New Studies on the Murchison Meteorite Shed Light on the Pre-RNA World

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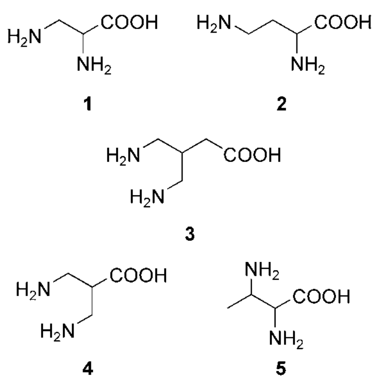
The Murchison Meteorite and Its Relevance to Prebiotic Chemistry

On September 28, 1969, pieces of a stony meteorite fell around the small town of Murchison, about 130 km north of Melbourne, Australia. More than 100 kg of fragments were collected, several of them shortly after the fall. It is reported that eyewitnesses noticed a strange smell reminiscent of methylated spirit, bitumen or kerosene. This was the first indication of organic compounds being present in the Murchison meteorite at relatively high concentrations. The subsequent chemical analyses were facilitated by the fact that NASA laboratories, at the time of the Apollo missions to the Moon, were well prepared to study extraterrestrial material. In a first report, which is now a classic paper in prebiotic chemistry, evidence was presented for amino acids and hydrocarbons in the Murchison meteorite.[1] It was shown by analysis of the $^{13}C/^{12}C$ ratios that these compounds were unambiguously of extraterrestrial origin. Since then about 500 soluble organic compounds, which belong to several different classes, have been identified in this meteorite.[2] Among them are amines, alcohols, aldehydes and ketones, aliphatic and aromatic hydrocarbons, carboxylic and dicarboxylic acids, hydroxy acids, amino acids, amides, phosphonic and sulfonic acids, sugar alcohols and acids and different types of N-heterocycles, such as purines and pyrimidines. Most of the carbon content of the Murchison meteorite (70–80%) is found, however, in insoluble macromolecular material that is difficult to characterize.

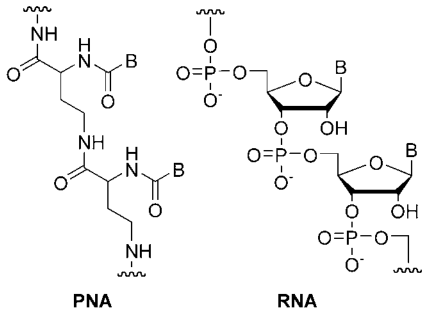
To date, we still have no consistent picture of the origin of organic compounds in the carbonaceous chondrites, the group of meteorites whose most prominent member is the Murchison meteorite. There are indications, however, that the organic molecules or close precursors of them formed in dense interstellar clouds. They became part of the asteroidal meteorite parent bodies when the interstellar ice and dust grains accreted during the formation of the solar system. At that time, further reactions, such as the hydrolysis of α-amino nitriles (the final step of the Strecker synthesis), might have occurred.[2,3] Simulation experiments strongly support the idea that interstellar chemistry forms the basis for the organic inventory of carbonaceous chondrites.[4,5] In these experiments, an interstellar ice analogue, typically consisting of H_2O, CH_3OH, NH_3, CO and CO_2, was irradiated with ultraviolet light under a high vacuum at 12 K. After the analogue had been warmed to room temperature and hydrolyzed, up to 16 amino acids were detected in the residue, among them glycine, alanine, valine, proline, serine and aspartic acid.[5] The meteoritic occurrence of organic molecules that are at least as old as our solar system has profound implications for prebiotic chemistry. The early Earth experienced a time of heavy bombardment by asteroids, meteorites and comets, that lasted until ~3.8×10^9 years ago. In the late phase of this period, large amounts of exogenously delivered organic compounds had probably accumulated on the Earth's surface and might have contributed to the raw material from which life emerged.[6]

