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Organic Compounds in Meteorites

They may have formed in the solar nebula, by catalytic reactions of carbon monoxide, hydrogen, and ammonia.

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Type 1 carbonaceous chondrites (C1) are the most primitive samples of matter known to man. They contain all stable elements in solar proportions, with the exception of the noble gases and the highly volatile major elements hydrogen, carbon, nitrogen, and oxygen. It is generally agreed that they are low-temperature condensates from a solar gas, though there still is some debate on the locale of the condensation. Most workers favor the solar nebula (*1, 2*). Others prefer atmospheres of red giants or interstellar space (*3*), or gaseous envelopes of meteorite parent bodies (*4, 5*).

The C1 chondrites contain 6 percent of their cosmic complement of carbon, mainly in the form of organic matter. The intense controversy which once surrounded the origin of this organic matter has subsided. Most authors now agree that this material represents primitive prebiotic matter, not vestiges of extraterrestrial life. The principal question remaining is just how primitive this material is: whether it is a primary condensate from a solar gas or a secondary product, introduced into the meteorite during residence in its parent body.

We can approach the problem in three stages. First, we try to reconstruct the physical conditions during condensation (temperature, pressure, time) from the clues contained in the inorganic matrix of the meteorite. Next, we determine the condensation behavior of carbon under these conditions, on the basis of thermodynamic calculations. Finally, we perform model experiments on the condensation of carbon, and compare the compounds synthesized with those actually found in the meteorites.

Formation Conditions of Carbonaceous Chondrites

Temperatures. Six different "cosmothermometers," based on kinetic or equilibrium isotope fractionations, or on chemical reactions, consistently give temperatures near 360°K for C1 chondrites (Table 1). These values represent the temperatures at which isotopic or chemical equilibria were frozen in, owing to sluggish reaction rates or physical isolation of the meteoritic dust from the ambient gas (accretion to larger bodies). These temperatures are lower than those for C2 chondrites, 380° to 400°K (*6*) or ordinary chondrites and achondrites, about 450° to 500°K (*1, 6*).

Pressure. A tentative value of roughly 4×10^{-6} atmosphere has been estimated for the C1 chondrite Orgueil from the ^{36}Ar content of its magnetite (*7*). Similar values, around 10^{-5} atm, were obtained for ordinary chondrites from their bismuth, thallium, and indium contents (*1*). An upper limit of less than 2×10^{-3} atm has been inferred (*2*) for C3 chondrites from the lack of evidence for gas-to-liquid condensation. These pressures agree with Cameron and Pine's (*8*) model of the solar nebula, based on Larson's adiabat (*9*) which gives 8×10^{-6} atm at 360°K. They do not appear to be consistent with Urey's gas spheres (*4*), which give pressures some five to seven orders of magnitude higher at this temperature.

Time. An age determination based on extinct 16-million-year ^{129}I suggests an interval as short as 2.0 ± 2.4 million years for the entire evolution of carbonaceous chondrites, from condensation through chondrule formation and accretion to end of metamorphism in the parent bodies (*10*). For our purposes, only the nebular stage is relevant, which has not yet been dated experimentally. Theoretical calculations of the lifetime of the nebula (*8*) suggest a time of no more than 10^4 years, perhaps as short as a few thousand years.

Behavior of Carbon in a Solar Gas

With the physical conditions thus defined, it is instructive to consider what happens to carbon in a cooling solar gas (Fig. 1). Carbon monoxide is the stable form at high temperatures, but becomes less stable on cooling and should transform to methane below 600°K, as shown by the solid lines in the right-hand portion of Fig. 1. However, CH_4 has a condensation temperature of less than 100°K, and if this reaction had gone as written, there should be no carbon and no life anywhere in the inner solar system. Since there is at least some evidence to the contrary (*11*), events must have taken a different course.

Urey (*12*) first noted this paradox in a classic paper. He suggested that the CO–CH_4 transformation might not have gone smoothly "in the absence of man-devised catalysts," but might instead have "proceed[ed] through graphite or complex tarry carbon compounds as intermediates. Such compounds have long been known to be constituents of the carbonaceous chondritic meteorites. It seems most probable to the writer that such compounds constitute the non-volatile carbon compounds which supplied the carbon to the earth and meteorites while other

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Table 1. Formation temperatures of C1 chondrites.

Thermometer	Temperature (°K)	Pressure (atm)	Reference
$^{18}O/^{16}O$ between $CaMg(CO_3)_2$ and H_2O	360 ± 5	Independent	(*6*)
$^{18}O/^{16}O$ between serpentine and H_2O	360 ± 15	Independent	(*6*)
$^{13}C/^{12}C$ between $CaMg(CO_3)_2$ and polymer	357 ± 21	Independent	(*35*)
$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2$	$\leqq 400$	Independent	(*79*)
Olivine + $H_2O \rightleftarrows$ serpentine	~ 350	10^{-4}	(*1*)
Thallium abundance	< 394	10^{-6}	(*1*)

gases, the hydrogen and inert gases, were lost from the region of the forming earth."

This idea soon fell into oblivion—ironically, due to the success of another of Urey's ideas. A major paradox facing all theories on the origin of life on the earth was that the carbon dioxide in the earth's atmosphere would not spontaneously transform to organic compounds, all of which are thermodynamically less stable. Calvin (*13*) showed in 1950 that the thermodynamic problem could be overcome by supplying energy in the form of ionizing radiation. But the crucial advance came 2 years later when Urey (*14*), following Oparin (*15*), realized that the primitive atmosphere must have been highly reduced (CH_4 rather than CO_2, along with NH_3, H_2O, and H_2). He suggested that ultraviolet light or electric discharges might have converted the molecules in the atmosphere to excited species or free radicals, which would then transform spontaneously into a variety of organic compounds, depending on the available kinetic pathways.

Urey's suggestion was soon confirmed by Miller (*16*) in a historic experiment, in which amino acids were produced from CH_4, H_2O, and NH_3 by an electric spark discharge. [The analogous synthesis with ultraviolet light was not achieved with high efficiency until 1971 (*17*).] A new scientific discipline, abiotic synthesis, was born. In the ensuing excitement, Urey's other suggestion (complex organic compounds from partial hydrogenation of CO) seems to have been forgotten.

Model experiments: the Fischer-Tropsch synthesis. We began to investigate this neglected idea in 1964, when it first became apparent that Miller-Urey reactions could not account for certain features of meteorite organic matter. Our approach was to see how CO and H_2 behaved in the presence of some natural catalysts expected in the solar nebula: nickel-iron, magnetite, hydrated silicates. We found (*18*) that the reaction indeed tends to stop at intermediate stages of hydrogenation, giving metastable products with an H/C ratio of about 2 (for example, $C_{20}H_{42}$) rather than stable methane with H/C equal to 4. In fact, this process (the Fischer-Tropsch synthesis, discovered in 1923) has been used industrially for the production of gasoline.

