THE ORIGIN OF THE POLYCYCLIC AROMATIC HYDROCARBONS IN METEORITES

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Abstract. Polycyclic aromatic hydrocarbons (PAHs) in C1 and C2 Carbonaceous Chondrites appear to be the product of a high-temperature synthesis. This observation counters a prevailing view that PAHs in meteorites are a thermal alternation product of preexisting aliphatic compounds, which in turn required the presence of low-temperature mineral phases such as magnetite and hydrated phyllosilicates for their formation. Such a process would necessarily lead to a more low-temperature assemblage of PAHs, as many low-temperature minerals and compounds are extant in meteorites.

Ivuna, a C1 carbonaceous chondrite, has been shown to contain abundant amounts of the three-ring PAHs phenanthrene/anthracene, but no detectable levels of the two- and four-ring PAHs naphthalene and pyrene/fluoranthene. Ivuna and other C1 carbonaceous chondrites are known to have been extensively altered by water. The aqueous solubilities of PAHs indicate that some PAHs would have been mobilized during the aqueous alteration phase in meteorite parent bodies. Model geochromatography experiments using crushed serpentine or beach sand as the solid phase and water for elution suggest that the complete separation of two, three, and four-ring PAHs could be expected to occur in the parent body of C1 carbonaceous chondrites. It is proposed that aqueous fluids driven by heat in the parent body of Ivuna migrated from the interior to the surface, in the process transporting, separating and concentrating PAHs at various zones in the parent body.

The presence of indigenous PAHs and absence of indigenous amino acids in the H4 ordinary chondrite Forest Vale provides support for the contention that different processes and environments contributed to the synthesis of the organic matter in the solar system.

Introduction

The analysis of PAHs (see Figure 1 for structures) in carbonaceous chondrites has been severely constrained by sample availability. Typically, several grams of sample are needed in order to obtain meaningful results using a combination of wet chemical isolation methods followed by detection and identification by gas chromatography/mass spectrometry. Most analyses have been performed on the Murchison C2 chondrite (Australia) and the Pueblito de Allende C3 chondrite (Mexico) in the early 1970's, soon after these meteorites fell (Cronin *et al.*, 1988). Meaningful comparisons of PAHs within and between each petrologic class have not been made.

In 1988 Hahn *et al.* analyzed PAHs in six carbonaceous chondrites and one ordinary chondrite utilizing the new analytical technique of two-step laser desorption/multiphoton ionization mass spectrometry (L^2MS). Their results for Murchison were consistent with the earlier studies (e.g. Pering and Ponnamperuma, 1971, Basile *et al.*, 1984). Three major features characterize the data for the various meteorites studies by Hahn and co-workers:
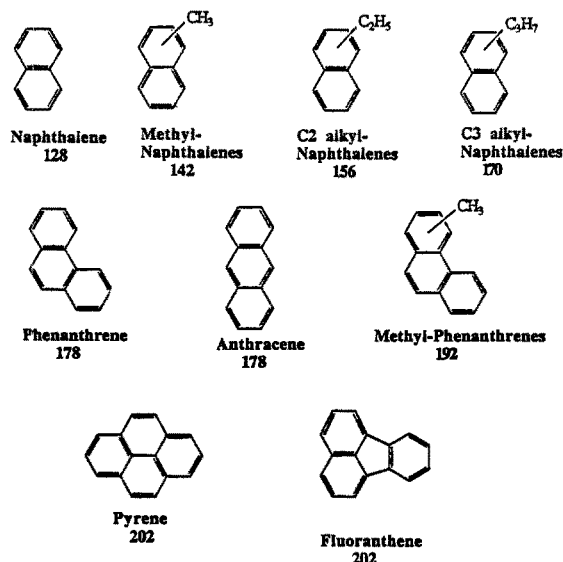
Fig. 1. Structures and molecular weights of some polycyclic aromatic hydrocarbons present in carbonaceous chondrites. The sites of alkylation are arbitrary.

