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DID METEORITES BRING THE INGREDIENTS OF LIFE ?

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Abstract. Carbonaceous chondrites are commonly considered as the most primitive meteorites and they accreted the primordial constituents of the Solar System. They are called "carbonaceous" due their high amount in extraterrestrial organic compounds. These compounds mainly formed 4.5 billion years ago by processes involving non-biologic chemical reactions, as shown by their isotopes. Among these molecules, several are considered as of biological interest because they could participate to processes equivalent to present day metabolic pathways in living cells; they include sugars, amino acids or nucleobases. These molecules being brought continuously on Earth, they may have induced the appearance of Life on Earth and/or could have an influence on the primitive forms of life.

Keywords: carbonaceous chondrites, organic molecules, astrobiology

1 Introduction

Carbonaceous chondrites are the witnesses of the formation of our solar system. They have trapped the remnants of the parent molecular cloud and the first components formed during the different phases of the solar system evolution. Since 4.56 Ga ago, they have preserved these constituents from the intense modifications that resulted from planet formation. However, almost all carbonaceous chondrites have undergone parent body processes. Due to the rapid decay of short lived radionucleides like ^{26}Al, the temperature increased up to partial melting on some parent bodies, inducing a thermal metamorphism (or fusion) of the accreted components. On others, when ice was present, the temperature increase generated a fluid circulation leading to hydrothermal alteration. During this hydrothermal alteration, accreted organic precursors may have reacted to produce new molecules. Pre-accretion chemistry (in the molecular cloud or the protosolar nebula) associated with parent body secondary processes resulted in a large diversity of the organic content of hydrated carbonaceous chondrites (Gilmour 2003). In contrast, on chondrites showing thermal metamorphism, the organic material has been carbonized and the soluble and reactive organic material is almost entirely lost (Remusat et al. 2008). Hence, only the organic content in hydrated objects will be described here.

It must be noted that there is no molecular evidence of any biological processes in the formation of these molecules. It is commonly accepted that all the extraterrestrial organic molecules are formed by non-biologic chemical reactions, and that any molecule with a biological signature is a contaminant (Anders et al. 1964). However, the organic content of carbonaceous chondrites may have influenced the prebiotic chemistry on the early Earth.

2 Diversity of organic compounds in meteorites

Organic matter in carbonaceous chondrites can be spread in an insoluble macromolecule (Derenne & Robert 2010) and a complex suite of soluble organic molecules (Krishnamurthy et al. 1992; Kvenvolden et al. 1970). The total organic content may reach 4 wt.% in some chondrites, with the macromolecular carbon representing more than 75wt.%. As recently shown (Schmitt-Kopplin et al. 2010), the soluble organic content in carbonaceous chondrites is very diverse. The use of very high mass resolution techniques revealed the occurrence of 14,000 different molecules, containing C, H, O, N and S. These molecules can be divided in several classes (see table 1), including sugar derivatives(Cooper et al. 2001), amino acids (Kvenvolden et al. 1970) and nucleobases (Martins et al. 2008) being potential metabolic reactants and genetic information recorders.

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Table 1. Soluble organic compounds detected in Murchison and Tagish Lake, from Pizzarello et al. (2006).

Meteorite	Murchison		Tagish Lake	
Class	Concentration (ppm)	Compounds identified	Concentration (ppm)	Compounds identified
Aliphatic hydrocarbons	> 35	140	5	12
Aromatic hydrocarbons	15-28	87	> 1	13
Polar hydrocarbons	< 120	10	n.d.	2
Carboxylic acids	> 300	48	40	7
Amino acids	60	74	<0.1	4
Hydroxy acids	15	7	n.d.	n.d.
Dicarboxylic acids	> 30	17	17.5	18
Dicarboximides	> 50	2	5.5	9
Pyridine carboxylic acids	> 7	7	7.5	7
Sulfonic acids	67	4	> 20	1
Phosphonic acids	2	4	n.d.	n.d.
N-heterocycles	7	31	n.d.	n.d.
Amines	13	20	< 0.1	3
Amides	n.d.	27	<0.1	1
Polyols	30	19	n.d.	n.d.
Imino acids	n.d	10	n.d.	n.d.