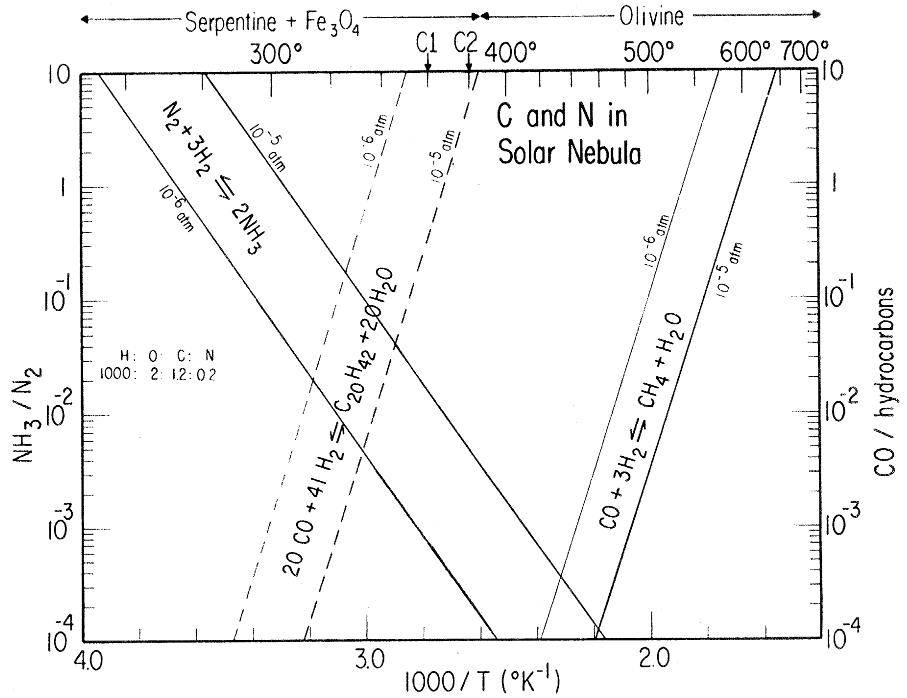

Fig. 1. If equilibrium is maintained on cooling, CO will be converted largely to CH_4 (solid lines) before metastable formation of more complex hydrocarbons by the Fischer-Tropsch reaction becomes possible (dashed lines). However, the reaction is very slow in the absence of catalysts, and may not have begun until about 400°K when catalysts such as serpentine and magnetite became available through the hydration of olivine.

It is not feasible to conduct such model experiments at the pressure and H_2/CO ratio of the solar nebula—the total amount of carbon in a 1-liter vessel would be only about 5×10^{-9} gram. Accordingly, we used higher pressures (0.1 to 10 atm), and lower H_2/CO ratios (generally 1, sometimes as high as 120). We shall show later on that these results are nonetheless applicable to the solar nebula.

As a safeguard against contamination, we used deuterium rather than light hydrogen in our syntheses, and identified reaction products by mass spectroscopy. Perdeuterated compounds give peaks only at even mass numbers (except for very minor peaks due to the rare isotope ^{13}C). Contaminants, on the other hand, give prominent peaks at both even and odd mass numbers. In general, products were separated by gas chromatography or other techniques (*19*) before mass spectrometry.

The reaction was always carried out under static conditions in a closed vessel, not in a flow system as in the industrial synthesis. We also broadened the range of experimental conditions beyond those of the classical Fischer-Tropsch synthesis. Reaction times ranged from a fraction of an hour to a few months, and the temperature was sometimes raised briefly from 150°–250°C to 500°–700°C. Such thermal pulses were intended to simulate short-term heating events in the nebula, such as collisions, shock waves, or the chondrule-forming process. When nitrogen compounds were sought we added ND_3 to the reactant gases, and occasionally used other types of catalysts, such as montmorillonite clay, Al_2O_3, or SiO_2. For want of a better term, we shall call this class of reactions "Fischer-Tropsch-type" (FTT).

Organic Compounds in Meteorites

There is little doubt that the bulk of the organic matter in meteorites is indigenous, judging from isotopic measurements on C, H, and S (*20, 21*). Such proof is not available for individual compounds, however, and it is therefore necessary to resort to less direct arguments to rule out terrestrial contamination. We shall briefly review the most reliably established features of organic matter in meteorites, and see how well FTT reactions can account for them. Owing to space limitations, we can only give a concise summary of the most pertinent data. The interested reader may wish to consult the original sources, as well as the reviews of Hayes (*22*), Vdovykin (*23*), and Oró and co-workers (*24*).

Heavy alkanes. The same few compounds dominate in meteoritic and FTT hydrocarbons (*18, 25, 26*). Normal (straight-chain) hydrocarbons are most prominent (Fig. 2), followed by five slightly branched (monomethyl and dimethyl) isomers (*27*). This resemblance is highly significant if one considers that some 10^4 structural isomers exist for saturated hydrocarbons with 16 carbon atoms. Apparently the meteoritic hydrocarbons were made by FTT reactions, or a process of the same extraordinary selectivity. The Miller-Urey reaction, incidentally, shows no such selectivity. Gas chromatograms of spark discharge hydrocarbons show no structure (*13*). Apparently all 10^4 possible isomers are made in comparable yield, as expected for random recombination of free radicals.

The indigenous nature of the alkanes in at least the Murray, Murchison, and Orgueil meteorites (*18*) is supported by four lines of evidence: absence of the isoprenoids pristane and phytane (*18*), which occur in nearly all terrestrial hydrocarbons (*13, 26, 28*); characteristic light hydrocarbon pattern (*18*); consistently low abundance of alkanes in the C3 chondrite Allende (*18, 29*), which is metamorphosed and hence may be regarded as a blank; and carbon isotope data (*21, 30*).

Most of the remaining compounds in the meteoritic chromatogram (acenaphthene, alkylbenzenes, olefins) can be made by FTT syntheses under appropriate conditions (*18*). Kvenvolden *et al.* (*30*) and Oró *et al.* (*31*) had reported alicyclic hydrocarbons in the Murchison meteorite on the basis of low-resolution chromatograms. These compounds were not confirmed at higher resolution (*18*), however, but can, in any event, be made in the FTT synthesis. The authors have found large amounts of cycloalkanes in a commercial Fischer-Tropsch sample.

Carbon isotope fractionations. Meteorites show a very large difference in $^{12}C/^{13}C$ ratio between carbonate and organic carbon: 60 to 80 per mil (*20, 21, 32*). This trend remained unexplained for a number of years, because coexisting carbonate and organic matter on the earth shows a much smaller difference, typically 25 to 30 per mil. It probably is a primary feature, unaffected by the later thermal history of the meteorite. Terrestrial calcium carbonate is not known to equilibrate with coexisting organic matter in sediments (*21*).

Although fractionations of 60 to 80 per mil are theoretically possible under equilibrium conditions at very low temperatures ($\leq 0°C$), they are not observed on the earth. Urey (*4*) therefore proposed that the two types of carbon came from two unrelated reservoirs while Arrhenius and Alfvén (*33*) suggested fractionation during carbonate growth from the gas phase, involving multiple desorption or metastable molecules.

It turns out, however, that the Fischer-Tropsch reaction gives an isotopic fractionation of just the right sign and magnitude, owing to a kinetic isotopic effect (*34, 35*). From the temperature dependence of the fractionation between 375° and 550°K, the observed fractionations in C1 and C2 chondrites correspond to about 360° and 400°K (Fig. 3). These values agree rather well with the formation temperatures of carbonates and silicates based on $^{18}O/^{16}O$ ratios, 360°K for C1's and 380°K for C2's (*6*). The Miller-Urey reaction gives a fractionation of only -0.4 ± 0.2 per mil (*35*).

