CHEMICAL EVOLUTION AND METEORITES: AN UPDATE

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Abstract. Carbonaceous chondrites are a primitive group of meteorites, which contain abundant organic material and provide a unique natural record of prebiotic chemical evolution. This material comprises a varied suite of soluble organic compounds that are similar, sometimes identical, to those found in the biosphere, such as amino acids, carboxylic acids, and sugar derivatives. Some amino acids of this suite also show L-enantiomeric excesses, and suggest the possibility they may have contributed to terrestrial homochirality by direct input of meteoritic material to the early Earth. This optical activity appears to be limited to the subgroup of α-methyl amino acids which, although not common in the extant biosphere, would have been well suited to provide the early earth with both enantiomeric excesses and means for their amplification by subsequent chemical evolution. We can also envision this exogenous delivery of carbonaceous material by meteorites and comets as having coincided with the endogenous formation of prebiotic precursors and influenced their evolution by complementary reactions or catalysis.

Keywords: amino acid, carbonaceous chondrite, chemical evolution, enantiomeric excess, exogenous delivery

1. Introduction

The idea of chemical evolution is a defining model in Exobiology. As first introduced independently by Oparin and Haldane in the 1920s, it proposes that the onset of planetary life was preceded by the abiotic formation of simple organic precursors and their subsequent evolution into increasingly complex molecules which ultimately yielded life. In more general terms, and to include newer astrophysical and cosmochemical data, it refers to the long cosmic history of the biogenic elements (H, C, O, N, S, and P; Wood and Chang, 1985), which have been shown to form numerous and complex abiotic organic molecules throughout interstellar, nebular, and planetary processes. Together with the observation of a terrestrial phylogeny that evolved from much simpler organisms, chemical evolution appears to offer a rationale for the proposal of a chemical continuum from abiotic chemistry to the precursors of life's molecules. Although corroborated by remote observations and coherent cosmogenic theories, to date, this chemical evolution has found a direct experimental scrutiny solely through the analyses of carbonaceous chondrite meteorites. They have provided a natural record of organic prebiotic chemistry in the early solar system as found in a planetary setting and at its closest to the onset of life.

2. Carbonaceous Meteorites

Carbonaceous chondrites (CC) are a group of primitive stony meteorites which display a solar-like elemental composition depleted only, to limited degree, of the most volatile elements H, C, O, and N. These meteorites are rare, 37 falls have been recorded since 1806, and are classified in several subgroups on the basis, inter alia, of water content, hydrous phases, and inclusional differences. All contain organic carbon, which consists of an abundant and varied suite of organics that may range in complexity from low molecular weight soluble compounds to insoluble macromolecular material that resembles kerogen.

This acid-insoluble material constitutes the larger portion (70–99%) of CC carbon and contains also lesser amounts of H, O, N, and S, 'presolar' grains, such as graphite, and silicon carbide. It is a complex residue, which is structurally and isotopically (Kerridge *et al.*, 1980) heterogeneous and is obtained only after extensive extraction and demineralization of the meteorite powders. It is of obvious interest to the understanding of the complexity and range of chemical evolution but has, nevertheless, resisted detailed characterization and is still poorly understood. So far, the analyses of the macromolecular solid have been limited to nuclear magnetic resonance (NMR) spectroscopy (Cronin *et al.*, 1987; Gardinier *et al.*, 2000; Cody *et al.*, 2002) and to its pyrolytic (Shephton *et al.*, 1999) or oxidative degradation (Hayatsu *et al.*, 1980) which have provided just an overview of its carbon content (NMR) and the identification of some of its constituent parts. Of the four meteorites analyzed so far, the most detailed analysis has been accomplished by Cody *et al.* (2002) for the Murchison meteorite. It shows a solid composed of two main constituents, an aromatic and an aliphatic component both with a wide range of respective functions, and having several oxygen containing groups as, for example, carboxylic and ether functions. The hydrous pyrolysis of samples that had been extracted but not demineralized (Gilmour *et al.*, 2001) showed several aromatic species which are dominant in the meteorite solvent extracts, raising the possibility of a relation between the soluble and insoluble material.

Still, no definitive and comprehensive structure for the insoluble carbon has yet been given to satisfactorily answer the many questions remaining about the history of this material and the relationship(s) between its constituents. For example, are the major aliphatic and aromatic constituents of this carbon integrated in an inclusive structure or independent? Can the material, if subjected to alteration that would realistically mimic parent body processes, produce some of the soluble organics we see in meteorites or is it truly kerogen-like and an end-product? These and more are still unanswered questions, which will require further and extensive analytical work.