Amino acids are emblematic organic compounds in meteorites. They are often cited as possible prebiotic molecules for the origin of life and are known to be indigenous in meteorites since the 70s (Kvenvolden et al. 1970; Lawless et al. 1972). To date, about 80 amino acids have been detected in CI, CM and CR chondrites; many of them have no terrestrial counterparts (Martins & Sephton 2009). Their abundance varies between meteorites from less than 1 ppm in some CI up to 250 ppm in some CR2 (Pizzarello & Holmes 2009). Amino acids in meteorites have from 2 to 8 carbon atoms; all the possible isomers are present. The distribution of amino acids differs from one meteorite to the other. For instance, in Murchison, glycine $>$ α-amino-isobutyric acid $>$ alanine, whereas in Orgueil β-alanine $>$ glycine $>$ γ-amino-butyric acid. Branched chains are more abundant than straight ones. Moreover, α, β and γ amino acids can be detected, with an abundance order $\alpha > \gamma > \beta$.

3 Enantiomeric excess and possible origin of homochirality on Earth

The question of chirality will only be addressed through the amino acids, however, it has been suggested to also occur in the insoluble macromolecule (Kawasaki et al. 2006) and in hydroxy acids (Pizzarello et al. 2010). Amino acids in meteorites have been found to be racemic when they were firstly reported, leading to the unambiguous interpretation of their indigenity (Kvenvolden et al. 1970). Nevertheless, progresses in GC-MS and protocols for analysis of enantiomeric excess in the 80*s* allowed the report of small excess of the L-form of some amino acids in Murchison (Engel & Nagy 1982), though doubts about contaminations raised (Bada et al. 1983). The question of contamination was solved years later with the use of compound specific isotopic measurements of ^{13}C and ^{15}N (Engel & Macko 1997). This was further confirmed by the discovery of L-excess in non-protein chiral amino acids and in other meteorites (Cronin & Pizzarello 1997).

Enantiomeric excesses are variable among meteorites (Glavin & Dworkin 2009), and also inside the same objects (Pizzarello et al. 2003) but never exceed 18%. The hydrated meteorites exhibit higher excess, pointing to a possible amplification during aqueous alteration (Glavin & Dworkin 2009). The exact process by which this amplification would occur is unknown, but some chemical reactions, like the Soai reaction (Soai et al. 1995) exhibit the property to enhance enantiomeric excess. Nevertheless, some amino acids, like 2- and 3- amino-pentanoic acids for instance, are known to undergo racemization (i.e. chemical reaction resulting in a racemic or homogeneous distribution of the two enantiomers) under hydrothermal alteration. Parent body processes hence tend to complicate the picture by amplifying, for some amino acids, the asymmetry in the distribution and, in the meantime, erasing any inherited excess (from a preaccretional process) for some others.

The primordial origin of enantiomeric excess is also an opened question. Effect of UV circularly polarized light has been suggested to explain the observed excesses (Rubenstein et al. 1983). This hypothesis is being tested by laboratory experiments (Noorduin et al. 2009; Nuevo et al. 2006; Takano et al. 2007; Meierhenrich et al. 2010) but the source of the CPL at the vicinity of the early solar system still needs to be assessed. Other processes driven by chiral mineral surfaces (Fig. 1) have also been suggested to produce the enantiomeric excesses observed in carbonaceous chondrites (Glavin & Dworkin 2009). These enantiomeric excesses found in organic matter in chondrites may have been transferred to prebiotic molecules at the moment of the emergence of Life by various processes, including asymmetric catalysis (Blackmond 2004). This would have led to the appearance of homochirality, a strong property of terrestrial forms of life. Such hypothesis is difficult to prove, although laboratory experiments involving for instance the Soai reaction (Soai et al. 1995) have succeeded in creating homochirality during non-biologic and purely chemical reactions.