Aromatic hydrocarbons; light alkanes. Carbonaceous chondrites contain a wide range of aromatic hydrocar-

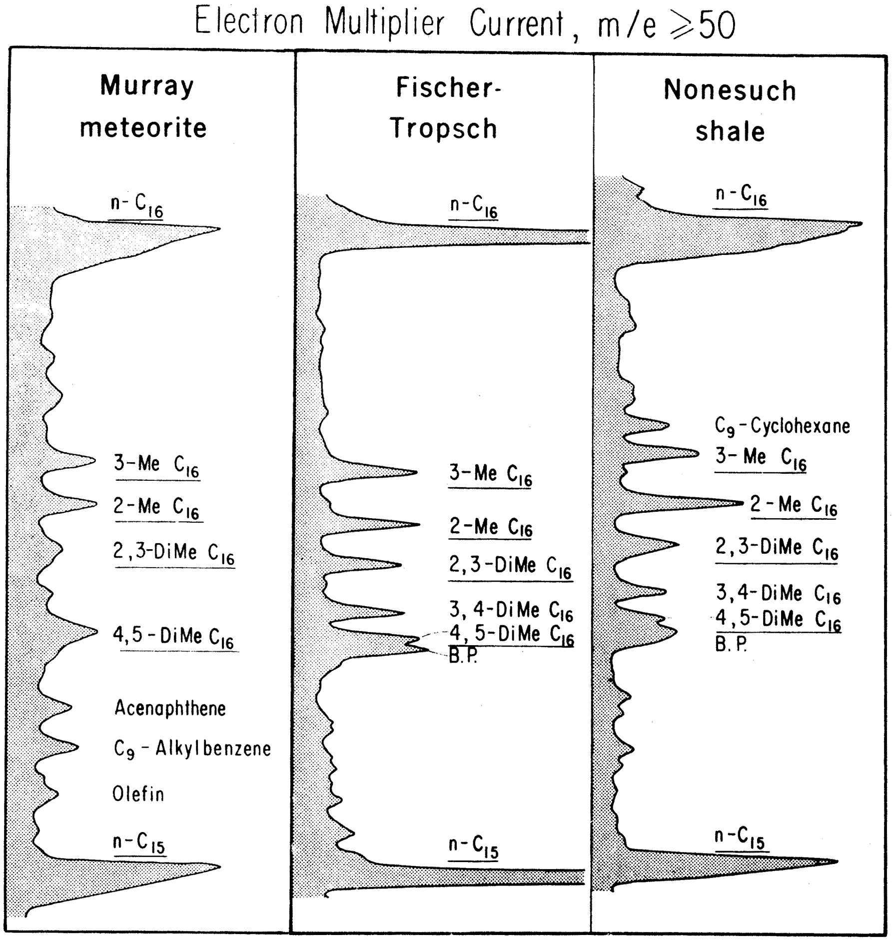

Fig. 2. Gas chromatogram of hydrocarbons in the range C_{15} to C_{16} (*18*). Only six of the approximately 10^4 isomeric hydrocarbons with 16 carbon atoms are present in appreciable abundance; five of these (underlined) are common to all three samples. The Nonesuch sample (courtesy W. G. Meinschein) is a pure aliphatic fraction from which aromatic hydrocarbons had been removed by silica gel chromatography. Abbreviations: Me, methyl; B.P., branched paraffin.

bons, from benzene through alkylbenzenes and alkylnaphthalenes to polynuclear hydrocarbons of up to six fused benzene rings (*18, 22, 23, 25, 36, 37*). At higher carbon numbers, aromatics tend to be less abundant than normal alkanes, but below about C_{11}, the reverse is true (Fig. 4A). In fact, virtually no normal alkanes at all are found between C_2 and C_8, their place having been taken largely by benzene, toluene, xylene, and various alkenes or branched alkanes (*18, 36*).

A pattern of this sort does not form directly in the primary Fischer-Tropsch reaction. It does, however, develop when a primary Fischer-Tropsch mixture remains in contact with the catalyst, for a day or so at 350° to 400°C (Fig. 4B), or longer times at lower temperatures (*18, 38*). Under such conditions, a metastable equilibrium is approached, with methane and aromatic hydrocarbons forming at the expense of ethane and heavier alkanes (*39*). The kinetics and mechanism of such aromatization on the catalyst surface has been discussed by Galwey (*38*). Of the 61 hydrocarbons in the meteorite, 42 (underlined in Fig. 4) are also seen in the synthetic sample, though often not in the same amount. It remains to be seen whether the match can be made more quantitative by changes in the reheating conditions.

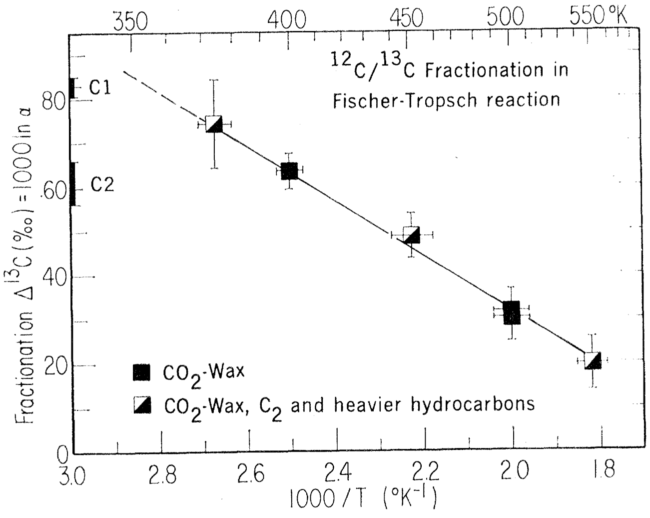

Fig. 3. The Fischer-Tropsch reaction shows a kinetic isotope fractionation between organic and carbonate carbon of the same sign and magnitude as that in meteorites (black bars on ordinate). Observed fractionations in C1 and C2 chondrites correspond to temperatures of about 360° and 400°K (*35*). [Fractionation factor α is defined as $(^{13}C/^{12}C)_{CO_2}/(^{13}C/^{12}C)_{wax}$.]

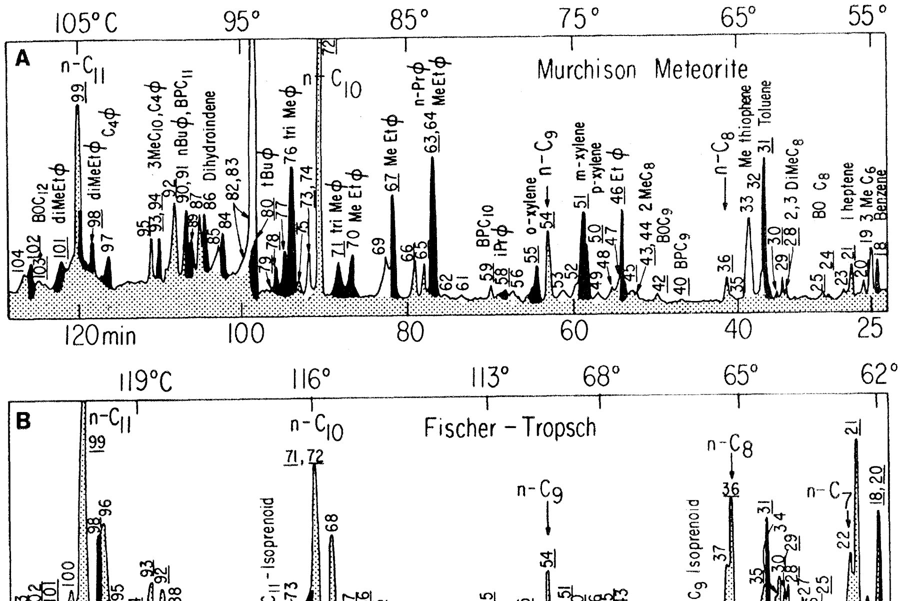

Fig. 4. Hydrocarbons from Murchison meteorite and Fischer-Tropsch synthesis; BP, branched paraffin; BO, branched olefin; Φ, phenyl radical. For additional peak identifications, see (*18*). Of the 61 hydrocarbons in the meteorite, 42 (underlined) are also present in the Fischer-Tropsch sample, though often not in comparable amount. (Solid area) Aromatic hydrocarbons, (stippled area) aliphatic hydrocarbons, (blank area) compounds containing Cl or S.

