COMETS: COSMIC CONNECTIONS WITH CARBONACEOUS METEORITES, INTERSTELLAR MOLECULES AND THE ORIGIN OF LIFE

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ABSTRACT

In discussing the possible relationships of comets to carbonaceous meteorites and interstellar matter, emphasis is placed on aspects of their carbon chemistry. The suites of volatile and organic compounds associated with these bodies overlap. Thus, the ions, radicals, and molecules observed in comets may be derived intact or by partial decomposition from parent compounds of the sort found either in the interstellar medium or in carbonaceous meteorites. However, there appears to be a closer correlation between the molecular structures of cometary and interstellar molecules in that cyanides are common to both, but are absent in carbonaceous meteorites. These observations do not conflict with the view that comets and carbonaceous meteorites represent nebula condensates formed at different temperatures nor with the view that comets were assembled in the interstellar medium. Ambiguities surrounding the interpretation of measured ratios of ^{12}C to ^{13}C in cometary and interstellar molecules, coupled with the imprecision of the data, make them unsuitable for distinguishing between a solar system and interstellar origin for comets. If comets accreted in the solar nebula, there may be isotopic affinity between cometary carbon and the carbonate carbon of meteorites.

The early loss of highly reducing primitive atmosphere and its replacement by a secondary atmosphere dominated by H_2O, CO_2 and N_2, as depicted in current models of the Earth's evolution, pose a dilemma for the origin of life: the synthesis of organic compounds necessary for life from components of the secondary atmosphere appears to be difficult, and plausible mechanisms have not been evaluated. It is estimated that carbonaceous meteorites cannot have made a significant direct contribution of organic compounds to

the primitive Earth. Direct input of cometary organic compounds cannot be estimated for lack of data on the organic content of comets. Both comets and carbonaceous meteorites, however, are implicated as sources for the Earth's atmophilic and organogenic elements. A mass balance argument involving the estimated ratios of hydrogen to carbon in carbonaceous meteorites, comets, and the crust and upper mantle suggests that comets supplied the Earth with a large fraction of its volatiles. The probability that comets contributed significantly to the Earth's volatile inventory suggests a chemical evolutionary link between comets, prebiotic organic synthesis, and the origin of life.

I. INTRODUCTION

Scientific observations made during recent apparitions of the bright comets West, Bennett, and Kohoutek and the prospect of seeing Halley's comet in 1985-86 have aroused considerable enthusiasm among cometary scientists for intensified study of these objects. As a consequence, the possibility exists that a space mission to a comet may become a NASA objective in the 1980's. This article examines various aspects of organic cosmochemistry so as to stimulate and focus widespread interest in the nature and origin of comets and their possible relationships to interstellar molecules, meteorites, and the origin of life.

A fundamental premise of this article is that the study of comets or of any other primordial matter in the solar system really is a study of origins. Indeed, the study of comets comprises an integral aspect of what might be considered a cosmic quest for an understanding of our origins, starting from the "big bang" and leading eventually to interstellar dust, solar nebula, sun, planets, and the origin of life. In this context, a comet mission is one that most people can understand and support. In fulfilling this mission, we may learn more about our own origins in the cosmos and also discover more about the constraints that stellar and planetary evolution impose on the origin and distribution of extraterrestrial life. The latter knowledge then helps narrow future searches for intelligent life among the stars.

Just as biological evolution assumes that all organisms have a common ancestry, so chemical evolution assumes that all matter in the solar system had a common origin. Consider the following scenario: an interstellar cloud of dust and molecules collapses, perhaps triggered by a nearby supernova, thus beginning the chemical evolution of the nascent solar system. From the solar nebula emerges the sun, planets, and other bodies of the solar system, including comets. The fall of meteoroids, meteorites, and cometary particles, large and small, contributes mass to the planets, as do particles injected by the solar wind. Sometime within 0.5 and 1.2 Gyr of the Earth's birth, life arises on its surface, and biological evolution begins. Eventually the death of the sun is perhaps accompanied by the ejection of matter back into the surrounding interstellar medium that originally spawned it. (This cycle in the condensation and dispersal of matter is depicted schematically in Fig. 1.)