(1) The unalkylated PAHs naphthalene (mass 128), phenanthrene/anthracene (mass 178) and pyrene/fluoranthene (mass 202) generally predominate over their methyl-, dimethyl-, and alkyl- homologs.

(2) Ivuna, the only C1 chondrite in their collection, contained only the three-ring PAHs phenanthrene/anthracene, and smaller amounts of their methyl- and dimethyl- homologs. No detectable amounts of naphthalene or pyrene, which have two and four rings, respectively, were found. In addition, Ivuna contained greater amounts of phenanthrene/anthracene than any of the other carbonaceous meteorites.

(3) The H3 ordinary chondrite Clovis was found to contain no PAHs. A negative result was expected in the case of Clovis, and the analysis provided a valuable control against the possibility of laboratory contamination.

Carbonaceous chrondrites contain many other organic species besides PAHs: detected compounds include amino acids, carboxylic acids, heterocyclic compounds, an aromatic polymer, and aliphatic hydrocarbons. Recent comments and reviews on the subject of organics in meteorites (e.g. Wright and Gilmour, 1990; Cronin et al., 1988; Mullie and Reisse, 1987) have focused chiefly on two alternative hypotheses for the formation of organics in meteorites: the Fischer-Tropsch type synthesis (CO and H_2 reacting on low-temperature catalytic surfaces), and the Miller-Urey synthesis (spark discharge in a reducing atmosphere). Three points have been overlooked in these discussions which are the focus of this paper. First, the Fischer-Tropsch type synthesis cannot account for the assemblage of PAHs observed in C1 and C2 carbonaceous chondrites; second, low-molecular weight organics which are not readily soluble in water can be selectively transported and concentrated

by hydrothermal fluids in the meteorite parent body; and finally, amino acids, PAHs, and aliphatic hydrocarbons indigenous in meteorites each likely originated from different processes.

The Synthesis of PAHs by Various Pathways: Relevance to Meteorites

According to the Fischer-Tropsch hypothesis, the aromatics in carbonaceous chondrites formed, along with all the other organic material, in the solar nebula by mineral-catalyzed reactions of CO, H_2, and NH_3 at 360 – 400 K and 10^{-5} atmospheres pressure. The reaction was supposedly triggered by the formation of the catalysts magnetite and hydrated phyllosilicates at around 400 K. The evidence for this view has been extensively reviewed by Anders et al., (1973) and Hayatsu and Anders (1981). Six different cosmothermometers give equilibration temperatures near 360 K for C1 meteorites and 380-400 K for C2's (Anders et al., 1973). The condensation pressures for carbonaceous chondrites are estimated to lie between 10^{-2} and 10^{-6} atmospheres. At 10^{-5} atmospheres and above 600 K, CO is the thermodynamically favored form of carbon. Below this temperature, CH_4 is most stable. However, CH_4 does not condense above 100 K and if the transition from CO to CH_4 had proceeded smoothly at 600 K there would be no carbon in meteorites, or anywhere in the inner solar system (Hayatsu and Anders, 1981). Urey (1953) suggested that the CO-CH_4 transition might have required catalysts, and might have proceeded through graphite or tarry intermediates. Anders et al., (1973) found that a Fisher-Tropsch type synthesis of H_2 and CO carried out in a static vessel at a range of temperatures and 0.1-1 atmospheres does indeed produce a complex, tarry mixture of metastable compounds of H/C -2 which resembles the polymer found in carbonaceous chondrites. They argue that CO survived the cooling from 600 to 400 K because of the absence of catalysts, the reaction proceeding once phyllosilicate and magnetite minerals had condensed. The Fischer-Tropsch type synthesis does not produce aromatics, but conversion of aliphatics to aromatics takes place readily on reheating of the primary Fischer-Tropsch type product (Studier et al., 1972). Continued contact with the catalyst at 350-400 °C yields methane and aromatics at the expense of aliphatics. Higher temperatures yield compounds of up to seven rings (Hayatsu and Anders, 1981). Hayatsu et al. (1977) surmise that polymer and aromatics were formed from aliphatics during brief excursions to 600 °C, perhaps caused by impact events, and that aliphatics were replenished by long incubation at 200 °C. However, recent work by Cronin and Pizzarello (1990) calls into question the long accepted existence of indigenous straight-chain aliphatic hydrocarbons in the Murchison meteorite.