When the heating is prolonged or carried out at higher temperatures, polynuclear aromatic hydrocarbons with up to seven rings are obtained (*18*). This reaction, with CH_4 as the starting material, was discovered by Berthelot over a century ago, and has lately been reinvestigated by several authors (*40*).

Opportunities for such secondary reactions certainly existed in the history of meteorites. Temperatures in the nebula (360° to 400°K, Table 1) may alone have been high enough for secondary reactions in the time available, on the order of 10^4 years. Kinetic studies of a similar reaction [formation of benzene from alcohols, amines, or fatty acids on Fe_2O_3 or iron-rich peat catalysts (*38*)] indicate a benzene formation rate of 5×10^{16} molecules per gram per year at 360°K. At this rate it would take only 5000 years to transform all the meteoritic carbon to benzene. Further opportunities were provided by brief thermal pulses during chondrule formation, impact, or transient shocks (*1*). Of course, any high-temperature episodes must have happened early or on a local scale, to permit survival of other, more temperature-sensitive compounds.

Isoprenoid alkanes. At one time it appeared (*26*) that nearly all carbonaceous chondrites contain the isoprenoid alkanes pristane and phytane (2,6,10,14-tetramethylpentadecane and 2,6,10,14-tetramethylhexadecane). These two hydrocarbons, which may formally be regarded as tetramers of isoprene, $CH_2 : C(CH_3)CH : CH_2$, serve as biological markers on the earth, being derived mainly from the phytol side chain of the chlorophyll molecule. Their presence in meteorites thus suggested either extraterrestrial life or an abiotic process that strongly favored isoprenoids over other types of branched hydrocarbons (*13, 41*).

It seems, however, that these results reflected terrestrial contamination. Studier *et al.* (*18*) found no tetrameric isoprenoids in Orgueil and Murray, only small amounts of dimeric isoprenoids from C_9 to C_{14}. These compounds can, however, be produced in FTT syntheses (*18*); in fact, they are more prominent in synthetic material than in meteorites (Fig. 4). The

Murchison meteorite did contain substantial amounts of tetrameric and trimeric isoprenoids; however, they are found only in a surface rinse of the stone, not in an interior extract (Fig. 5). Yet the other alkanes persisted, and since most terrestrial alkane mixtures contain isoprenoids (*13, 28*), this would seem to strengthen the case for an extraterrestrial origin of these alkanes. Gelpi *et al.* (*28*) cast further doubt on the earlier identifications by showing that pristane, phytane, and other heavy isoprenoids were prominent in house dust and even in hydrocarbon extracts from FeS nodules in iron meteorites.

Fatty acids. Nagy and Bitz (*42*) reported fatty acids from C_{14} to C_{28} in Orgueil. This work was subtantially confirmed by Hayatsu (*43*) and Smith and Kaplan (*21*). The latter authors found 3 to 91 parts per million (ppm) of fatty acids from C_{12} to C_{20} in seven carbonaceous chondrites. Smith and Kaplan believe that these acids are largely or entirely terrestrial contaminants, because unstable unsaturated acids comprise about 30 percent of the total, and C_{16} and C_{18} acids are predominant. No attempts have yet been made to look for fatty acids in the model experiments described here, but it is well known that they can be produced in the Fischer-Tropsch and related syntheses (*44*).

Purines, pyrimidines, and other nitrogen bases. Several of the constituent bases of DNA and RNA (adenine, guanine, and so forth) have been found in the Orgueil meteorite, along with structurally similar nitrogen compounds (melamine, ammeline, guanyl urea) of no biological significance (*45, 46*). All these compounds are produced, in yields of 0.1 to 0.6 percent, by an FTT reaction in the presence of NH_3 (*46*). Other compounds observed in FTT syntheses but not yet found in meteorites include several of biological importance: xanthine, thymine, uracil and derivatives, guanidines, pteridines, cyanuric acid, biuret, and, of course, urea (*46*). It is interesting that adenine, one of the bases of DNA and RNA, forms in the same yield (0.16 percent) as urea, a compound of simpler structure and far longer history of abiotic production.

A somewhat different set of *N*-heterocyclic compounds, including 4-hydroxypyrimidines but no biological heterocyclics, was reported by Folsome *et al.* (*47*) in three carbonaceous chondrites. However, this seems to reflect problems of technique. With suitable extraction methods, biological heterocyclics such as adenine and guanine are readily identified (Fig. 6).

Amino acids. Early reports of amino acids in meteorites were discredited by the discovery that fingerprints give an equally rich spectrum of amino acids, in comparable quantities (*48*). However, Kvenvolden *et al.* (*30*) showed by an elegant, contamination-proof technique (gas chromatography of diastereomeric derivatives) that the Murchison meteorite contains at least 17 indigenous amino acids, or compounds hydrolyzable thereto. The abiotic character of this assemblage is

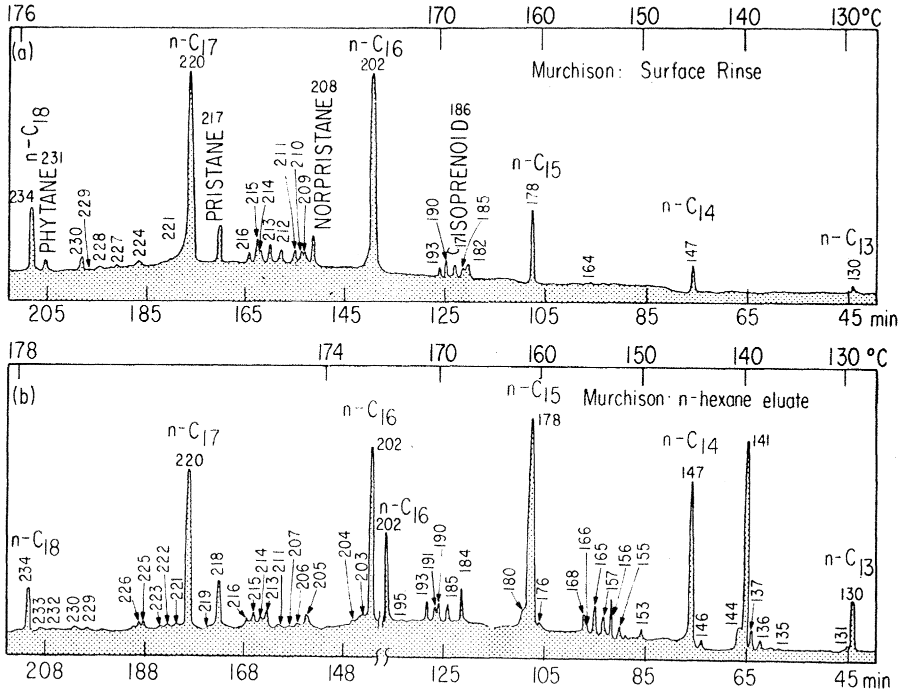

Fig. 5. (a) A surface rinse of Murchison (benzene-methanol and *n*-hexane at room temperature) contains four isoprenoid hydrocarbons (capitalized). For peak identifications, see (*18*). (b) Benzene-methanol extract of the same sample after grinding still yields a variety of alkanes and alkenes, but no isoprenoids. Peak 218 preceding *n*-C_{17} is not pristane but an alkene. Apparently the heavier isoprenoids are surficial contaminants of terrestrial origin.