According to this scenario, the origin and evolution of life on Earth was, and will continue to be, inextricably bound to the evolution of the sun and the Earth. Ironically, life evolved on a planet in which hydrogen, carbon, and nitrogen among the four major organogenic elements, hydrogen, carbon, nitrogen, and oxygen, are severely depleted with respect to the parent sun (Table I). Yet, there is satisfaction in knowing that the chemistry of life is based on four of the five most abundant elements in the cosmos (Table I). From this knowledge springs the conviction that organic chemistry constitutes an integral and fundamental aspect of cosmochemistry. Therein lies the anticipation that, despite the seeming improbability of its origin on Earth, life may be widely distributed in the cosmos.

In an evolutionary sense, human beings are the products of countless changes in the form and content of primitive matter wrought by processes of chemical and biological evolution. Biological evolution, as taught by Darwin, proceeds by accidental mutations; we are, therefore, the products of innumerable chance occurrences. Surely, in a cosmos whose order and harmony cannot be clearly discerned, cosmic events that we can only classify now as accidental or fortuitous must have occurred along the path of chemical evolution

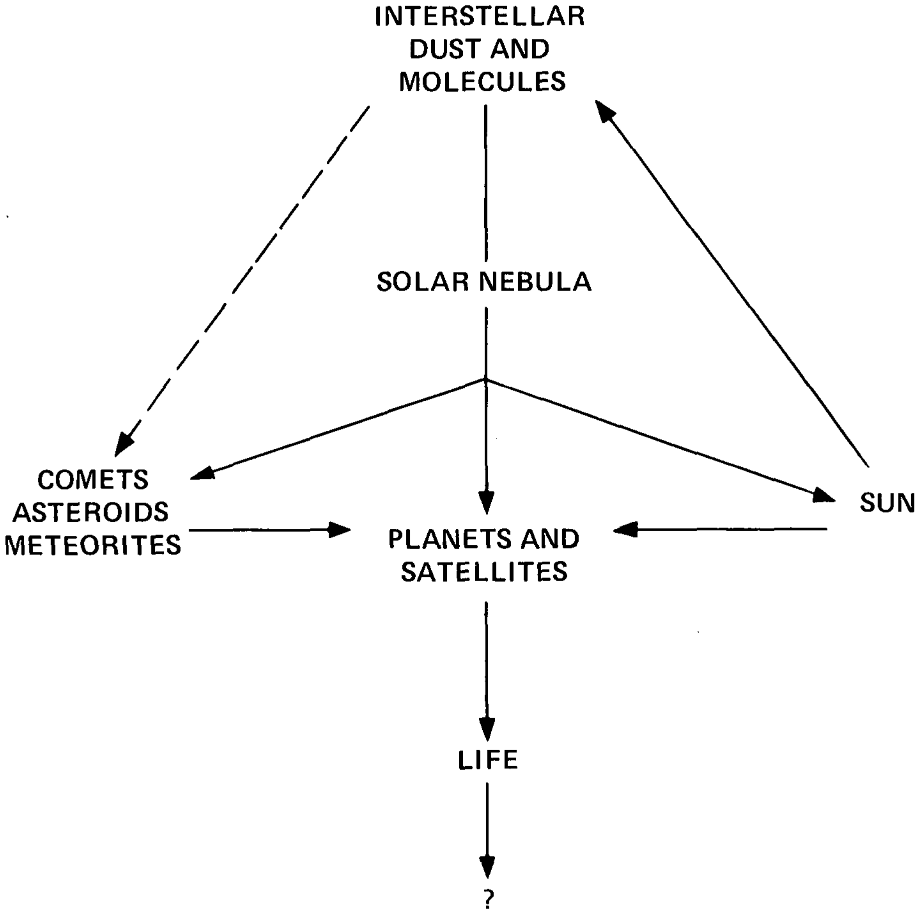

Fig. 1. Interrelationships between various bodies during chemical evolution of the solar system. Solid arrows indicate contributions of matter from one source to another. The dashed line signifies uncertainty regarding direct condensation of comets from interstellar matter. The arrow from "LIFE" implies its eventual dispersal from Earth.

