtained in the case of nitrogen (ref. 28). Together with gaseous molecules and grain molecules, the Solar Nebula also contained dust particles of silicon carbide (SiC) graphite, diamond and carbyne synthesized in the vicinity of one (or more) red giant. The particles had been injected into the dark cloud and remained unchanged until the Solar Nebula stage.

Some of the SiC grains are ≥ 200 million years older than the Solar Nebula (ref. 34). These grains are found unchanged today, as minor components of meteorites, including carbonaceous chondrites. The study of these grains is very interesting and a great number of papers have been devoted to this subject in the very recent literature. Very anomalous $^{13}\text{C}/^{12}\text{C}$ ratios are observed in these grains with $\delta^{13}\text{C}$ values as high as 30,000 (ref. 35). In the case of carbon ($^{13}\text{C}/^{12}\text{C}$) standard corresponds to Pee Dee Belemnite (PDB) characterized by $^{13}\text{C}/^{12}\text{C} = 1.12372 \cdot 10^{-2}$ (1). Nevertheless, these grains represent only a very tiny amount of meteoritic matter, 6 ppm by weight, while organic matter is present at the 10^4 ppm level, for example (ref. 36). Interstellar graphite grains have also been detected at the few ppm level (ref. 36).

Diamond has been found in meteorites at the 500 ppm level (37), but in this case the $^{13}\text{C}/^{12}\text{C}$ ratio is within the terrestrial range. Nevertheless, their presolar origin is attested by the anomalous isotopic composition of xenon, krypton and nitrogen trapped in the diamond particles.

Since 1980, it has been speculated that carbynes i.e. the elemental carbon formed by the association of long linear carbon chains of the polyacetylene type, are present in meteorites (38). During the 80-90 period the existence of this new allotropic form of carbon was questioned by many authors, but very recently Gilkes et al (ref. 39) confirmed the presence of carbynes in meteoritic matter. These carbynes may also have a presolar origin (ref. 39).

It is interesting to observe that until now the C_{60} Buckminster fullerene has not been detected either in interstellar space or as constituent of meteorites (ref. 38).

These carbons-containing dust-particles of presolar origin are generally the hosts of various noble gases trapped by ion implantation. These gases are frequently characterized by highly abnormal isotopic ratios which are proof of the presolar origin. The study of these grains therefore provides a lot of information on the latest stage of evolution of the dark cloud, and on nucleosynthetic pathways in red giants (particularly the s-process in AGB red giants, where AGB refers to Asymptotic Giant Branch). Complementary information on the nucleosynthetic pathways can be obtained via the study of the so-called Fun Type CAI inclusions found in carbonaceous chondrites (CAI = Calcium-Aluminium Inclusion) like Vigirano and Allende (ref. 40).

From the point of view of the origin of organic matter in carbonaceous chondrites, the discovery of SiC, graphite, carbyne and diamond grains provides additional proof that the Solar Nebula was a heterogeneous ensemble of isotopically distinct reservoirs characterized by isotopic abundances different from those of the average solar system. Many of these reservoirs were quantitatively small. This explains why the average composition of CI carbonaceous chondrites, for example, is very similar to the average composition of the solar photosphere. An average value is usually obtained for a 0.1 g-1 g sample. It is perhaps useful to remember here that 1 mg of micron-size grains contains approximately 10^9 grains (ref. 41) and that many SiC, graphite or diamond grains have a size of one to a few microns.

ORGANIC MATTER IN CARBONACEOUS CHONDRITES

As previously discussed in detail (ref. 1,2,3) various organic molecules have been detected in carbonaceous chondrites. Carboxylic acids, hydrocarbons, aminoacids, ketones, amines and many other classes of molecules have been detected. Table 3 (see reference 1 for the original references) gives an estimate of the total amount of some classes of organic molecules in the Murchison meteorite (CM2).