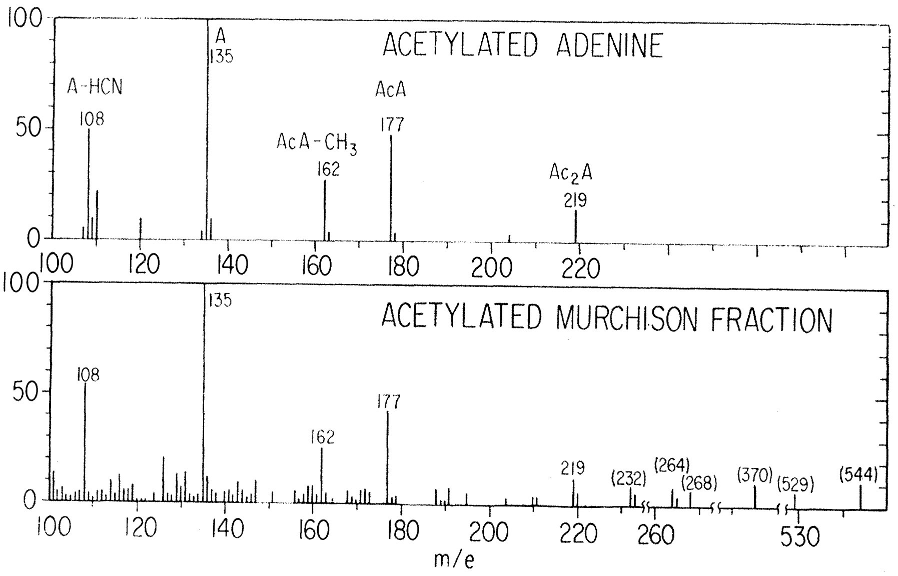

Fig. 6. Mass spectra of acetylated authentic adenine (top) and a trifluoroacetic acid extract from the Murchison meteorite (bottom), hydrolyzed in 3*M* HCl for 6 hours at 120°C; A, adenine; Ac, acetyl. High-mass peaks in the meteoritic sample indicate that the precursor material was not completely hydrolyzed (*56*).

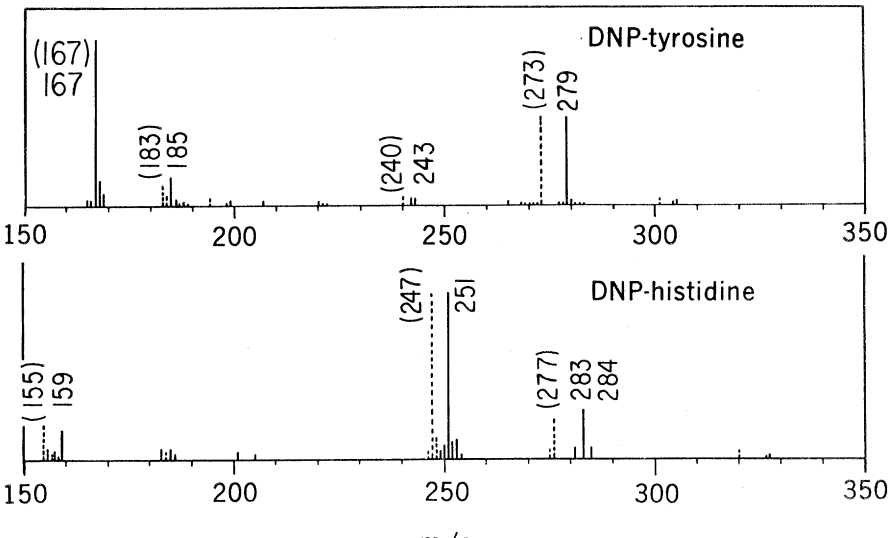

Fig. 7. Mass spectra of dinitrophenyl (DNP) derivatives of amino acids, separated by paper chromatography (*50*). (Solid lines) Deuterated amino acids synthesized from CO, D_2, and ND_3 by an FTT reaction. (Dashed lines) "Light" (protonated) amino acid standards.

underscored by the racemic nature of several of the amino acids, and by the fact that ten of them are not commonly found in terrestrial proteins. These results were substantially confirmed by other authors (*49*).

A somewhat similar distribution of amino acids (Table 2) is produced in FTT syntheses involving a brief initial heating to 500° to 700°C (*50*). Yields are low (0.01 to 0.1 percent), but the products include structurally complex aromatic or heterocyclic amino acids such as tyrosine and histidine (Fig. 7) that cannot be made by conventional Miller-Urey syntheses. Regrettably, this work was completed before the meteorite analyses became available, and so the nonprotein amino acids were not systematically looked for. Some were tentatively identified when seen in large amounts; others may have comprised the up to six unidentified compounds that were observed in most of these syntheses.

A directed search for these amino acids in the Miller-Urey synthesis has been largely successful (*51*), yielding all those seen in Murchison. Interestingly, the proportions of amino acids in the synthesis agree to within one or two orders of magnitude with those in the meteorite. To the extent that such a comparison can be made from the more limited data, this also appears to be true of the FTT synthesis.

Porphyrins. Hodgson and Baker (*52*) have detected pigments resembling porphyrins in several carbonaceous chondrites. It is not clear whether these were true (cyclic) porphyrins or linear pyrrole polymers. Both kinds have been seen in FTT syntheses. The cyclic pigment illustrated in Fig. 8 has a major peak at mass 580, as expected for an alkyl-substituted porphine $C_{20}D_{14}N_4 + 16CD_2$. Though it does not show a doubly charged ion at mass 290, it displays other characteristics of porphyrins: strong absorption at 394 nanometers (in the Soret band range), formation of a red copper complex, and chromatographic and solvent extraction behavior similar to that of porphyrins (*34*).

Table 2. Amino acids in the Murchison meteorite and in FTT syntheses. The abbreviations are Def., definite; Tent., tentative; N.S., not sought.