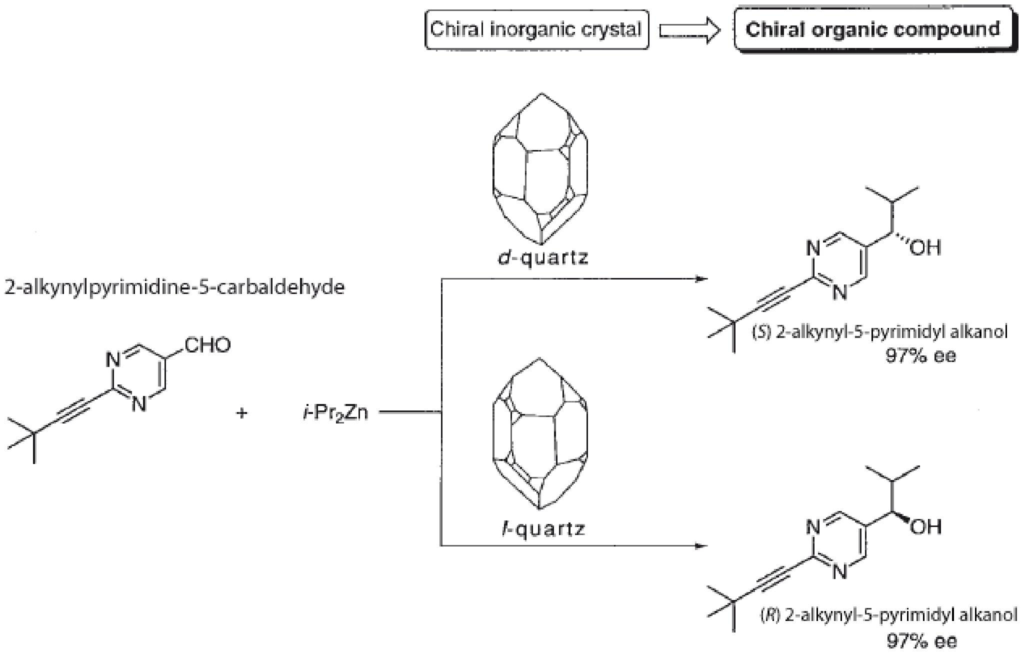

Fig. 1. Principle of the Soai reaction with the influence of a chiral inorganic mineral, from Soai et al. (2001)

4 Isotopic composition of soluble organic molecules in meteorites: understanding their origin

Organic molecules in carbonaceous chondrites are often enriched in heavy isotopes of C, N or H compared to their terrestrial counterparts. This has been used to discard contamination in many studies. Moreover, isotopic composition can be used to constrain the synthetic processes.

Amino acids constitute the best documented case for isotopic characterization in meteorites. In Murchison (Pizzarello et al. 2004), N isotopic composition seems homogeneous with δ^{15}N = 60 ‰(compared to around 1‰in terrestrial proteins), whereas in the two CR2 LAP02342 and GRA95229, it is more heterogeneous and δ^{15}N ranges between 70 and 130 ‰(Pizzarello & Holmes 2009). δ^{13}C is variable (Pizzarello et al. 2004), with values ranging from -6 to +50‰(terrestrial values from -35 to -25‰). Amino acids are usually enriched in ^{13}C by 40‰compared to the other extraterrestrial soluble organic compounds except the carboxylic acids (Gilmour 2003). For C isotopes in α-amino acids, it must be noted that branched chains have higher ^{13}C content than straight ones; this may sign a secondary addition of the methyl groups. Moreover, δ^{13}C decreases with the carbon number; this has been interpreted as the result of a C addition process in the formation of the carbon chain. Amino acids have high δD, indicating low temperature chemistry during the formation of the carbon chain (Sandford et al. 2001). In Murchison Pizzarello & Huang (2005) reported δD up to 3500 ‰(i.e. $D/H=701\times10^{-6}$). Pizzarello & Holmes (2009) measured even higher values in GRA95229 (CR2 chondrite): $\delta D=$ 7245 ‰($D/H=1284\times10^{-6}$). Like for C isotopes, D distribution is heterogeneous among amino acids. There is no clear trend or correlation with any molecular parameter, indicating a complex origin for the extraterrestrial amino acids fraction. It must be noted that the 2-methyl amino acids and branched chains tend to have higher D/H than 2-H amino acids and straight chains.

The correlation between the distribution of amino acids and hydroxy acids has led to the suggestion that amino acids were synthesized by Strecker-cyanohydrin synthesis (Cronin et al. 1995). Indeed, this reaction can form, from aldehyde or ketone precursors, α-amino acids and α-hydroxy acids that will have parallel distribution. This reaction requires HCN and water as co-reactants. But this reaction can not produce the non α-amino acids and other mechanisms like hydrolysis of lactams and Michael addition has been proposed to account for the β- and γ- amino acids (Cronin & Chang 1993). Molecular properties and isotopic ratios of both the insoluble macromolecule and the amino acids rule out an origin from the hydrolysis of the macromolecule (Remusat et al. 2005). Molecular and isotopic data on extraterrestrial amino acids thus indicate a complex origin for this fraction, with superimposition of preaccretion reactions and secondary processes. So far there is no simple mechanism adopted to explain the molecular distribution of amino acids or their isotopic compositions.