An alternative process for the abiotic synthesis of organics is the Miller-Urey synthesis (Miller, 1953; Miller, 1987). This proceeds by the exposure of gaseous CH_4, NH_3, H_2O and H_2 to electric discharges. HCN is an intermediate product made in this process. Aqueous HCN, aldehydes, and NH_3 react to produce amino and hydroxy acids by the Strecker-cyanohydrin synthesis (Peltzer et al., 1984; Miller,

1987). The synthetic product from spark discharge experiments strongly resembles Murchison in its suite of amino acids (Wolman *et al.*, 1972). The Miller-Urey synthesis, or at least its essential steps, seems to account for the amino acids in Murchison (Hayatsu and Anders, 1981; Peltzer *et al.*, 1984). Although the main focus of the Miller-Urey synthesis has been on amino acids and other organic acids, variations of the synthesis have been shown to produce PAHs as well. For example, methane and other reduced gasses yield naphthalene in electric discharge experiments (Friedmann *et al.*, 1971). The Miller-Urey synthesis cannot be ruled out as a source for PAHs in meteorites.

Recently, evidence from the infrared spectra of a number of celestial objects has been presented that suggests PAHs are ubiquitous in interstellar space (Allamandola *et al.*, 1985; but see Donn *et al.*, 1989, for a discussion of this hypothesis' deficiencies in the visible-ultraviolet portion of the spectrum.) A likely source of these interstellar PAHs is condensation in the carbon-rich envelopes of some stars (Allamandola *et al.*, 1987) or photochemical reactions in the interstellar medium (Mullie and Reisse, 1987). Such origins share in common that the PAHs thus generated would predate the formation of the solar system, and any PAHs of pre-solar origin in meteorites would then have to be survivors of a relatively non-destructive transportation and accretion process.

To evaluate the Fischer-Tropsch hypothesis for the production of PAHs in meteorites, it is necessary to review several aspects of PAH occurrence in the geochemical and cosmochemical literature. In C1 and C2 carbonaceous chondrites, unalkylated PAHs (naphthalene, phenanthrene, pyrene, etc) predominate over their alkylated homologs. This observation has been documented in Murchison by Basile *et al.* (1984), Pering and Ponnamperuma (1971), Hahn *et al.* (1988) and Wing (1991). Various Antarctic meteorites (Shimoyama and Harada, 1989; Murae *et al.*, 1987) as well as the other carbonaceous meteorites analyzed by Hahn *et al.* (1988) also show a strong predominance of unsubstituted naphthalene, phenanthrene and pyrene over their alkylated homologs. The only exception to this pattern is the study by Studier *et al.* (1972) which appears to show the opposite: higher concentrations of methyl-naphthalene and dimethyl-naphthalene than of naphthalene were reported in Murchison. These results are at odds with the other studies cited above, and because Studier *et al.* subjected their samples to vacuum evaporation, it is probable that part of their naphthalene (which sublimes at room temperature) was lost in sample processing.

