

# ACCOUNTS of CHEMICAL RESEARCH<sup>®</sup>

APRIL 2006

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## The Chemistry of Life's Origin: A Carbonaceous Meteorite Perspective

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Received November 7, 2005

### ABSTRACT

Carbonaceous chondrite meteorites are primitive asteroidal fragments that contain organic carbon and offer a glimpse of the abiotic chemical processes that preceded the onset of life. Their organic material displays structures as diverse as kerogen-like macromolecules and simpler soluble compounds that range from polar amino acids and polyols to nonpolar hydrocarbons. Several of these compounds have identical counterparts in terrestrial biomolecules and some of the amino acids show a unique L-asymmetry, suggesting their possible contribution to terrestrial molecular evolution and the origin of biological homochirality.

### Introduction

Niels Bohr once remarked<sup>1</sup> "the existence of life must be considered as an elementary fact that cannot be explained, but must be taken as a starting point in biology." It was not a dismissive or general "vitalistic" comment but rather part of an optimistic lecture he gave in 1933 titled *Light and Life*, where he expressed confidence that the physical approach that had led to the understanding of atomic processes and light phenomena will help biology greatly. His statements were predictive in many respects. In fact,

Sandra Pizzarello was born in Venice (Italy) in 1933 and studied in nearby Padua, where she obtained a Doctorate in Biological Sciences. After a brief fellowship, she "stayed home" to raise a family of four children, and it took 15 years. She moved to the U.S. with this group and joined the Chemistry and Biochemistry Department of Arizona State University in 1977, where she still is a Research Professor. Her research has been devoted to the study of the organic material in carbonaceous chondrite meteorites with emphasis on the molecular, isotopic, and chiral characterization of their soluble compounds. More recently, she has focused on the study of the nonracemic amino acids of meteorites with compound-specific isotopic analyses, as well as model syntheses that would mimic their prebiotic catalytic activity and reactions.

molecular biology now offers a clear operational account of extant life, so much so that we may describe it in simplified chemical terms, for example, as a chemical process (metabolism and biopolymer synthesis) that is controlled by its products (protein and nucleic acids).<sup>2</sup> On the other hand, if we attempt to account for life's full evolutionary history, we find that the origin of the complex macromolecular chemistry that defines and sustains life is still not understood and much less amenable to simplification. Extant biopolymers are the structurally specific and stereochemically homogeneous products of a rigorous compositional selection. Their complexity and specificity are hard to reconcile with simple beginnings and their origin from an abiotic chemical environment remains unsolved.<sup>3</sup> Given the difficulty of the problem, origin of life studies have undertaken a multidisciplinary path and focused on the known natural phenomena of chemical and biological evolution, as well as model experiments, to elucidate the processes that could have led to, and away from, life's origin.

The former approach is based on the premise that the onset of planetary life was preceded by a lengthy period of abiogenic chemistry, during which the formation of increasingly complex molecules led to life's precursor molecules. The biogenic elements (C, H, N, O, and S) have a long cosmic history, during which complex organic molecules are known to have formed in diverse environments from the gas and dust of the interstellar clouds to small solar system bodies.<sup>4</sup> The primitive organic record of the early Earth was lost to ensuing geological and biological changes, but examples of the organic chemistry in the early solar system can be found recorded in carbonaceous chondrite meteorites. These are asteroidal fragments having an elemental composition that is only slightly altered from that of the sun and are considered to resemble closely primitive solar nebular aggregates. As their name indicates, they contain relatively abundant organic carbon and have reached the Earth repeatedly through the ages. Although cometary and asteroidal return samples may soon become available, so far, meteorites represent the only sample of chemical evolution available for direct analyses.<sup>5</sup> Their organic material, therefore,

offers a unique opportunity to answer critical questions concerning prebiotic chemical evolution, for example, how compounds important to extant biochemistry could have formed abiotically and whether we can reasonably assume that they were important to the origin of life. This Account gives an overview of the organic composition of carbonaceous meteorites and the possible involvement they might have had in the origin of terrestrial life upon delivery to the early Earth. Several extensive reviews have been written on the chemistry and mineralogy of these meteorites<sup>6–9</sup> that can be searched for further details and references.