It is obvious that the kerogen - an ill-defined macromolecular substance - is by far the most abundant organic compound. It is highly unsaturated, with an approximate elemental composition equal to $\text{C}_{100}\text{H}_{48}\text{N}_{1.8}\text{S}_2\text{O}_{12}$ (ref. 28). Such a composition implies the presence of polycyclic aromatic moieties. Indeed, the C/H ratio is similar to what is observed for coronene. Moreover Murchison's insoluble carbon (kerogen) shows two broad signals in

TABLE 3 : Carbonaceous compounds in the Murchison meteorite (ref. 2)

	Relative Abundance* (by weight)
Kerogen	1.45.10 ⁻²
carbonate	1-2.10 ⁻³
monocarboxylicacids	3.10 ⁻⁴
amino acids	1-2.10 ⁻⁵
hydrocarbon (aliphatic)	1-3.10 ⁻⁵

* with respect to whole rock.

the ¹³C NMR spectrum, obtained by the CP-MAS technique on a partially demineralized sample (ref. 2). These two signals correspond to the Csp³ and Csp² atoms.

The aromatic units are linked by bridges (ref. 42) in a three-dimensional macromolecular structure similar to, but not identical to, type III terrestrial kerogen (ref. 2).

The isotopic characterization of kerogen material in the Murchison carbonaceous chondrite was performed mainly by Robert and Epstein (ref. 43), and more recently by Kerridge et al (ref. 44). In the context of the present paper it is interesting to observe firstly, that the isotopic composition of H released during combustion is always positive (D-enrichment) and secondly, that different δD values are obtained depending on the combustion temperature. This last result led Kerridge et al (ref. 44) to suggest the existence of different D/H values depending on whether the hydrogen atoms are aliphatic, aromatic or linked to oxygen. The prominent aliphatic component, labelled H(I) could apparently be characterized by an upper limit of the δD values of about 1800 ‰. On the other hand, the H(III) fraction from aromatic moieties would be relatively D-depleted, with an upper limit of δD equal to 400 ‰ (ref. 44). Another aromatic fraction H(II) also seems to be D-rich, with a δD value of 1,300 ‰. In the same work δ¹³C and δ¹⁵N values were also measured, but their variations are much smaller than those observed for δD. δ¹³C of the aliphatic carbon atoms associated with the heaviest H(I) fraction is positive (+7 ‰), while δ¹³C is negative for C(II) (-18.7 ‰) and C(III) (-22 ‰).

Interesting also is the estimation of the aliphatic C, which gives a value between 5 and 18 ‰.

These δD values observed for kerogen are considered by the authors to be a proof of interstellar origin. It means that the Murchison meteorite contains presolar matter, probably chemically modified but which had never been submitted to any process leading to a complete H exchange either with H₂, or with H₂O in the Solar Nebula. This absence of complete exchange with water is interesting and also surprising. Indeed, carbonaceous chondrites show evidences of aqueous alteration (ref. 45,46). This alteration is particularly ubiquitous in CM2 carbonaceous chondrites like Murchison, but even the CV3 Kaba carbonaceous chondrite - considered to be the least altered and thus as the most primitive of the carbonaceous chondrite, group - shows evidence of aqueous alteration (ref. 47). In this last case, the presence of Fe-bearing saponite is a definitive proof of this alteration. Indeed saponite is commonly observed on Earth as a hydrothermal alteration of basalts and gabbros at temperatures below 100 °C. On the basis of similarities between the alteration of the mineral matrix and the chondrites, Keller et al (ref. 47) consider that the alteration occurred in the parent body and not in the protosolar nebula before accretion. It is difficult to imagine that what is true for the less altered parent body of a CV3 meteorite should not also be true for the parent bodies of CM or CI carbonaceous chondrites. Thus, the kerogen in Murchison, which had been present in the parent body since the beginning of accretion (kerogen and mineral matrix are intimately mixed) had most probably been in contact with water molecules which were not D-rich. Aliphatic and even aromatic CH bonds are not easily interchangeable but we must take into account that the contact between organic and water molecules occurred in the presence of phyllosilicates which are efficient catalysts in many reactions.