Amino acid	Meteorite (*30, 49*)	FTT (*50*)
Protein amino acids		
Glycine	Def.	Def.
Alanine	Def.	Def.
Valine	Def.	Tent.
Leucine		Tent.
Isoleucine		Tent.
Aspartic acid	Def.	Def.
Glutamic acid	Def.	Def.
Tyrosine		Def.
Proline	Def.	Tent.
Ornithine		Def.
Lysine		Def.
Histidine		Def.
Arginine		Def.
Nonprotein amino acids		
N-Methylglycine	Def.	Def.
N-Ethylglycine	Def.	N.S.
β-Alanine	Def.	Def.
N-Methylalanine	Def.	N.S.
Isovaline	Def.	N.S.
Norvaline	Def.	N.S.
α-Aminoisobutyric acid	Def.	Tent.
α-Amino-*n*-butyric acid	Def.	Tent.
β-Aminoisobutyric acid	Def.	Tent.
β-Amino-*n*-butyric acid	Def.	N.S.
γ-Aminobutyric acid	Def.	Tent.
Pipecolic acid	Def.	N.S.

Porphyrin-like pigments of similar properties have been made by the Miller-Urey synthesis (*53*), but they have not yet been characterized by mass spectrometry.

Chloro and thio compounds. Mono- and dichlorobenzenes have been found in several carbonaceous chondrites (*18*), but in view of the widespread human use of such compounds, it is not at all certain that they are indigenous. Benzothiophenes, first reported by Hayes and Biemann (*36*) in pyrolysis experiments, have also been seen in solvent extracts at room temperature (*18*) and hence must be original constituents of the meteorites, not thermal degradation products. It is not known whether these compounds can be made in FTT syntheses, because the necessary experiments have not yet been attempted.

Macromolecular material. At least 70 percent of the organic matter in meteorites consists of an ill-defined, insoluble solid, said to resemble humic acids in soils (*54*). It has an aromatic skeleton bearing functional groups such as –COOH and –OH (*18, 22, 23, 55*). A similar material was obtained in an FTT synthesis extended over 6 months. The mass spectra of the meteoritic and synthetic polymers (Fig. 9) show mainly benzene, naphthalene, and their alkyl derivatives, as well as alkylindanes, fluorene, anthracene or phenanthrene, alkenes, alkanes, and alkylphenols (*56*).

A Miller-Urey reaction in the presence of H_2S (*57*) also gives a polymer, but of aliphatic rather than aromatic structure.

Relevance to the Solar Nebula

It appears that FTT reactions can account reasonably well for all features of organic matter in meteorites. The only alternative process, the Miller-Urey synthesis, fails to account for the aliphatic and aromatic hydrocarbons, purines and pyrimidines, the polymer, and carbon isotope fractionations, though it remains an alternative and perhaps superior source of amino acids.

However, it is not immediately obvious that the FTT model experiments are relevant to the solar nebula. First and foremost, it must be shown that CO was still present at the time the nebula had cooled to 360°K. How did CO traverse the no-man's-land between 600°K where it becomes unstable with respect to CH_4, and about 400°K where formation of heavy hydrocarbons first becomes thermodynamically feasible (Fig. 1)? Second, was the reaction rate fast enough at the extremely low pressures in the nebula?

Survival of CO. An answer to the first question was suggested by Lancet and Anders (*34*). The principal meteoritic phases stable above about 350° to 400°K (olivine, pyroxene, Fe, FeS) are not effective catalysts for the Fischer-Tropsch reaction, while the phases forming below this temperature (hydrated silicates, magnetite) are. [Though metallic iron is often regarded as a catalyst for this synthesis, the catalytically active phase actually is a thin coating of Fe_3O_4 formed on the surface of the metal (*58*).] Thus, CO may have survived metastably until catalysts became available by reactions such as

$$12(Mg,Fe)_2SiO_4 + 14H_2O \rightarrow 2Fe_3O_4 + 2H_2 + 3(Mg,Fe)_6(OH)_8Si_4O_{10}$$

$$4(Mg,Fe)_2SiO_4 + 4H_2O + 2CO_2 \rightarrow 2(Mg,Fe)CO_3 + (Mg,Fe)_6(OH)_8Si_4O_{10}$$

This would also explain why the hydrated silicates, carbonates, and organic compounds all have the same formation temperature (Table 1).

Rate of reaction in the nebula. The second question cannot be answered unequivocally because the kinetics of the Fischer-Tropsch reaction are not well enough understood to permit reliable extrapolations to very low pressures. Still, a tentative analysis based on Langmuir's adsorption isotherm suggests that the rate may be adequate even at 4×10^{-6} atm (*35*).

Since H_2 is much more strongly adsorbed than is CO and covers nearly the entire surface at pressures greater than 10^{-10} atm (*59*), the Langmuir rate expression simplifies to:

$$R = k(b_C/b_H)\,(P_C/P_H^{\frac{1}{2}})$$

where P is the pressure, k the rate constant, and b the adsorption coefficient, and the subscripts C and H stand for CO and H_2. (The exponent ½ reflects the fact that H_2 dissociates to H atoms upon adsorption.) With the symbols N for nebula and L for laboratory, the half-time t in the nebula is:

$$t_N = t_L P_{CL} P_{HN}^{\frac{1}{2}} / P_{CN} P_{HL}^{\frac{1}{2}}$$

A conservative estimate of t_L may be obtained from the experiments of Lancet (*35*), who studied the rate of the Fischer-Tropsch reaction on a cobalt catalyst between 500° and 375°K (Fig. 10). The data gave an activation energy of 27 ± 1 kilocalories per mole, similar to earlier determinations (*58*). The laboratory half-time t_L extrapolated to 360°K is 8600 hours, or about 1 year. With $P_{HL} = P_{CL} = 0.5$ atm, $P_{HN} = 4 \times 10^{-6}$ atm, and $P_{CN} = 3 \times 10^{-9}$ atm, we obtain $t_N = 5 \times 10^5$ years.

However, this value almost certainly is a gross overestimate. Lancet's experiments were done in a static system at 1 atm, where the mean distance between gas molecules and catalyst was about 10 cm or 10^6 mean free paths. In the nebula, this distance would be only about 0.04 cm or 0.01 mean free path (*60*). A better estimate may therefore be obtained from industrial flow-type syntheses, where contact between gas and catalyst is more intimate than in a static system. Rates at 440° to 470°K (*58*) are typically (1 to 2) × 10^3 times faster (bottom curve in Fig. 10) than in Lancet's static experiments (middle curve). Accordingly, the half-time in the nebula (top curve) may be 500 years or less, somewhat shorter than the expected lifetime of the nebula, on the order of 10^4 years.

We can reexamine the question of CO survival in the light of these rate data. From the relation between surface density and cooling time (*61*), it

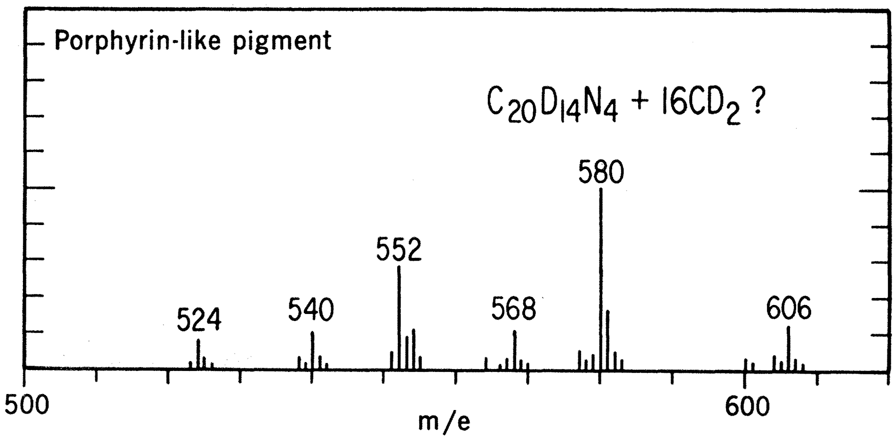

Fig. 8. Mass spectrum of porphyrin-like pigment, made from CO, D_2, and ND_3 by an FTT synthesis (*46*). It resembles porphyrins in optical and chemical characteristics, but lacks a peak at mass 290 due to the doubly charged molecular ion.