## The Molecular Distribution of Meteorite Organics

The organic content of the rare carbonaceous meteorites (only 18 fell in the last 2 centuries) have been long known to chemists,<sup>10</sup> but it was the fall of two meteorites in 1969, the Murchison and Allende meteorites, and the unequivocal finding of indigenous amino acids in Murchison,<sup>11</sup> that spurred the comprehensive analyses of carbonaceous meteorite organics that continue today. The Murchison meteorite in particular has been extensively studied and found to contain organic material as diverse as kerogen-like macromolecules, simple soluble organic compounds, and, likely,<sup>12</sup> several unknowns. Macromolecular and acid-insoluble organic material (IOM) represents the larger portion (~75–99%) of the carbon in these meteorites and can be isolated only by dissolution of the more abundant silicates; it also contains trapped noble gases and “exotic” (presolar) material such as diamonds, silicon carbide, graphite, and fullerenes in fractional percent amounts.<sup>9</sup> Because it is insoluble, the IOM has been hard to characterize in detail at the molecular level and is known mostly through spectroscopic and pyrolytic analyses. Its structure contains condensed aromatic, hydroaromatic, and heteroaromatic clusters plus alkyl branching, functional groups such as OH and COOH, and alkyl chain, ether, and sulfide linkages.<sup>6</sup> However, the material is not homogeneous or entirely resistant to further treatment. Self-contained entities such as nanometer-sized flakes, solid or hollow spheres, and tubes of mostly aromatic composition imbedded in the main phase are observed by transmission electron microscopy and electron energy-loss spectroscopy<sup>13</sup> and represent some 10% of total IOM. Also, hydrothermal treatment at temperatures and pressures not too dissimilar from those found in some terrestrial undersea hydrothermal vents<sup>14</sup> releases from the IOM a variety of solvent<sup>15</sup> and water-soluble compounds.<sup>16</sup> The freeing of a water-soluble suite is particularly interesting because it was found to contain organic compounds, such as a series of dicarboxylic acids of C<sub>3</sub> to C<sub>17</sub> chain length, imidazoles, and branched pyridines that surpass in their structural range those observed in the meteorites prior to this treatment. These recent results, and the heterogeneity of elemental and isotopic composition established for the materials of several meteorites,<sup>9</sup> suggest that the insoluble organic portion of meteorites is com-

**Table 1. Soluble Organic Compounds in the Murchison Meteorite<sup>9</sup>**

Class of Compounds	ppm	<i>n</i> <sup>a</sup>
aliphatic hydrocarbons	>35	140
aromatic hydrocarbons	15–28	87
polar hydrocarbons	<120	10 <sup>c</sup>
carboxylic acids	>300	48 <sup>c</sup>
amino acids	60	75 <sup>c</sup>
imino acids <sup>47</sup>	nd <sup>b</sup>	10
hydroxy acids	15	7
dicarboxylic acids	>30	17 <sup>c</sup>
dicarboximides	>50	2
pyridine carboxylic acids	>7	7
sulfonic acids	67	4
phosphonic acids	2	4
<i>N</i> -heterocycles	7	31
amines	13	20 <sup>c</sup>
amides	nd <sup>b</sup>	27
polyols	30	19

<sup>a</sup> Number of compounds identified with reference standards or with unequivocal matching of compound and library mass spectra.

<sup>b</sup> Not determined. <sup>c</sup> Groups where larger number of compounds are recognized by their mass spectra in the absence of standards or library references.

positionally complex and may consist of several independent phases, perhaps of diverse origin that is not yet fully understood.

By contrast, the low molecular weight compounds found in the Murchison meteorite, which represent about 30% of its total carbon, have been extensively characterized.<sup>9</sup> They make up a complex suite that includes aliphatic and aromatic hydrocarbons; alcohols and carbonyl compounds; carboxylic, dicarboxylic, sulfonic, and phosphonic acids; amines, amides, and nitrogen heterocycles (Table 1). Most classes of these compounds show common characteristics of comprehensive structural diversity and isomerism, exponential abundance decline within the homologous series, and a predominance of branched chain isomers. Overall, their molecular composition appears to fulfill the expectations of abiotic syntheses governed by purely physicochemical processes and is quite dissimilar to the structural specificity characterizing biochemistry, a contrast that also vouches for meteorite organics' indigeneity. Typical in this respect are the meteoritic amino acids, a diverse suite of well over 80 linear and cyclic alkyl compounds of up to nine-carbon chain length, as compared to only 20 major amino acids that comprise terrestrial proteins.