Our understanding is more precise for the soluble organic content of CC, which represents up to 20% of total carbon in some of these meteorites (Figure 1). A soluble carbon fraction is found in the CI, CM, and CR chondritic subgroups (named after the representative meteorites for the type: Ivuna, Murray, and Renazzo, re-

spectively) where it can be present as an abundant, complex, and varied suite of organic compounds which includes low molecular weight species, such as amino acids and hydrocarbons. A good example is offered by the Murchison meteorite, a CM which fell in 1969 in Australia and is one of the most rich in soluble organics of the CC analyzed to date; its carbon distribution and molecular abundances are listed in Table I. As the table shows, most of the classes of meteoritic compounds are also common in the biosphere and several of these have identical terrestrial counterparts. Organic compounds in meteorites, however, display some common characteristics that differentiate them from biomolecules, these are: complete structural diversity, abundance decline with increasing chain-length within homologous series, and a predominance of branched chain isomers. Overall, their molecular composition appears to fulfill the expectations of abiotic processes governed by purely physico-chemical processes and contrasts with the structural specificity characteristic of biomolecules. Typical in this respect are the meteoritic amino acids, a diverse suite of over seventy compounds, compared to only twenty major amino acids that make up the whole of terrestrial proteins (Cronin *et al.*, 1988; Cronin and Chang, 1993). Notwithstanding this random distribution, however, the list in Table I also allows us to conclude that abiotic chemical evolution, as represented by some CC meteorites, already comprises an abundant inventory of the low molecular weight organics and monomers contained in terrestrial biomolecules.

One trait of structural specificity that at least some chiral meteoritic compounds appear to share with biomolecules is that of enantiomeric selection. Interestingly, enantiomeric excesses (*ee*) had been searched for since the first analysis of the Murchison meteorite (Kvenvolden *et al.*, 1970). The finding there of amino acids that were approximately racemic, including some of those common in terrestrial proteins, had helped establish these compounds as the product of abiotic syntheses and not contamination. The attempts that followed to detect *ee* in meteoritic amino acids (Engel and Nagy, 1982; Engel and Mako, 1997) remained frustrated by the many possibilities of terrestrial contamination (Bada *et al.* 1983; Pizzarello and Cronin, 1998). Indigenous L-*ee*, however, appear now to be established (Cronin and Pizzarello, 1997; Pizzarello and Cronin, 2000; Pizzarello *et al.*, 2003) for a sub-group of α-amino acids which are rare or unknown in the biosphere, the α-methyl-α-amino acids. These *ee* have been described for both Murchison and Murray amino acids (Pizzarello and Cronin, 2000) and can reach a magnitude of up to 15% (Pizzarello *et al.*, 2003). Since it is generally believed that life would be impossible without the exclusive one-handedness of its molecules, which is required for the three-dimensional assembly and function of biopolymer, these findings of optical activity in meteoritic amino acids allow us to extend our assessment of prebiotic evolution in meteorites as one that includes properties intimately associated with life, such as chiral selection.

TABLE I

Carbon distribution in the Murchison meteorite

Form		Total C (%)
A.	Interstellar grains:	2
	Diamonds (400 ppm)	
	SiC (7 ppm)	
	Graphite (< 2 ppm)	
	Fullerenes (≥ 400 ppm)	
B.	Carbonate minerals	2–10
C.	Macromolecular (insoluble) carbon	70–80
D.	Organic compounds (soluble)	10–20 .

Amino acids [b]	Amides [b]
Carboxylic acides [c]	Amines [b]
Dicarboxylic acids [b]	Alcohols [b]
Hydroxy acids [b]	Aldehydes and ketones [b]
Phosphonic acids [a]	Aliphatic hydrocarbons [b]
Sulfonic acids [d]	Aromatic hydrocarbons [b]
Basic N-heterocycles [a]	Polar hydrocarbons [c]
Purines and pyrimidines [a]	Sugar alcohols and acids [b]
Pyridine carboxylic acids [a]	

[a] >1 ppm, [b] >10 ppm, [c] >100 ppm, [d] >1000 ppm

2.1. THE ORIGIN OF METEORITE ORGANICS

The origin of meteorite organics has been the subject of much interest and debate in terms of both the physicochemical processes and the locales involved in their formation. Two models were proposed after the fall of the Murchison meteorite, one hypothesis was that of a Fisher Tropsch type (FTT) catalytic synthesis of organics from simple gases (CO, H_2, NH_3) in a cooling nebula. A second one envisioned organics synthesis in a reduced planetary atmosphere by the energetic production, recombination, and ultimate reaction in water of radicals (see Cronin and Chang, 1993 for a review). Both these early theories fell short of matching the molecular and/or isotopic distribution of organics later found in meteorites. In retrospect, however, we also find they suffered by oversimplification, in that both ideas tried to limit the complex and, likely, lengthy formation of organics in meteorites to just one locale or pathway.