The kerogen itself was probably not present as such in the dark cloud even if the composition of the grain mantles remains essentially unknown and this means that what may be involved is a

macromolecular material with some similarities to kerogen (ref. 48, 49). The molecular composition of dark clouds involves a far-from-equilibrium situation with highly oxidized molecules coexisting with highly reduced ones. It is difficult to say if the pre-kerogen material (mantle grains and gaseous molecules) was more or less hydrogenated than kerogen itself. Some of the small molecules of the pre-kerogen remain probably unchanged or slightly modified and were trapped in the kerogen itself. They constitute, perhaps, a part of what is today the extractable molecules (hydrocarbons, carboxylic acids, amino acids and so on) of carbonaceous chondrites. Later, during the hydrothermal processes taking place in the parent body, the kerogen itself was, probably, partially degraded during events perhaps similar to what happens during the catagenesis of a terrestrial sediment. It is interesting to note that catagenesis takes place at a moderate temperature (50-200°C) (ref. 50). During the catagenesis of terrestrial sediments, 85 % of the oil and 75 % of the gas are formed together with a highly unsaturated mixture called asphalt (ref.50). We do not establish a strong parallelism between catagenesis and the evolution of the kerogen in the parent body, but it is tempting to suggest that the extractable molecules from carbonaceous chondrites have multiple origins i.e.

- 1) interstellar molecules trapped during accretion
- 2) molecules synthesized during accretion itself.
- 3) molecules deriving from a catagenesis-like process
- 4) terrestrial contaminants (clearly demonstrated by Cronin and Pizzarello (ref. 51) in the case of non volatile hydrocarbons
- 5) cleavage products resulting of the extraction procedures

Scenario 2) was the most popular for many years (ref. 1,2,3). The Fischer-Tropsch Type synthesis (FTT) (starting from CO (or eventually CO₂ and H₂) and the Urey-Miller (U-M) synthesis (starting from CH₄ and various other reduced gases) were generally considered to be the best candidates. A lot of work was done to substantiate FTT versus UM or vice versa. Also, we performed FTT simulation experiments (see the next section). Nevertheless, scenarios 1) and 3) have recently become more and more popular due to the discovery that not only kerogen is D-rich, but also aminoacids (with δD values as high as 2500 ‰ (ref. 52)) and organic acids (ref. 53,54) with δD values between +377 and +697 ‰). It is interesting to observe that δD values follow the sequence :

amino acids > kerogen > carboxylic acids.

Nevertheless, it is also important to observe that δD values for the same meteorite (Murchison) vary from sample to sample as a consequence of samples inhomogeneities.

THE VOLATILE HYDROCARBONS CASE

Volatile hydrocarbons are present in the Murchison carbonaceous chondrite as free molecules trapped in the mineral matrix and (or) the kerogen. In 1985 when we started our work on the origins of organic matter in meteorites, we decided to consider the origins of hydrocarbons first. This choice was dictated by the fact that Yuen et al (ref. 55) had just described the isolation of C₁-C₅ hydrocarbons by the freeze-thaw disaggregation of a Murchison sample. This smooth method did not lead to a complete extraction of volatile hydrocarbons, which therefore appeared as a minor component of the organic matter (ref. 54). The indigenous character of the molecules was demonstrated by the $\delta^{13}C$ value which was clearly different from terrestrial ones. As was shown later (ref. 51), higher hydrocarbon analysis was difficult due to contamination problems.

In 1985 and as mentioned previously, the origin of small molecules like volatile hydrocarbons was considered very generally in the context of FTT or UM synthesis (ref. 1,2,3). The measurement of Yuen et al (ref. 55) of $\delta^{13}C$ in the hydrocarbons series prompted us to perform a series of simulation experiments in order to see if the trend observed ($\delta^{13}C$ decreasing from CH₄ to C₅H₁₀ in chondritic hydrocarbons) (see figure 1) could be reproduced experimentally. The $\delta^{13}C$ variation in the series is small (below 30 ‰). Indeed, Freeman et al (ref. 57) have observed a $\delta^{13}C$ difference between two sedimentary terpenoids : norpristane ($\delta^{13}C = -23$ ‰) and 17 β (H), 21 β (H) -30-norhopane ($\delta^{13}C = -65$ ‰). This difference is larger than the one

observed between meteoritic CH_4 and C_5H_{10} . Considering the dependence of $\delta^{13}\text{C}$ with respect to the experimental conditions during simulation experiments (for example the conversion factor) and the fact that the meteoritic hydrocarbon sampling might be skewed (ref. 54), it is difficult to draw any definitive conclusion on the basis of a comparison between figures 1 and 2, even if our results (figure 2) are in satisfactory agreement with results obtained by Yuen et al. (ref. 56)