Within this abiotic complexity, several meteoritic organic compounds have identical counterparts in terrestrial biochemistry, such as eight protein amino acids (glycine, alanine, valine, aspartic acid, glutamic acid, leucine, isoleucine, proline), pyridine carboxylic acids (e.g., nicotinic acid), glycerol and other sugar alcohols, and many others that can be commonly found in extant organisms. Moreover, while the vast majority of chiral compounds are found to be racemic, as expected of indigenous abiotic compounds, a subgroup of the meteoritic amino acids, the 2-methyl-2-amino acids, display small but significant L-enantiomeric excesses (*ee*) that are detected throughout the homologous series in the range of 1–15%.<sup>17–19</sup> These findings, relating to amino acids either unknown or rare

in the biosphere, have been shown to be minimally affected by contamination.<sup>19,20</sup>

Based on the organic composition of carbonaceous chondrites, one would conclude that abiotic syntheses are capable of yielding a large variety of organic compounds of remarkable complexity, some identical to biomolecules. Also the molecular asymmetry of some meteoritic amino acids presents evidence that the overall abiotic chemical process that produced meteorite organics may include a degree of chiral selection, a property known since the time of Pasteur to be intimately associated with life.

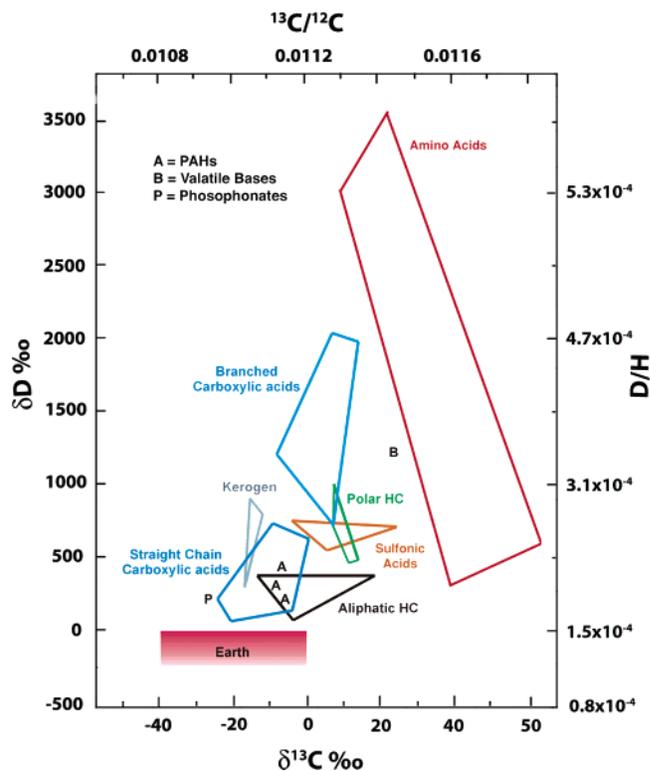
## The Origin of Meteorite Organics

Where and how were the organics of meteorites formed? As geochemists well know, the best diagnostic tool at our disposal for understanding the synthetic history of a natural compound is its isotopic composition; this is because the bond energies of isotopomers are different and lead to mass-dependent fractionation in reactions where bonds are broken and formed. This isotopic fractionation, which is proportional to  $e^{-\Delta E/RT}$ , will be larger the larger the mass ratio of the isotopic species (e.g., D/H = 2 compared to  $^{13}\text{C}/^{12}\text{C} = 1.084$ ) and the lower the temperature. The most dramatic example of fractionation under these conditions is that offered by the spectroscopic observations of the D/H ratios of molecules formed in the dense clouds of the interstellar medium, where temperatures are in the 10–30 K range. Over 100 such molecules have been described,<sup>21</sup> many of which show extremely high D/H ratios; for example, the average D/H ratio in terrestrial organic compounds is approximately  $1.5 \times 10^{-4}$ , whereas D/H ratios as high as 0.33 have been measured for deuterated formaldehyde in a star-forming region<sup>22</sup> (using the more common  $\delta\text{D}$  notation<sup>23</sup> as in Figure 1, the above comparison would be 0 to 384400).