5 Conclusions

Carbonaceous chondrites contain a diverse suite of molecules that could constitute the seeds of life on Earth. However this remains debated and no laboratory experiment has proven that the organic content in chondrites could induce the emergence of life. It is nevertheless sure that the chondrites infall on the early Earth has released organic molecules in the prebiotic oceans. Interestingly, organic matter in chondrites may produce spheres (Deamer 1985) that could have helped the formation of the first cell membranes (Deamer et al. 2002). As shown in Figure 2, carbonaceous chondrites also contain hollow organic globules (Nakamura et al. 2002) that could be templates for the formation of the first chemical reactors that could have then evolved into living cells.

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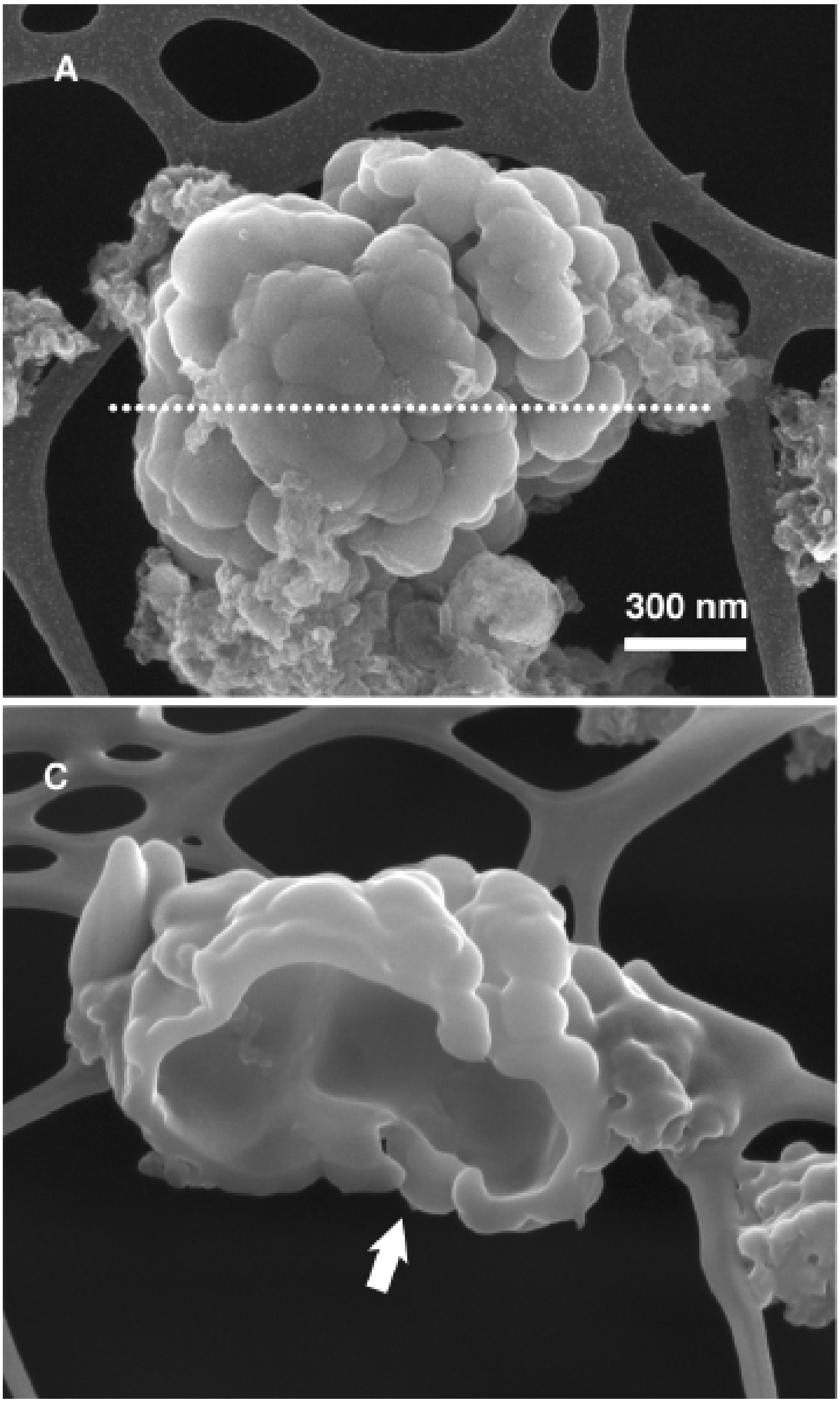

Fig. 2. Top: Image of nanoglobules found in carbonaceous chondrites, from Garvie et al. (2008). **Bottom:** cross section.

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