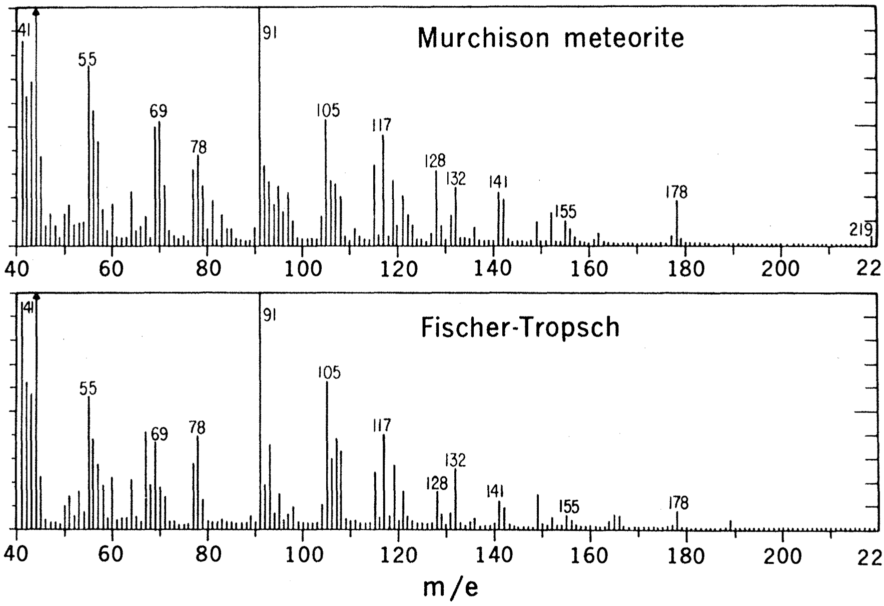

Fig. 9. Mass spectra of polymeric materials from the Murchison meteorite and a Fischer-Tropsch synthesis extended over 6 months. The principal peaks are due to aromatic hydrocarbons, their alkyl derivatives, and alkenes (*56*).

seems that the pertinent region of the nebula took 10 years or 3×10^8 seconds to cool from 600° to 400°K. The requirement that one-half the initial CO survive this stage is equivalent to the condition that the half-time at 600°K, in the absence of good catalysts, be greater than 3×10^6 seconds (*62*). This is nearly three orders of magnitude longer than the half-life of 7×10^3 seconds extrapolated from the top curve in Fig. 10, which applies in the presence of good catalysts. The available experimental data do indeed suggest a difference of at least this order. No trace of a reaction was observed when CO and D_2 were heated to 620°K in the presence of the L6 chondrite Bruderheim (*18*), which is representative of the mineral assemblage expected in the nebula between 600° and 400°K. The lower limit to the half-life inferred from this experiment is 4×10^8 seconds (triangle in Fig. 10), that is eight orders of magnitude above the value for a Co catalyst. It appears that survival of CO between 600° and 400°K is not a problem.

It is not clear whether enough NH_3 was present in the nebula for the synthesis of nitrogen compounds. Figure 1 shows that NH_3 becomes less abundant at lower pressures. Only about 2×10^{-3} of the total N will be present as NH_3 at 360°K and 4×10^{-6} atm, if equilibrium is reached. Perhaps this was sufficient for the synthesis of nitrogen compounds; if not, it is conceivable that some NH_3 was brought in from denser parts of the nebula, or synthesized by shock waves.

Catalysts. The availability of a catalyst is another important question. Industrial Fischer-Tropsch syntheses generally use metallic catalysts and since these are easily poisoned by sulfur, Oró and co-workers (*26*) have questioned the catalytic effectiveness of meteoritic dust in the solar nebula, because of the high sulfur content of meteorites.

However, this objection does not seem serious. In a poisoned industrial catalyst, the entire surface is coated with sulfide, rendering it ineffective. But in carbonaceous chondrites, discrete and spatially separated sulfide, magnetite, metal, and phyllosilicate grains are present. The last three phases are catalytically active (*38, 58, 63*). Grains suspended in the nebula cannot intercommunicate with each other, hence a sulfide grain cannot inhibit catalytic reactions at the surface of an Fe_3O_4 grain 0.1 cm distant. Indeed, Studier *et al.* (*18*) showed that the Cold Bokkeveld carbonaceous chondrite was able to catalyze an FTT reaction.

There are some indications that the organic compounds were indeed synthesized on the surfaces of meteoritic mineral grains. Vdovykin (*23*) and Alpern and Benkheiri (*64*) have shown that much of the organic matter is present as rounded, fluorescent particles 1 to 3 micrometers in diameter, containing cores of magnetite or silicate.

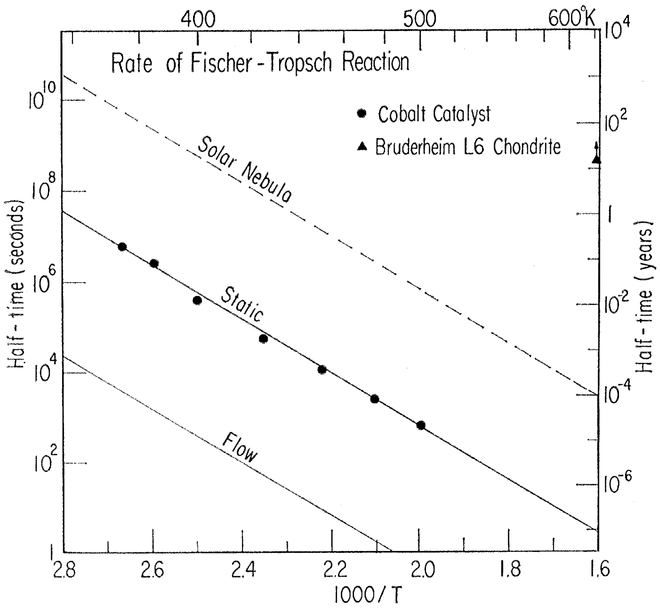

Fig. 10. The Fischer-Tropsch reaction at 1 atm is first-order in CO, with an activation energy of 27 kcal/mole (*35*). The reaction in a flow system is about 10^3 times faster than in the static system used here. The dashed line shows an extrapolation to the solar nebula; the rate is assumed proportional to (P_{CO}) $(P_{H_2})^{-\frac{1}{2}}$. The reaction proceeds at an undetectable rate when the Bruderheim L6 chondrite is used as a catalyst. Apparently, the high-temperature minerals in this meteorite (olivine, orthopyroxene, troilite, and nickel-iron) do not catalyze the hydrogenation of CO. Thus CO can survive in the solar nebula down to 400°K, when catalytically active minerals first form (Fig. 1).