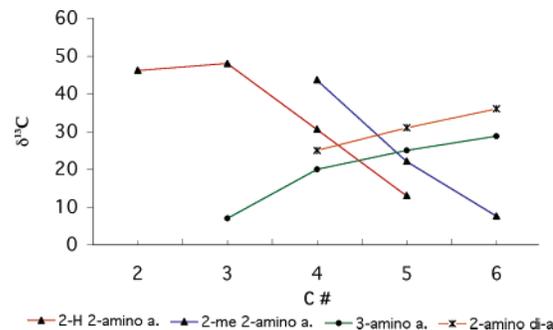
As expected, the measurements of the stable isotopes of the light elements also proved invaluable in the general understanding of the formation of meteorite organics, from first establishing their extraterrestrial origin<sup>24,25</sup> to the assessment of the possible processes involved in their formation.<sup>26</sup> The results obtained to date from carbon and hydrogen analyses of various classes of Murchison meteorite organics are shown in Figure 1, which summarizes the isotopic values obtained for groups as well as for individual molecules within a group of compounds.<sup>20,27–29</sup>

All meteorite organics are, to varying degrees, enriched in  $^{13}\text{C}$  and deuterium compared to terrestrial material; the analyses of N-containing compounds are not included in the figure but have shown enrichment in  $^{15}\text{N}$  as well, with Murchison total amines and individual amino acids reaching  $\delta^{15}\text{N}$  values of +93‰<sup>30</sup> and +50‰ to 184‰,<sup>18</sup> respectively. Because of the stable isotope enrichment of the light elements observed in cold interstellar clouds, these data and in particular the magnitude of the  $\delta\text{D}$  values have suggested a synthetic relation between meteoritic compounds and interstellar precursors.

Based on this view, a general theory has emerged in the past decade that proposes that cold asteroidal bodies



**FIGURE 1.** The carbon and hydrogen isotopic distribution of the organic material in the Murchison meteorite. Redrawn from Cronin and Chang<sup>27</sup> with added refs 20, 28, and 29.



**FIGURE 2.**  $\delta^{13}\text{C}$  values of Murchison amino acids versus carbon number.<sup>26</sup>

accreted with abundant volatiles, including water and deuterium-rich interstellar organics, which, upon warming by isotopic decay and a subsequent period of aqueous phase chemistry, yielded the various soluble organic compounds of these meteorites.

As Figure 1 shows, however, there is also a large spread of isotopic values for each compound series that accompanies the large compositional diversity of meteorite organics. For example, compound-specific isotopic analyses of meteoritic amino acids<sup>28</sup> (Figure 2) showed that the various isomeric subgroups of these compounds differ in  $^{13}\text{C}$  fractionation trends and were likely the products of diverse synthetic pathways. The 2-amino acids show a decline in  $^{13}\text{C}$  content within the homologous series, a trend similar to the one determined for monocarboxylic acids<sup>26</sup> that could result from a kinetically controlled growth of the compound alkyl chains by addition of single

moieties. Intramolecular differences in  $^{13}\text{C}$  between alkyl and carboxyl moieties, such as that measured for Murchison acetic acid,<sup>31</sup> could account for it as well but remain to be explored for amino acids. Dicarboxylic amino acids as well as the alkyl dicarboxylic acids<sup>32</sup> do not display similar  $^{13}\text{C}$  distributions, and it is speculated that these classes of compounds could derive from long chain partially unsaturated nitriles, which are detected in the cold dark clouds of the interstellar medium. From nitriles, the more direct dinitrile precursors for diacids could have derived, for example, by HCN addition, possibly at conditions that may have differed from those that produced the monocarboxylic and amino acid precursors.<sup>33</sup>