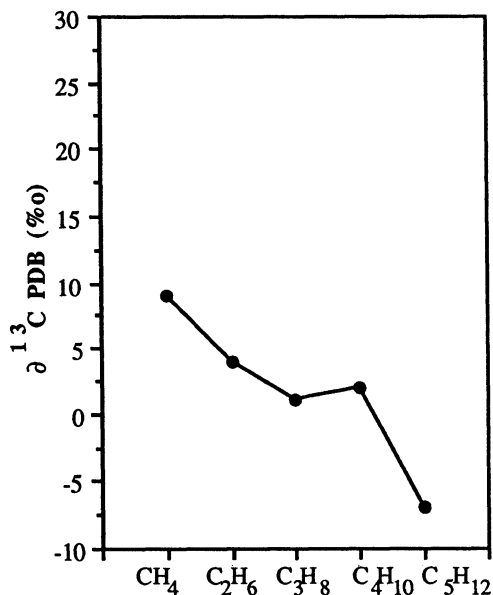


Fig. 1: Isotopic composition of individual aliphatic linear saturated hydrocarbons (CH_4 to $n\text{-C}_5\text{H}_{12}$) (From ref. 55).

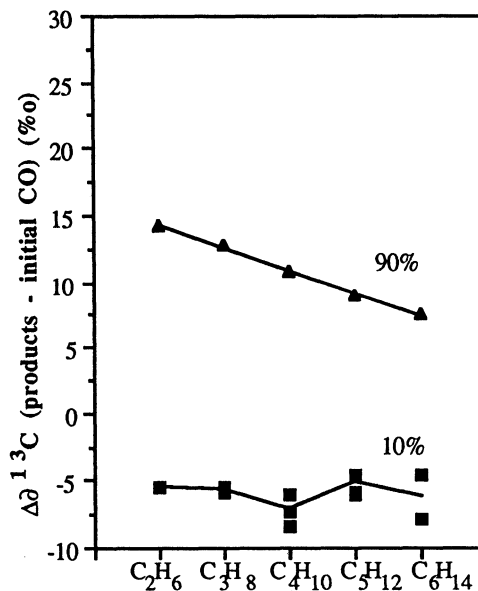


Fig. 2: FTFT experiments on reduced magnetite ($\text{CO}/\text{H}_2 = 1$; $T = 523\text{K}$; $P_{\text{in}} = 1,5 \text{ atm}$) reaction time: 6h and 26h corresponding to 10% and 90% of conversion.

An isotopic effect as described in figure 1 may have a kinetical as well as a thermodynamical origin. Indeed, an equilibration process between isotopomers is conceivable a priori. We performed statistical mechanics calculations and we were able to demonstrate that except for the CO/CO_2 case, the δD values observed cannot be explained by equilibration processes.

When the $\delta^{13}\text{C}$ values are not an unambiguous signature of the origin of volatile hydrocarbons, it is necessary to use other information. On the basis of what has already been said, it is clear that δD values would be welcome. These data remained unknown until very recently but are now available. Indeed the unpublished results of Krishnamurty et al (ref. 54) show that the δD values for volatile hydrocarbons analyzed as a mixture range from -72 to +410, depending on the technique used to recuperate the hydrocarbon mixture. The freeze-thaw disaggregation method gives a negative value, while an acid treatment of the matrix leads to the release of D-rich hydrocarbons. The more positive δD values are associated with more positive $\delta^{13}\text{C}$ values. It means that the average value of $\delta^{13}\text{C}$ goes from 0 ‰ for the freeze-thaw disaggregation sample to +17 ‰ for the acid treated one. The authors conclude that a D-rich reservoir (also ^{13}C rich) contributes increasingly to the gas release, and that this D-rich reservoir is directly related to D-rich interstellar molecules processed during the accretion process.