Meteoritic PNA Building Blocks

Recently, Meierhenrich et al. identified at least five different diamino monocarboxylic acids ("diamino acids"; Scheme 1) in the Murchison meteorite.[7] This finding is intriguing because diamino acids have been proposed as backbone building blocks of so-called peptide nucleic acids (PNAs). PNAs are RNA analogues, in which a peptide chain replaces the sugar–phosphate backbone (Scheme 2). This type of polymer has been discussed in a prebiotic context as a possible pre-



Scheme 1. *Diamino acids in the Murchison meteorite:*[7] *DL-2,3-diaminopropanoic acid (**1**), DL-2,4-diaminobutanoic acid (**2**), 4,4′-diaminoisopentanoic acid (**3**), 3,3′-diaminoisobutanoic acid (**4**) and 2,3-diaminobutanoic acid (**5**). Individual concentrations range from ~32 ppb (**3**) to ~100 ppb (**1**). For comparison, the most abundant monoamino acids glycine and alanine are present at concentrations of ~5 ppm and ~3 ppm, respectively.*



Scheme 2. *Comparison of 2,4-diaminobutanoic acid-based peptide nucleic acid (PNA) and RNA; B = nucleic acid base.*

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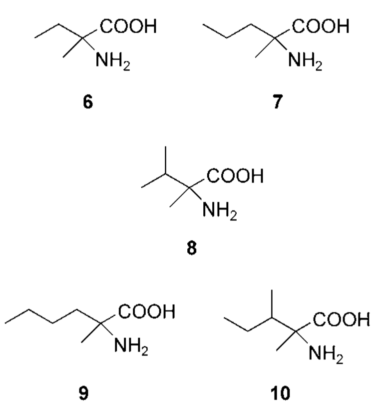
RNA genetic material. More than a decade ago, Nielsen proposed that PNA could be based on 2,4-diaminobutanoic acid (**2**), among others.[8] This compound is one of the diamino acids that have been found in the Murchison meteorite.[7] It is now widely accepted that our present-day "two-polymer world" of nucleic acids and proteins was preceded by a "one-polymer world" of RNA. The "RNA world" concept is strongly supported by the fact that RNA combines the properties of a biological catalyst (ribozyme) and a carrier of genetic information. There are, however, serious doubts about the possibility of a de novo prebiotic synthesis of RNA.[9] It is therefore appealing to assume the former existence of precursor molecules that acted as templates for RNA polymerization. PNA are good candidates for this because i) their components can be easily synthesized under presumed prebiotic conditions[10] and ii) PNA and complementary RNA form stable 1:1 complexes by Watson–Crick base pairing.[11] The occurrence of diamino acids in the Murchison meteorite proves that these compounds can also be formed by one or more extraterrestrial abiotic routes. Thus, not only endogenous synthesis but also exogenous delivery could have been a source of these PNA components on the young Earth. Information transfer from PNA to RNA, that is, the ability of PNA to act as a template for RNA synthesis (and vice versa) has been demonstrated experimentally.[12] It is conceivable that the prebiotic PNA→RNA transition occurred in chemically advanced precellular compartments that could already synthesize activated RNA nucleotides. In aqueous solution, PNA molecules undergo two slow chemical transformations, namely *N*-acyl rearrangement and autodegradation, but these do not necessarily conflict with the possible role of PNA as a primordial genetic material.[13] Formation of complete PNA molecules in a simulated prebiotic environment, however, has not yet been accomplished. In addition to PNA, other chemical systems have been suggested as the earliest carriers of genetic information. Among them are phyllosilicates, which naturally occur as clay minerals.[14] But apparently no experimental evidence exists that clays can act as suitable replicators or transfer information to RNA or DNA. It should be mentioned that some phyllosilicates, particularly montmorillonite, possess prebiotically interesting catalytic properties that have been studied experimentally.[15] The basic idea that clays could have played a role in the origin of life dates back to the work of Bernal more than half a century ago.[16]