Compound-specific D/H analyses of the meteorites' amino<sup>20</sup> and monocarboxylic acids,<sup>29</sup> on the other hand, found that the deuterium distributions in these series of compounds are quite different from those determined for  $^{13}\text{C}$  and  $\delta\text{D}$  values vary not between subgroups or with chain length but rather within the subgroups and solely on the basis of their alkyl chain branching. For instance, the 2-amino acids (2-H as well as 2-methyl) do not display D-content declines as for  $\delta^{13}\text{C}$  and  $\delta\text{D}$  values average +1251‰ for the 2-H-2-amino acids and +3238‰ for the 2-methyl-2-amino acids. The 2-methyl-2-amino acid  $\delta\text{D}$  values are the largest ever recorded in the laboratory for extraterrestrial organic molecules and are not much lower than those determined remotely (spectroscopically) for interstellar molecules, whose lower range is +5400‰. These isotopic analyses also proved beyond doubt the extraterrestrial origin of the nonracemic amino acids in meteorites by establishing the same  $\delta\text{D}$  values for the L and combined DL enantiomers of isovaline (2-amino-2-methylbutyric acid). Isovaline is the most abundant nonracemic amino acid in the Murchison and Murray meteorites and may display L-*ee* of up to 15%.<sup>19</sup>

The isotopic data obtained for individual organic compounds in meteorites allow significant inferences in regard to their formation. The high  $\delta\text{D}$  values found for the branched amino acids suggest that some of the meteoritic amino acids, or their direct precursors, may have predated planetary processes and were formed in the cold environments of the interstellar medium. Such environments could also account for the chiral and molecular traits of these compounds, in that they could have provided asymmetric influences leading to *ee* (as discussed below) and an abundance of radicals and ions for the syntheses of highly branched species. The fact that high  $\delta\text{D}$  values are shared by amino acids that differ in structure and  $^{13}\text{C}$  composition, differences that suggest diverse synthetic histories, would further indicate that presolar regimes were capable of producing a large variety of amino acids or their precursors, that is, that molecules important to biochemistry were within the synthetic capabilities of such regimes. From a cosmochemical perspective, the organics in meteorites appear to link presolar chemistry, of which most carry the isotopic signature, and the biosphere, with which they share identical molecules.

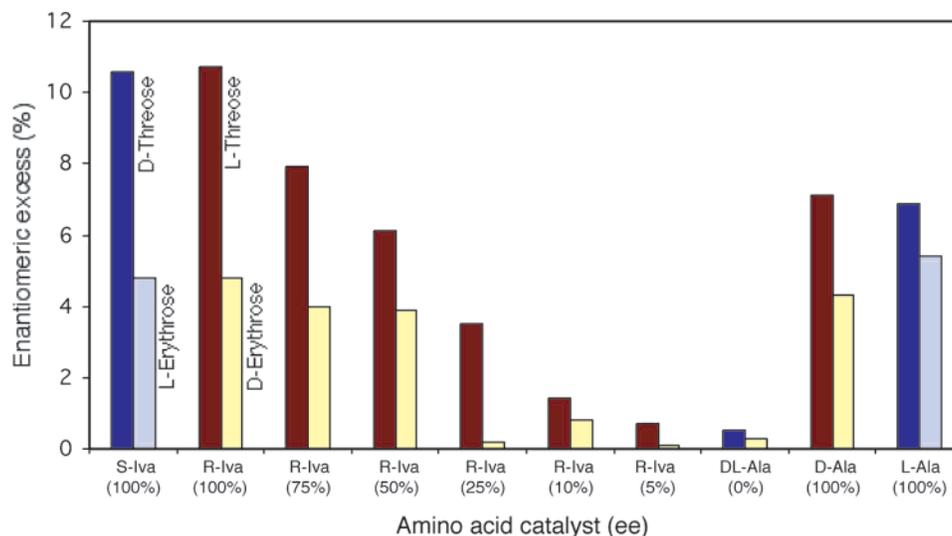
## Molecular Asymmetry in Meteorites and the Origin of Life

In broad terms, the finding that diverse biomolecules were attained abiotically in presolar environments is appealing and would encourage the suggestion of possible, even widespread, exobiology. Because extant life is based on the unique properties of carbon chemistry and the essential organic compounds that derive from it, it is reasonable to hypothesize that life elsewhere could likely be carbon-based as well. If so, we should expect common terrestrial biomolecules, for example, the amino acids, possibly including the extraterrestrial amino acids of the kind we find in meteorites, to be integral to the framework and catalytic functions of such life.