Our current understanding of the synthesis of soluble compounds in carbonaceous chondrites is that of a multi-step process in which organic precursors were formed in the interstellar cloud, incorporated with many volatiles into icy plan-

etesimals, and upon aqueous processing produced the variety of compounds we find in meteorites. By relating them to cold interstellar chemistry, this model appears able to account for the high deuterium and ^{13}C content found in meteorite organics as well as for the CM and CI petrologies, where hydrous phases are found (Cronin and Chang, 1993). In the case of α-amino and α-hydroxy acids, a specific pathway of formation from aldehydes and ketones, HCN, water, and ammonia (the Strecker synthesis, Peltzer and Bada, 1978) appeared confirmed by the detection in Murchison water extracts of imino acids, compounds expected from such reaction (Pizzarello and Cooper, 2001).

However, some recent findings have raised questions about the overall inclusiveness of this theory also. Tagish Lake is a CM meteorite that fell in the winter of 2000 on a frozen lake of the Yukon Territory of Canada. Both his fall and retrieval were quite exceptional in that the meteorite was left only a few days at subfreezing temperatures before being collected by an amateur geologist who, aware of the possibility of contamination, proceeded to store it frozen and protected. Recent analyses of this pristine meteorite (Pizzarello *et al.*, 2001) have found that its organic composition, while poor in the majority of soluble organics observed in the Murchison meteorite, contained two distinct groups of compounds, the pyridine carboxylic acids and the dicarboxylic acids, which are practically identical to those of Murchison. These findings have suggested that the synthetic processes of organic matter in primitive meteorites may have been multiple and distinct and that the various soluble organics of carbonaceous chondrites, or at least groups within the suite, may be the result of separate synthetic pathways. That is, we have to think of some processes (interstellar, nebular, planetesimal, or some combination thereof) which eventually yielded in Tagish Lake dicarboxylic acids and pyridine carboxylic acids with the precise molecular and isotopic distribution as in Murchison (Pizzarello and Huang, 2002) but to the exclusion of other Murchison soluble organic species. Moreover, some of the Tagish Lake compounds, which are present, as aliphatic n-alkanes, carboxylic acids, and sulfonic acids, display a definite linear chain preference and a preponderant abundance of few lower homologues of each series. This appears to contradict the likelihood of precursor species derived from radical and/or ion-molecule reactions and would point instead to catalytic processes. The sites where these processes took place could have been planetary, nebular, as well as a combination of the two.

These analyses lead to the commentary that nebular processes, which are largely unknown, may have been under-represented in the interstellar-parent body formation hypotheses of meteorite organics. The relatively 'gentle' planetary aggregation processes that appear to have produced the primitive and undifferentiated meteorites, especially meteorites with low density as Tagish Lake, would leave ample time for reactions of organic precursors on nebular grains or small aggregate of grains. Here, reactions of less volatile interstellar molecules could take place, as those of dinitriles to dicarboxylic acids (Pizzarello *et al.*, 2001), while volatile species, as the aldehydes and ketones precursors to amino acids, would be lost. On these grains

and upon warming we can also conceive that some catalytic reactions of the Fisher Tropsch type (Pizzarello, 2002) were possible and produced the unusual soluble organic distribution we find in Tagish Lake.

The findings of *ee* in some Murchison and Murray amino acid has also required us to revisit the possible synthetic scenario for these compounds as one that ought to include symmetry breaking. The first hypothesis that was proposed for the causation of *ee* in meteorites was that of an asymmetric photolysis of meteorite organics by UV circularly polarized light (CPL) irradiation during their synthesis (Rubenstein *et al.*, 1983; Cronin and Pizzarello, 1997; Engel and Macko, 1997). This proposal appeared to shift the locale of formation of the compounds, or at least of meteoritic amino acids, to the interstellar medium, since it is likely that an asymmetry-causing radiation would have been shielded in the meteorite parent bodies (Pizzarello and Cronin, 2000).

Recent analyses (Pizzarello *et al.*, 2003), however, have obtained data that were unexpected in the context of this hypothesis and again challenge our detailed understanding of the formation of amino acids in meteorites. The study found hat *ee* for these compounds can be larger than would be theoretically allowed (Balavoine *et al.*, 1974) if photolysis by UV CPL had been the only source of their asymmetry and also indicated that the distribution of non-racemic amino acids may correlate with the abundance of hydrous silicates. This work, therefore, while shifting back the likely formation of non-racemic amino acids to a planetesimal and/or nebular locale, raises the prospect of a possible mineral participation. The formation of primary asymmetric mineral phases and the possible influence they may have yielded on the asymmetry of meteorite organics is still undefined and will require extensive new studies.

In light of the many meteoritic studies which have been and are still being undertaken, it is reasonable to conclude that meteorite organics represent the product of long and complex formation processes that combined, to various extent and degrees, interstellar, nebular, and planetary abiotic syntheses.