Meteoritic Amino Acids and Biological Homochirality

A striking property of living systems on Earth is that their proteins and nucleic acids contain almost exclusively L-amino acids and D-(deoxy)ribose, respectively. This homochirality is obviously a prerequisite for the proper function of enzymes, DNA and RNA. How biomolecular homochirality originated is a long-standing question in prebiotic chemistry. Again, the Murchison meteorite might provide an answer. Meteoritic amino acids were originally thought to be racemic, but in recent years enantiomeric excesses (*ee*) of L-amino acids have been discovered. These excesses were unambiguously shown not to be caused by terrestrial contaminations. In the case of isovaline (**6**; Scheme 3), for example, contaminations are virtually impossible because this non-protein amino acid very rarely occurs in the biosphere. This argument is even stronger for other α,α-dialkyl-α-amino acids for which L-excesses have been found, because on Earth they have no natural occurrence at all. In the Murchison meteorite, L-enantiomeric excesses for these amino acids range from 2.8 to 9.1% (Table 1; see below for a recently reported higher value).[17] A possible causal relation to the origin of biomolecular homochirality is obvious, since exogenously delivered nonracemic amino acids may have constituted an initial "chiral pool" on the early Earth. In fact, Pizzarello and Weber have recently succeeded in demonstrating that L-isovaline can transfer its chirality to sugars, for example in the formation of tetroses by aldol addition of glycolaldehyde.[18] In this context it is also interesting that a special type of autocatalytic reaction exists that can amplify even small enantiomeric excesses.[19] α,α-Dialkyl-α-amino acids, such as isovaline, are well suited as stable long-term carriers of chiral information because their rate of racemization is usually very low.



Scheme 3. *α,α-Dialkyl-α-amino acids with L-enantiomeric excesses found in carbonaceous chondrites:[17] 2-amino-2-methylbutanoic acid (isovaline, **6**), 2-amino-2-methylpentanoic acid (**7**), 2-amino-2,3-dimethylbutanoic acid (**8**), 2-amino-2-methylhexanoic acid (**9**) and 2-amino-2,3-dimethylpentanoic acid (**10**).*

Table 1. *L-Enantiomeric excesses (% L ee) in α,α-dialkyl-α-amino acids in the meteorites Murchison and Murray.[17] Formulae and names of the amino acids are given in Scheme 3.*

Amino acid	Murchison	Murray
6	8.4	6.0
7	2.8	1.4
8	2.8	1.0
9	4.4	1.8
2*S*,3*S*/2*R*,3*R*-**10**	7.0	1.0
2*S*,3*R*/2*R*,3*S*-**10**	9.1	2.2

It has been proposed that L-enantiomeric excesses in carbonaceous chondrites were produced by irradiation with ultraviolet circularly polarized light (UV CPL). Circular polarization occurs in reflection nebulae in star-forming regions, for example in the Orion nebula.[20] These are exactly the locations where organic compounds are present (see above)! During UV CPL irradiation of a racemic mixture of an amino acid or a precursor, one enantiomer decomposes faster than the other. In the laboratory, *ee*'s of a few percent have been achieved by this method of asymmetric photolysis. A significant enantiomeric enrichment is, however, always accompanied by a high degree of decomposition and therefore can only be obtained at the expense of the amount of substance. Recently, Pizzarello et al. reported an L *ee* of up to 15.2% for isovaline in the Murchison meteorite.[21] This surprisingly high value is difficult to explain solely by UV CPL irradiation of the amino acid. Alternatively, the authors suggest a role of the mineral matrix because the observed high *ee* values appear to be associated with the phyllosilicate serpentine $[Mg_3Si_2O_5(OH)_4]$. Enantioselective catalysis by a phyllosilicate seems plausible, provided the mineral itself—by an as yet unknown mechanism—has acquired an enantiomorphic excess. It has already been pointed out by others that chirally selective surfaces of minerals such as calcite ($CaCO_3$)[22] and pyrite (FeS_2)[23] could have been involved in prebiotic chiral separation and enantioselective reactions. In general, little is known about how amino acids and their precursors interact with and react in/at phyllosilicates. This opens a large field for future prebiotic research.

From the results described in this Highlight, the view emerges that the chemical roots of life might ultimately lie beyond Earth and may be widespread across the universe. If this is true, then at least the first steps in the origin of life perhaps were more or less inevitable.