In contrast to the PAHs in carbonaceous chondrites, those in terrestrial petroleums, which are formed at temperatures of 60-150 °C, always show alkylated PAHs predominating over unsubstituted PAHs (Tissot and Welte, 1984). Blumer (1976) has shown that a predominance of unalkylated PAHs in natural or synthetic mixtures indicates a high temperature of formation (400-800 °C) whereas the presence of excess alkylated PAHs indicates a low temperature of formation (100-150 °C); these results are summarized in Figure 2. Blumer's results suggest that the PAHs in Murchison and other carbonaceous chondrites were generated at temperatures
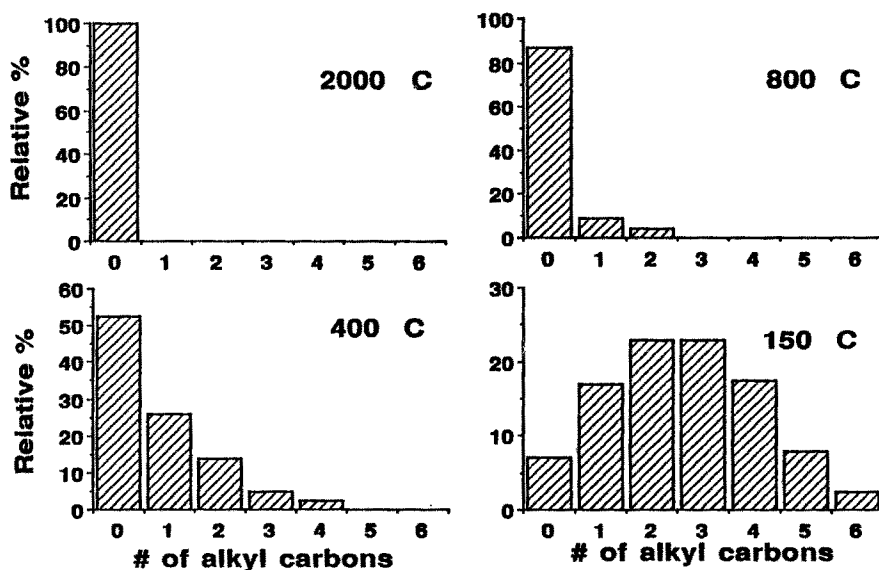
Fig. 2. Relationship of PAH alkylation to temperature of formation (after BLUMER, 1976).

between 400 °C and 800 °C, and probably closer to 800 °C. This is inconsistent with the Fischer-Tropsch hypothesis. An impact event may heat a small region of the meteorite's parent body to 800 °C or more, but it will necessarily warm a larger region of the parent body surrounding the impact site to a lower maximum temperature. It is difficult to imagine how an assemblage of high-temperature PAHs could be generated at one site without generating an even greater amount of low-temperature PAHs somewhere else. Yet PAHs in Murchison are homogeneously distributed and their distribution does not appear to vary from one milligram-sized sample to the next (Hahn et al., 1988). If every site on the parent body were to experience such heating, the resulting meteorites would not be C1 or C2 chondrites. Carbonaceous chondrites contain numerous low-temperature organic and inorganic phases including the hydrated phyllosilicate minerals and magnetite that Hayatsu and Anders (1981) suppose to be responsible for the presence of organics in the first place. Amino acids decompose in seconds at 350 °C (Miller and Bada, 1988), yet amino acids are plentiful in carbonaceous chondrites.

Despite its geochemical implausibility, the synthesis of PAHs by thermal alteration of aliphatics in the meteorite's parent body has been the dominant mechanism of formation proposed in recent review articles (Hayatsu and Anders, 1981; Mullie and Reisse, 1987; Cronin et al., 1988.) The possibility that different classes of organics (e.g. amino acids, PAHs, aliphatics) were formed at different times and by different processes has not been sufficiently explored. Meteorite review papers tend to lump all of the organics together into one section (e.g. Cronin et al., 1988) but their origins may be as diverse as those of the mineral phases. PAHs in meteorites appear to have formed before the accretion of meteorite parent bodies and thus could be presolar as proposed by Allamandola et al. (1987).

Cosmogeochromatography on the Parent Body of the Carbonaceous Chondrite Ivuna

The reported presence of abundant phenanthrene/anthracene (the three-ring PAHs) and absence of detectable amounts of naphthalene, pyrene or fluoranthene (the two- and four-ring PAHs) in Ivuna (Hahn *et al.*, 1988) is very curious. Either the phenanthrene/anthracene in Ivuna was synthesized in a process that did not produce naphthalene or pyrene, or all of these compounds were synthesized together and subsequently separated by some chemical or physical process. Wing and Bada (1991) have considered the problem and found little theoretical or experimental support for the selective synthesis of only three-ring PAHs. Enthalpies of formation (Stull *et al.*, 1969) for these compounds are so similar on a stoichiometric basis that they are generated together over a very wide range of temperatures, pressures and chemical conditions. Instead, it appears that the differing solubilities of these compounds in water (naphthalene 31 mg kg^{-1}, phenanthrene 1.2 mg kg^{-1}, pyrene 0.13 mg kg^{-1} at 25 °C: Futoma *et al.*, 1981) provide the most likely explanation. C1 carbonaceous chondrites are known from their mineralogies to be extensively altered by water (McSween, 1987) and it does seem reasonable to expect that a few parts per million of PAHs in Ivuna could have been dissolved and transported in Ivuna's hydrothermal milieu.