3.   Meteoritic Chemical Evolution and the Origin of Terrestrial Life

Finding ample proof in meteorites, and several other cosmic environments, of an extensive and varied organic chemical evolution does not give any conclusive indication that the origin of terrestrial life was continuous within this evolution. Certainly, much of the abiotic chemistry which we have been recording may represent evolutionary dead-ends, just as many opportunities in biological evolution came to an end. Many origin of life theories are based, in fact, on the 'de novo' syntheses, and subsequent evolution, of simple organic molecules in an early Earth environment under favorable energetic conditions. This was in 1953 the thesis of the Miller-Urey hypothesis, with Miller (1955) giving later experimental proof of the syntheses of numerous organic species under 'possible primitive Earth condi-

tions'. In spite of the fact that the Miller-Urey premise of a reducing early earth atmosphere has since changed (it is estimated now to have been non reducing, Owen *et al.*, 1979), this mechanism could still have produced several key organic precursors, such as formaldehyde. Another proposed model of molecular evolution is found in the 'hot' hydrothermal systems scenario, which predicts that organic compounds could be synthesized from simple inorganic precursors (e.g., CO_2, CO, metal sulfides) in geochemical environments and has accomplished some success in model experiments (see Shock, 1992; Simoneit, 1995; for reviews).

However, we do not know the evolutionary extent of these 'endogenous' pathways nor is our understanding of a prebiotic environment firmly established. For example, the fundamental question of how this planet became habitable i.e. accreted and retained water, is still hotly debated (see Morbidelli *et al.*, 2000 for a recent discussion). Given the detailed understanding of chemical evolution which we have obtained from meteorite analyses, it appears reasonable and relevant to speculate how this chemistry that we know well might have evolved on the early earth and contributed to the origins of life.

We can see this relation as a simple evolutionary analogy between meteorite and early terrestrial chemistry or as a direct delivery of meteoritic and cometary material to the early Earth. While the former requires too large a number of uncertainties to be debated, the exogenous delivery of asteroidal material is a possibility which is directly proven today and has been established indirectly for the Earth's prior history (Delsemme, 1992; Chyba and Sagan, 1992). Although estimates of this delivery may vary still, as different planetary formation models are proposed and constraints on the extent of chondritic input are determined (Drake and Righter, 2002), a large amount of meteoritic material has undoubtedly showered the Earth through time. If we limit our assessment of organic carbon input to the Earth to that delivered by meteorites today (Dodd, 1986), and in particular by the subgroups of CC containing soluble compounds which is ∼1% of the total influx, and estimate their average carbon content to be ∼2%, the amounts of organics accreted by Earth would be substantial ($\leq 8 \cdot 10^4$ Kg/year). After the primary collisional period, at ∼4 Gy, this amount would have been larger by at least two factors and during this time an influx of just one million years would have delivered to the Earth $\geq 10^{12}$ kg of organic carbon.

Did any of the meteoritic components, which were accreted by this delivery, hold any evolutionary advantage? α-methyl amino acids, generally unimportant in terrestrial biochemistry and not viewed as relevant to the origin of life, are abundant in meteorites and may be well suited for such a role. First, these meteoritic amino acids carry *ee* that can be as high as 15% and we may assume chiral selection to have been an initial evolutionary achievement. Although the early chemistry of bio-precursors may have been largely different from contemporary metabolism, today, homochirality is essential to the structural organization and function of both metabolic and information biopolymers necessary to life. Second, α-substituted amino acids do not racemize, a definite advantage in water chemistry on which,

again we have to assume, even early life was based. Conversely, α-H isomers readily racemize and would have 'catastrophically' lost any *ee*, however gained, in water (Bada and Miller, 1987). Third, it has been shown that polymerization accompanied by formation of regular secondary structures, as α-helices and β-sheets, can be an effective way to amplify modest initial *ee* (see Reiss and Cronin, 2003 for a review) and α-methyl amino acids are known to have strong helix inducing and stabilizing effects (Altman *et al.*, 1988; Formaggio *et al.*, 1995). Therefore, it is conceivable that meteoritic amino acids may have played a significant early role in the chemical evolution of homochirality and, perhaps, the biochemistry of a pre-RNA world.

Finally, it should be noted that, while most origin of life theories so far seem to have proceeded in parallel model tracks of either endogenous formation or exogenous delivery as possibilities of organic early molecular evolution, it is most likely that the two processes coincided and, to various extents, collaborated. In this 'collaborative' context, and amongst other effects by exogenous material, meteoritic amino acids could have provided the symmetry-breaking spark to pre-RNA evolution both directly, by the formation of homochiral assemblages, and indirectly, as catalysts or promoters of asymmetric syntheses leading to RNA.

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