From these very recent results, it appears that the $\delta^{13}\text{C}$ values depicted in figure 1 are probably not representative of the total content of volatile hydrocarbons. On the other hand, an acid treatment could lead to the partial hydrolysis of the kerogen, and it is possible that a fraction of hydrocarbons released under more drastic extraction conditions does not exist as such in the meteorite. Whatever the true situation is, it now becomes necessary to see if these very recent results rule out the possibility that the Fischer-Tropsch Type synthesis during the accretion

process contributed to the volatile hydrocarbon content found in the Murchison meteorite. A survey of the literature on the Fischer-Tropsch synthesis shows clearly that D-enrichments were indeed observed, especially in the case of CH₄. For example, Kellner et al (ref. 58) have observed an inverse isotopic effect (D₂ faster than H₂) in the case of the CH₄ formation (kinetical factor of 1.5). The isotopic effect decreases with the number of carbon atoms in the chain, and becomes "normal" for hydrocarbons heavier than pentane. This work shows how important the role of the catalyst is: Ru/SiO₂ does not give the same results as Ru/Al₂O₃.

From this survey, we can conclude that an isotopic effect, qualitatively similar to that observed for hydrocarbons in the Murchison meteorite can be obtained during a Fischer-Tropsch synthesis.

Faced with this conclusion, we decided to perform FTT experiments using experimental conditions which are more similar to those existing in the Solar Nebula and using a reduced Fe₃O₄ powder as a catalyst. The very preliminary results obtained during two completely independent experiments show that, with respect to the δD value of the starting H₂, FTT synthesis leads to a D-enrichment which is equal to + 303 ‰ and + 346 ‰ respectively. It proves that FTT synthesis can be associated with D-enrichment which is of the same order of magnitude as that observed in volatile meteoritic hydrocarbons. Indeed, with respect to protosolar H₂, the D-enrichment of meteoritic hydrocarbons ranges from 800 per mil to 1,300 per mil and nothing proves that the experimental 340 per mil corresponds to an upper limit.

GENERAL CONCLUSIONS

Our ability to perform more accurate analysis on increasingly smaller meteoritic samples gives us a better insight on how complex the problem of the origins of organic matter in carbonaceous chondrites is. A meteoritic sample is highly inhomogeneous and this inhomogeneity reflects not only the fundamental inhomogeneity of the Solar Nebula, but also the complexity of the accretion and hydrothermal alteration processes of the parent body.

Twelve years ago, the majority of scientists involved in the cosmochemistry of carbonaceous chondrites were convinced that most of the organic matter was synthesized during accretion.

Progressively, the interstellar origin of organic matter has become the favoured scenario, and it has been demonstrated that at least a part of organic matter has indeed an interstellar origin. Nevertheless, it would be dangerous to reject the "synthesis during accretion" scenario too rapidly. H₂ and CO were probably the most abundant gases in the Solar Nebula. Reactions between these two gases were not necessarily prevented. A D/H isotopic effect of few hundredths is not always the signature of a very low temperature process. Simulation experiments may probably never lead to a clear-cut conclusion because the chosen experimental conditions are neither identical, nor perhaps even similar to the (not so well-known) conditions prevailing in the solar nebula 4.6 billion year ago. So, our simulation experiments do not prove that the FTT synthesis is at the origin of the volatile hydrocarbons in the Murchison carbonaceous chondrite, but from our point of view, they do demonstrate that enrichments of a few hundredths with respect to H₂, are not per se, a proof of extrasolar origin. When δD and $\delta^{13}C$ values are not completely out of the range with respect to terrestrial values and when other observations (like the presence of trapped noble gases in diamond) are not available to support a presolar origin, it remains necessary to examine all the other possibilities. Nothing precludes that a part of volatile hydrocarbons has a presolar origin while an other part (CH₄ for example) was synthesized during accretion.

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