To test the feasibility of this explantation, a model geochromatography experiment was conducted; experimental details and results have been presented by Wing and Bada (1991). Glass columns were packed with either crushed serpentine or Southern California beach sand (consisting of quartz, feldspar, hornblende and biotite). Mixtures of three PAHs (naphthalene, phenanthrene and pyrene) were introduced into the tops of the columns, and then water was allowed to drip through the columns over a period of several hours. The PAH composition of the effluent was analyzed by reversed-phase high performance liquid chromatography utilizing the technique given by Ogan *et al.* (1979). Naphthalene was the dominant PAH in the early effluent for both columns, compromising at least 96% of the total. As the elution progressed, the concentration of naphthalene fell and the concentration of phenanthrene rose, reaching 80% of the total PAHs. Pyrene was leached off the columns more slowly, and at the end of the experiment most of the pyrene was still absorbed on the solid phase of the columns. This was removed for analysis by acetronitrile washes.

Complete resolution of PAHs was not achieved in these experiments, but the results strongly suggest the ease with which a complete separation of PAHs could be made in a C1 parent body. The latter medium would be expected to have a smaller porosity, a longer length, a higher pressure gradient, and more time than in the model experiment. In a more detailed analysis, the chromatographic efficiency of Ivuna's parent body was found by Wing and Bada (1991) to be at least 20 × greater than that of the 19 cm long columns used in the model cosmogeo-chromatography experiment.

It would not be unexpected for cosmogeochromatography to occur on meteorite

parent bodies, for it also happens in hydrothermal systems on Earth. Pendletonite, a mineral found in San Benito Co., California, consist of 99% pure coronene, a seven-ring PAH (Blumer, 1975). The remainder is mostly 1-methyl coronene. Schmidt (1987) has noted that this is more pure than commercially available coronene, and that a similar mineral (carpathite) occurs in Eastern Europe, which also appears to consist chiefly of coronene. The association of pyrene and fluoranthene with the mercury ore cinnabar has been noted for over a century (Schmidt, 1987). PAH migration in steam distillates in Yellowstone National Park has been observed by Clifton *et al.* (1990). The potential for natural chromatographic separation appears to exist wherever PAHs and liquid water are found.

PAHs and Amino Acids in the H4 Ordinary Chondrite Forest Vale

Despite the expected lack of PAHs in the H3 ordinary chondrite Clovis (Hahn *et al.*, 1988) the H4 ordinary chondrite Forest Vale was recently found by Zenobi *et al.* (1992) to contain abundant PAHs (mostly phenanthrenes). Contamination by terrestrial sources appears to have been ruled out as a cause, as the meteorite has no apparent PAH concentration gradient from the exterior to the interior of the sample. The detection of PAHs in Forest Vale led to the search for another class of organic molecules abundant in carbonaceous chondrites: the animo acids (Zenobi *et al.*, 1992). More than 60 amino acids have been positively identified in extracts of Murchison and other carbonaceous chondrites (Cronin *et al.*, 1988). When chiral and free of terrestrial contamination, these amino acids are found to be racemic (Bada *et al.*, 1983). Nonprotein amino acids are present in significant amounts, especially α-amino isobutyric acid (AIB), the most abundant single amino acid in Murchison, and racemic isovaline (D/l ISOVAL). The Forest Vale study concentrated on these two amino acids because they are extremely rare in organisms, and not known to be breakdown products of the terrestrial amino acids (Zhao and Bada, 1989).