Based on the same findings, however, it might seem difficult to argue in favor of the hypothesis that abiotic organic compounds could have acted as “seeds” for prebiotic molecules, a thesis of prebiotic chemical evolution studies. In fact, the chemistry of meteorites appears to confirm what we have learned from several model experiments, which is that all abiotic chemical processes leading to the syntheses of prebiotically relevant organic molecules appear to do so within complex mixtures of compounds. The synthesis of sugars from formaldehyde and glycolaldehyde (the formose reaction<sup>2</sup>) offers just one of many examples. In these mixtures, the “desired” compounds may be a small fraction of the total and are, in the absence of catalysts, racemic. Because this randomness appears to be inherent to abiotic processes, an explanation of life's selection of chemically homogeneous polymers such as RNA from an abiotic mixture needs to invoke “some” evolutionary means of induction, selection, or catalysis.

Of late, several authors have addressed the predicament in relation to prebiotic sugars. For example, Müller et al.<sup>34</sup> showed that the phosphorylation of glycolaldehyde in a formose reaction would lead to condensation products enhanced in the pentoses and hexoses we find in the biosphere, while Zubay<sup>35</sup> and Ricardo et al.<sup>36</sup> demonstrated that the addition of lead or boron salts in the same reaction impedes the run-away formation of complex polymeric material. Following a different rationale, Springsteen and Joyce<sup>37</sup> demonstrated that the high reactivity of ribose, the RNA sugar, could have been an advantage in prebiotic mixtures if it led to sequestration into stable compounds, for example, ribose-cyanamide crystals. The common question these authors asked is whether early Earth environments or the chemical property of some biomolecule precursors could have helped in the choice of selected species for the ensuing molecular evolution toward the origins of life.

A different and more general question can also be asked, that is, whether there are in the *natural* samples of chemical evolution, such as we find in meteorites, any discernible traits that would match life's requisites or would indicate an opening toward specificity. The overwhelming importance of homochirality for terrestrial life and the uniqueness of molecular asymmetry in meteorites



**FIGURE 3.** Effect of amino acid catalyst *ee* upon the asymmetric synthesis of tetroses from glycolaldehyde (*S*- and *R*-Iva are equivalent to *L*- and *D*-2-amino-2-methylbutyric acid). Reprinted from S. Pizzarello, A. L. Weber, *Science* **303**, 1151 (2004).

as well as the similarity of configuration between terrestrial and some meteoritic amino acids suggest that molecular asymmetry could be an important prebiotic attribute in chemical evolution. Extant life is characterized by chiral homogeneity; not only are biopolymers rigorously composed of one enantiomeric form of their monomers (*L*-amino acids for proteins and *D*-sugars for RNA and DNA) but so are the chiral molecules involved in the myriad reactions of metabolism. Outside the biosphere, by contrast, the natural world offers several examples of enantiomorphs and enantiomers, such as the *d*- and *l*-quartz crystals, right- and left-handed circularly polarized light, and chiral molecules from uncatalyzed syntheses, but very few examples of excess of one over the other. As for *ee*, there are only two known natural cases: (a) the predicted energy difference between enantiomers of a chiral molecule due to parity violation during weak force interactions, which is estimated at  $10^{-11}$  J mol<sup>-1</sup> but has not yet been measured,<sup>38</sup> and (b) the *ee* we find in the amino acids of meteorites.

Enantiomeric excesses in meteorites are found within the  $\alpha$ -methyl amino acid series, favor the *L*-configuration, vary from 1 to 15%, and have an unknown origin. The first hypothesis proposed to account for these *ee*, that is, an asymmetric photolysis of meteorite organics by UV circularly polarized light (CPL) during their syntheses,<sup>39</sup> does not seem consistent with the data at hand<sup>19</sup> because isovaline's *ee* in meteorites (15%) extends beyond the theoretical boundaries set for amino acid decomposition by UV CPL.<sup>40</sup> It is still possible,<sup>40</sup> however, that photolytic processes may produce larger amino acid *ee* in conditions where large amounts of organic material was accumulated and subjected to repeat exposure to UV CPL, that is, by starting each time with small *ee* achieved previously, such as could be envisioned to occur as an interstellar cloud collapses during nebula formation.<sup>41</sup> Another possibility would be that the formation of amino acids in meteorites was secondary to that of asymmetric catalysts, residing either in the organic or in the mineral phases. In the case

of organics, the preferential photolysis of a racemic compound having a higher extinction coefficient than that of the aliphatic amino acids could have achieved greater chiral purity in the process and subsequently acted as an asymmetric catalyst.<sup>41</sup> In the case of minerals, crystallization often leads to spatially asymmetric structures, such as are seen in tartrates and quartz; in meteorites there could be similar opportunities for asymmetric morphologies. For example, magnetite (Fe<sub>3</sub>O<sub>4</sub>) has been described<sup>42,43</sup> in the Orgueil meteorite in a barrel-shaped stack of disks that appears connected at the center and suggests a spiral structure. These are all possibilities that we are just starting to explore.