Interstellar Molecules

It seems that FTT reactions in solar nebulas may also be responsible for interstellar molecules, as first suggested by Herbig (*65*). Main sequence stars show a marked discontinuity of rotation rates at 1.5 solar masses ($M_{\odot}$) suggestive of angular momentum transfer to extrastellar material. Thus solar nebulas may be a common by-product of star formation. Such nebulas, embedded in interstellar clouds, provide a high-density environment ($\sim 10^{14}$ molecules per cubic centimeter) in which matter can be transformed to grains and molecules which are then returned to the interstellar cloud when the nebula is dissipated. The denser parts of such clouds are well shielded from ultraviolet radiation, and may serve as a long-term source of interstellar molecules.

In our own solar system, nearly all volatiles complementary to the inner planets ($3 \times 10^{-3} M_{\odot}$) were so lost. Earth and Venus contain only about 10^{-4} of their complement of C, and even lesser amounts of H_2O, N, and noble gases. The chemical state of the lost C may never be known with certainty, but since the retained C appears to show the imprint of the Fischer-Tropsch reaction, it seems likely that the lost C, too, had been involved in this process. Of the 12 known interstellar molecules with three or more atoms, at least 10 are found in meteorites or in FTT syntheses (*66*): H_2O, $HCHO$, CH_3OH, $HCOOH$, HCN, $HC{\equiv}CCN$, $HNCO$, $CH_3C{\equiv}CH$, CH_3CN, and COS. This is not a compelling argument in favor of the FTT synthesis, because these structurally simple molecules can also be made by the Miller-Urey synthesis (*67*). A choice may become possible when more complex molecules are discovered in interstellar space.

There also exists circumstantial evidence linking interstellar molecules to protostars. Interstellar molecules tend to occur in regions of very high density (10^6 H_2 molecules per cubic centimeter or more), such as the infrared nebula in Orion (*68*). Star formation proceeds at a rapid rate in such clouds, and thus solar nebulas must have formed and dissipated. The lifetime of our solar nebula seems to have been rather short: not over 10^4 years, or two or three orders of magnitude less than the age of a typical cloud, such as the Orion Nebula. If these values are typical, even a young cloud should contain appreciable amounts of carbon cycled through solar nebulas. Abundances of interstellar molecules relative to CO are at least two orders of magnitude lower than yields in FTT syntheses (*68, 69*). Even though part of this difference reflects their shorter photolytic lifetimes (*70*), it appears that only a moderate degree of star formation and CO processing would suffice to account for the interstellar molecules.

It should be noted in passing that no other explanation has yet been found for polyatomic interstellar molecules. Collisions of individual atoms in interstellar clouds can at best account only for the diatomic molecules (*71*), not for the polyatomic molecules with up to seven atoms. Reactions on grain surfaces are a more promising mechanism for polyatomic molecules (*67, 72*), but judged from our above estimates for the Fischer-Tropsch reaction at an H_2 density of about 10^{14} cm^{-3}, rates may be far too slow at the lower densities of interstellar clouds.

Origin of Volatiles on Inner Planets

Some of the most volatile substances occur in the earth's crust in nearly the same proportions as in carbonaceous chondrites (*73*). This has led to the suggestion that the inner planets obtained their volatiles from carbonaceous-chondrite-like dust or larger bodies that had formed in colder parts of the nebula (*74*). Such material might have made a significant contribution to the earth's initial endowment of organic matter. Bodies of meteoritic size (1 to 100 cm) would survive atmospheric entry, and deliver their organic compounds intact. Larger bodies would vaporize on impact, causing any organic compounds to revert to CO and H_2. But on expansion and cooling of the gas ball (*75*), catalytic reactions would commence on the surfaces of dust grains. Apart from prebiotic organic matter, some portion of the earth's petroleum may have originated by this route, as argued by Robinson (*76*), Porfir'ev (*77*), and others.

FTT reactions on the earth. There are indications that FTT reactions also take place in petroleum deposits. Friedel and Sharkey (*78*) have shown that the alkane isomer distribution up to C_9 in crude oils can be quantitatively represented by a formula first devised for the Fischer-Tropsch reaction, in which the only two parameters are the probabilities of chain branching and chain lengthening. The resemblance of the ostensibly biogenic Nonesuch shale hydrocarbons to Fischer-Tropsch hydrocarbons (Fig. 2) suggests that this similarity holds also at higher carbon numbers. The most straightforward explanation of the quantitative applicability of the Fischer-Tropsch formula is that surface-catalyzed FTT reactions are involved in the formation of petroleum, at least under more extreme conditions of diagenesis. Several authors (*18, 38, 50, 63*) have shown that clay minerals are good catalysts for such reactions.

Summary

Organic compounds in meteorites seem to have formed by catalytic reactions of CO, H_2, and NH_3 in the solar nebula, at 360° to 400°K and (4 to 10) $\times 10^{-6}$ atm. The onset of these reactions was triggered by the formation of suitable catalysts (magnetite, hydrated silicates) at these temperatures. These reactions may be a source of prebiotic carbon compounds on the inner planets, and interstellar molecules.

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Geneticists and the Biology of Race Crossing

Geneticists changed their minds about the biological effects of race crossing.

William B. Provine

"Education is to man what manure is to the pea," (*1*) wrote the young geneticist Reginald C. Punnett in 1907. He was obviously keenly aware of the social significance of his work on peas for human affairs. Like many other geneticists then and now, he believed that he should publicize the social implications of his research. In this paper I examine historically only one aspect of the social significance of genetics: the attitude of United States and British geneticists on the topic of race crossing.

Beween 1860 and 1900 Europeans and Americans felt a new urgency about race problems. The Civil War and the freeing of slaves in the United States stimulated a huge outpouring of books and pamphlets about race, in Europe as well as America. Europeans divided up the entire continent of Africa and carved out spheres of imperialistic activity throughout the world, dramatically increasing their contacts with other races. Race-related social problems grew accordingly.

Most whites from Europe and the United States believed these problems resulted from the mental inferiority of nonwhite races. Nineteenth-century biologists concurred. They believed that races of man differed in hereditary physical and mental characteristics, and viewed crossing between distant races with suspicion or outright antagonism (*2*). Specifically, they argued that Negroes were, on an average, mentally inferior to European whites. In 1869 Francis Galton provided a simple quantitative model for the distribution of intelligence within and between populations (*3*). He theorized that the intelligence of Negroes was, on an average, two grades below that of Englishmen, while the intelligence of the "Athenian race" of the Fifth Century B.C. was two grades above that of Englishmen. One of Galton's grades corresponds to approximately ten points on current IQ distributions. Galton based his quantitative analysis of hereditary mental differences between races upon faulty assumptions and scanty evidence. But in the late 19th century his analysis convinced almost all biologists. Galton merely made quantitative what biologists already assumed: that races differed hereditarily in mental traits.

Galton's analysis of racial differences indicated that an intellectually superior race should not breed with an inferior race because a small reduction in average intelligence caused a much greater reduction in the proportion of individuals in the highest grades of intelligence. And, he said, "We know how intimately the course of events is dependent upon the thoughts of a few illustrious men" (*3*, p. 343). Other biologists condemned wide race crosses because some evidence indicated that racial hybrids had weak constitutions, especially if bred among themselves. But the evidence was meager and conflicting. Some anthropologists and political thinkers advocated race amalgamation as the best solution to rising race-related problems. A greater understanding of human heredity seemed

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