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[1] K. Kvenvolden, J. Lawless, K. Pering, E. Peterson, J. Flores, C. Ponnamperuma, I. R. Kaplan, C. Moore, *Nature* **1970**, *228*, 923–926.

[2] J. R. Cronin in *The Molecular Origins of Life* (Ed.: A. Brack), Cambridge University Press, Cambridge, **1998**, pp. 119–146.

[3] S. Pizzarello, *Origins Life Evol. Biosphere* **2004**, *34*, 25–34.

[4] M. P. Bernstein, J. P. Dworkin, S. A. Sandford, G. W. Cooper, L. J. Allamandola, *Nature* **2002**, *416*, 401–403.

[5] G. M. Muñoz Caro, U. J. Meierhenrich, W. A. Schutte, B. Barbier, A. Arcones Segovia, H. Rosenbauer, W. H.-P. Thiemann, A. Brack, J. M. Greenberg, *Nature* **2002**, *416*, 403–406.

[6] C. Chyba, C. Sagan, *Nature* **1992**, *355*, 125–132.

[7] U. J. Meierhenrich, G. M. Muñoz Caro, J. H. Bredehöft, E. K. Jessberger, W. H.-P. Thiemann, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 9182–9186.

[8] P. E. Nielsen, *Origins Life Evol. Biosphere* **1993**, *23*, 323–327.

[9] L. E. Orgel, *Crit. Rev. Biochem. Mol. Biol.* **2004**, *39*, 99–123.

[10] K. E. Nelson, M. Levy, S. L. Miller, *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 3868–3871.

[11] a) M. Egholm, O. Buchardt, L. Christensen, C. Behrens, S. M. Freier, D. A. Driver, R. H. Berg, S. K. Kim, B. Norden, P. E. Nielsen, *Nature* **1993**, *365*, 566–568; b) S. C. Brown, S. A. Thomson, J. M. Veal, D. G. Davis, *Science* **1994**, *265*, 777–780.

[12] C. Böhler, P. E. Nielsen, L. E. Orgel, *Nature* **1995**, *376*, 578–581.

[13] M. Eriksson, L. Christensen, J. Schmidt, G. Haaima, L. Orgel, P. E. Nielsen, *New J. Chem.* **1998**, 1055–1059.

[14] A. G. Cairns-Smith, *Genetic Takeover and the Mineral Origins of Life*, Cambridge University Press, Cambridge, **1982**.

[15] See for example: a) J. P. Ferris in *The Molecular Origins of Life* (Ed.: A. Brack), Cambridge University Press, Cambridge, **1998**, pp. 255–268; b) M. M. Hanczyc, S. M. Fujikawa, J. W. Szostak, *Science* **2003**, *302*, 618–622.

[16] a) J. D. Bernal, *Proc. Phys. Soc. London Sect. A* **1949**, *62*, 537–558; b) J. D. Bernal, *The Physical Basis of Life*, Routledge and Kegan Paul, London, **1951**.

[17] J. R. Cronin, S. Pizzarello, *Adv. Space Res.* **1999**, *23*, 293–299.

[18] S. Pizzarello, A. L. Weber, *Science* **2004**, *303*, 1151.

[19] a) K. Soai, T. Shibata, H. Morioka, K. Choji, *Nature* **1995**, *378*, 767–768; b) D. G. Blackmond, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5732–5736.

[20] a) J. Bailey, A. Chrysostomou, J. H. Hough, T. M. Gledhill, A. McCall, S. Clark, F. Ménard, M. Tamura, *Science* **1998**, *281*, 672–674; b) J. Bailey, *Origins Life Evol. Biosphere* **2001**, *31*, 167–183.

[21] S. Pizzarello, M. Zolensky, K. A. Turk, *Geochim. Cosmochim. Acta* **2003**, *67*, 1589–1595.

[22] R. M. Hazen, T. R. Filley, G. A. Goodfriend, *Proc. Natl. Acad. Sci. USA* **2001**, *98*, 5487–5490.

[23] G. Wächtershäuser, *Prog. Biophys. Mol. Biol.* **1992**, *58*, 85–201.

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