Three samples (54-122 mg) of Forest Vale from different sources and one sample of Murchison (91 mg) were hydrolyzed in HCl and desalted according to a standard procedure; the extracts were then analyzed for amino acids by the high-performance liquid chromatography technique given by Zhao and Bada (1989). Although amino acids were detected in Forest Vale, they consisted entirely of biological amino acids such as glycine, L-aspartic acid, and L-alanine. No detectable amounts of D-alanine, D-aspartic acid, AIB or racemic ISOVAL were observed. The limits of detection were < 0.08 ppm AIB and < 0.05 ppm ISOVAL. The amino acids detected in Forest Vale are thus presumed to be terrestrial contaminants. In contrast to Forest Vale, 5.5 ppm AIB and 4.0 ppm ISOVAL were detected in the Murchison sample, which is consistent with previously reported values (Cronin and Pizzarello, 1983).

The amino acids in Murchison are thought to have been synthesized from HCN and ammonia by a Strecker-cyanohydrin pathway in a aqueous environment, probably in the pore fluids of the parent body (Peltzer *et al.*, 1984). Forest Vale

was never subjected to the action of aqueous fluids as is evident from its high petrologic grade and absence of aqueous alteration products in matrix minerals (Marti *et al.*, 1989.) So the presence of indigenous PAHs and absence of indigenous amino acids in Forest Vale strongly supports the contention that amino acids require the presence of liquid water for their formation (by the Strecker-cyanohydrin synthesis), whereas PAHs do not, and were probably formed by a completely different process.

Conclusions

The Fischer-Tropsch hypothesis for the formation of PAHs in carbonaceous chondrites is not consistent with the available evidence. Because of the high temperatures needed to generate unsubstituted PAHs, this type of synthesis could not have occurred without destroying the low-temperature phases in carbonaceous chondrites, including minerals (hydrated phyllosilicates, magnetite, etc.) that are thought to be responsible for the presence of organics in the first place, and fragile, heat-sensitive organics such as amino acids. Thus, PAH formation was probably completed before the accretion of the parent body began. The abundance of phenanthrene/anthracene in Ivuna and the absence of any other PAHs does not appear to be due to any selective synthesis of the three-ring PAHs. Instead, considerations of PAH solubility and the history of aqueous alteration in the meteorite make it likely that chromatographic separation by hydrothermal fluids was the cause. The presence of indigenous PAHs and the absence of indigenous amino acids in the H4 ordinary chondrite Forest Vale supports the contention that PAHs and amino acids in meteorites are synthesized by different processes: amino acids by a process which requires the presence of liquid water, and PAHs by a non-aqueous, high temperature process which occurred before the accretion of meteorite parent bodies.

Acknowledgements

References

Allamandola, L. J., Sandford, S. A., and Wopenka, B.: 1987, *Science* 237, 56.
Allamandola, L. J., Tielens, A. G. G. M., and Barker, J. R.: 1985, *The Astrophysical Journal* 290, L25.
Anders, E., Hayatsu, R., and Studier, M. H.: 1973, *Science* 182, 781.
Bada, J. L., Cronin, J. R., Ho, M., Kvenvolden, K. A., Lawles, J. G., Miller, S. L., Oro, J., and

Steinberg, S.: 1983, *Nature* **301**, 494.

Basile, B. P., Middleditch, B. S., and Oro, J.: 1984, *Org. Geochem.* **5**, 211.

Blumer, M.: 1975, *Chem. Geol.* **16**, 245.

Blumer, M.: 1976, *Sci. Amer.* **234** (3), 34.

Clifton, C. G., Walters, C. C., and Simoneit, B. R. T.: 1990, *Appl. Geochem.* **5**, 169.

Cronin, J. R. and Pizzarello, S.: 1983, *Adv Space Res.* **3**, 5.

Cronin, J. R. and Pizzarello, S.: 1990, *Geochim. Cosmochim. Acta* **54**, 2859.