Could the limited molecular asymmetry found in meteorites set off an abiotic mixture on the path of prebiotic evolution? We do not know, but this is a question worth pursuing. For example, we have explored the possibility that the nonracemic amino acids of meteorites could have acted as catalysts during early Earth molecular evolution and transferred their asymmetry to other prebiotic building blocks such as sugars. We studied the synthesis of tetrose sugars from glycolaldehyde under the catalytic influence of two nonracemic amino acids, alanine and isovaline. The method, involving the reaction of glycolaldehyde in a buffered water solution, at 50 °C or less, and for a few hours, represented a realistic prebiotic model. We found<sup>44</sup> that under these aqueous conditions, the aldol condensation of glycolaldehyde produced tetroses whose chiral configuration was affected significantly by the chirality of the amino acid catalyst; *ee* were the largest for threose produced with enantiomerically pure isovaline catalyst and decreased linearly with the decrease of the catalyst's *ee* (Figure 3). More recent studies<sup>45</sup> have shown that dipeptide catalysts, whose formation would arguably be a simple prebiotic step for prebiotic amino acids to undertake, display a greatly enhanced asymmetric effect in the same syntheses, with *ee* that surpass 80%.

These data would appear to suggest that the 2-methylamino acids, although generally unimportant in ter-

restrial biochemistry, might have had a role in early molecular evolution. They are abundant in carbonaceous chondrites and may hold advantages in other evolutionary roles; for example, these amino acids are stable to chemical racemization and would not be subjected to what has been called the "catastrophe of racemization"<sup>46</sup> for early molecules, that is, sugars and amino acids lacking substituents at the weakly acidic C2 could have lost to racemization any *ee* advantage<sup>47</sup> in prebiotic chemistry. Also, polymerization accompanied by formation of regular secondary structure, such as  $\alpha$ -helices and  $\beta$ -sheets, has been shown to be an effective way to amplify modest initial *ee*<sup>48,49</sup> and 2-methyl amino acids are known to have strong helix-inducing and stabilizing effects.<sup>50</sup> Small peptides containing 2-methylamino acids, such as 2-aminoisobutyric acid and isovaline, are found today imbedded in cell membranes of fungal paptabols as ion channels; their lineage is estimated to be very old, based on the sequencing of the RNA controlling their metabolism.<sup>51</sup> If these amino acids were involved in molecular evolution, a transition to 2-H-amino acids must have occurred later, perhaps to allow amino acid formation by transamination of 2-keto analogues, a process that is very important in the metabolism of protein amino acids but impossible for the 2-methylamino acids.

## Concluding Comments

While the origin of life remains an inscrutable event, the study of chemical evolution offers means for learning the range of abiotic molecules available to prebiotic chemistry as well as to explore the physicochemical regimes that may have led to a selected chemical pool that was amenable to the onset of life. Furthermore, the unique natural samples of carbonaceous meteorites allow us to evaluate whether selective prebiotic events, such as symmetry-breaking, might have played a significant early role in the molecular evolution of homochirality and the biochemistry of a pre-RNA world.

*I am grateful for the support of many years by the NASA Exobiology Division and to Carleton Moore and the Center for Meteorite Studies at Arizona State University for providing samples of the Murchison meteorite. I also thank George Cooper, John Cronin, and Arthur Weber for many discussions and helpful comments.*

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- The  $\delta$  notation is used in geochemistry and biochemistry for the easy comparison of small fractionations between isotopes. It expresses the isotopic ratio *R* as follows:  $\delta\text{‰} = (R_{\text{sample}} - R_{\text{standard}}/R_{\text{standard}}) \times 10^3$ ;  $\text{D}/\text{H}_{\text{standard}} = 1.5575 \times 10^{-4}$ .
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AR050049F