Cronin, J. R., Pizzarello, S., and Cruikshank, D. P.: 1988, in J. F. Kerridge and M. S. Matthews (eds.), *Meteorites and the Early Solar System*, University of Arizona Press, p. 819.

Donn, B. D., Allen, J. E., and Khanna, R. K.: 1989, in L. J. Allamandola and A. G. G. M. Tielens (eds.), *Interstellar Dust*, IAU Symposium 135, Kluwer Acad. Publ., Dordrecht, p. 181.

Friedmann, N., Bovee, H. H., and Miller, S. L.: 1971, *J. Org. Chem.* **36**, 2894.

Futoma, D. J., Smith, S. R., Smith, T. E., and Tanaka, J.: 1981, *Polycyclic Aromatic Hydrocarbons in Water Systems*, CRC Press.

Hahn, J. H., Zenobi, R., Bada, J. L., and Zare, R. N.: 1988, *Science* **239**, 1523.

Hayatsu, R. and Anders, E.: 1981, in *Topics in Current Chemistry* **99**, Springer-Verlag, p. 1.

Hayatsu, R., Matsuoka, S., Scott, R. G., Studier, M. H., and Anders, E.: 1977, *Geochim Cosmochim. Acta* **41**, 1325.

Marti, K., Kim, J. S., Lavielle, B., Pellas, P., and Perron, C.: 1989, *Z. Naturforsch* **44a**, 963.

McSween, H. Y. Jr.: 1987, *Meteorites and Their Parent Planets*, Cambridge University Press.

Miller, S. L.: 1953, *Science* **117**, 528.

Miller, S. L.: 1987, *Cold Spring Harb. Symp. Quant. Biol. LII*, 17.

Miller, S. L. and Bada, J. L.: 1988, *Nature* **334**, 609.

Mullie, F. and Reisse, J.: 1987, in *Topics in Current Chemistry* **139**, Springer-Verlag. p. 83.

Murae, T., Masuda, A., and Takahashi, T.: 1987, in *Mem. Natl. Inst. Polar Res., Special Issue* **46**, 196.

Ogan, K., Katz, E., and Slavin, W.: 1979, *Anal. Chem.* **51**, 1315.

Peltzer, E. T., Bada, J. L., Schlesinger, G., and Miller, S. L.: 1984, *Adv. Space Res.* **4** (12), 69.

Pering, K. L. and Ponnamperuma, C.: 1971, *Science* **173**, 237.

Schmidt, W.: 1987, in A. Leger, L. B. d'Hendecourt and N. Bocarra (eds.), *Plycyclic Aromatic Hydrocarbons and Astrophysics*, Kluwer Acad. Publ., Dordrecht.

Shimoyama, A. and Harada, K.: 1989, *Geochem. J.* **23**, 181.

Studier, M. H., Hayatsu, R., and Anders, E.: 1972, *Geochim. Cosmochim. Acta* **36**, 189.

Stull, D. R., Westrum, E. F. Jr., and Sinke, G. C.: 1969, *The Chemical Thermodynamics of Organic Compounds*, J. Wiley ‑ Sons.

Tissot, B. P. and Welte, D. H.: 1984, *Petroleum Formation and Occurrence*, 2nd ed. Springer-Verlag. p. 699.

Urey, H.: 1953, *XIII International Congress of Pure and Applied Chemistry: Plenary Lectures.*

Wing, M. R.: 1991, Ph. D. Dissertation, University of California, San Diego, p. 120.

Wing, M. R. and Bada, J. L.: 1991, *Geochim. Cosmochim. Acta* **55**, 2937.

Wolman, Y., Hverland, W. J., and Miller, S. L.: 1972, *Proc. Nat. Acad. Sci. U.S.A.* **69**, 809.

Wright, I. P. and Gilmour, I.: 1990, *Nature* **345**, 110.

Zenobi, R., Philippoz, J. -M., Zare, R. N., Wing, M. R., Bada, J. L., and Marti, K.: 1992, *Geochim. Cosmochim. Acta* (in press).

Zhao, M. and Bada, J. L.: 1989, *Nature* **339**, 463.