TABLE I

RELATIVE ABUNDANCES OF SELECTED ELEMENTS

(In atom percent)

Element	Sun[a]	Earth[b]	Biosphere[c]
Hydrogen	94	0.08	64
Helium	6	~0	0
Carbon	0.04	0.01	9.1
Nitrogen	0.008	0.00002	0.1
Oxygen	0.07	49	27
Neon	0.004	~0	0
Sodium	0.0002	0.7	0.005
Magnesium	0.004	14	0.02
Aluminum	0.0003	4	0.0004
Silicon	0.004	14	0.03
Argon	0.0001	~0	0
Calcium	0.002	0.8	0.008
Iron	0.003	17	0.002

[a] Adapted from Ross and Aller (1976).

[b] Hydrogen, carbon, nitrogen data from Turekian and Clark (1975) for hydrosphere, atmosphere, crust, and upper mantle; other data adapted from Mason (1966) for total Earth.

[c] Mean percentages in terrestrial vegetation: adapted from Hutchinson (1968).

from interstellar matter to origin of life. How many of these events were essential to the origin of life? Is it possible, for example, that if the solar system had no comets, no life would have appeared? This last question is addressed in Section IV.

II. RELATIONSHIPS BETWEEN COMETS, SOLAR SYSTEM BODIES, AND THE INTERSTELLAR MEDIUM

At this point it is appropriate to indicate briefly the variety of cosmochemical issues that would be clarified by a better knowledge of comets. These issues focus on the relationships between comets, meteorites, and other bodies, both inside and outside the solar system. More detailed discussions of most of these issues, accompanied by leading references, can be found in Delsemme (1977). A widely held hypothesis states that the mineralogy and chemistry of carbonaceous meteorites reflect in part the equilibrium condensation of minerals from a cooling nebula gas of solar composition (Grossman and Larimer, 1974). Thus, carbonaceous meteorites are viewed as having accreted as mixtures in varying proportions of high- (>1,250 K) and low-temperature condensates and products resulting from subsequent alteration of these primary condensates in a relatively cool (<700 K) gas of solar composition and/or on the surface of a parent body. Wetherill (1976) argued persuasively that carbonaceous and chondritic meteorites are derived from Earth-approaching Apollo-Amor asteroidal bodies which, in turn, comprised the outgassed and compacted cores of moribund comets. Anders (1975) presented evidence of an alternative derivation of meteorites from main belt asteroids.

The birthplace of comets has been assigned a vast range of locations, from the asteroid belt to the distant interstellar medium. In a recent assessment of their place of origin, Delsemme (1977b) concluded that comets originated in the outer regions of the solar nebula, in and beyond the space now traversed by the giant planets. Accordingly, comets, which have an apparently high endowment of volatile elements and compounds, may represent material accreted at low temperatures (Delsemme and Rud, 1977; Barshay and Lewis, 1976) at the distant edge of the solar nebula. Although an interstellar origin for comets has gained little support (see Delsemme, 1977b; Noerdlinger, 1977; and references therein), the recent discovery of similar molecular species in comets and in the interstellar medium suggests that contributions of interstellar matter to comets cannot be wholly discounted. If comets and interstellar clouds were genetically related, then spectroscopic observations of similarities in the chemistries of both would reflect commonalities in composition and origin. Meteorites may also be woven into this hypothetical relationship of comets and interstellar clouds. Recent analyses of trace mineral phases in carbonaceous meteorites reveal anomalous isotopic compositions for the elements oxygen, neon, magnesium, silicon, calcium, krypton, strontium, xenon, barium, neodymium, and samarium. (See Clayton, 1977; Frick, 1977; Lee *et al.*, 1978; Lugmair *et al.*, 1978; McCulloch and Wasserburg, 1978; Papanastassiou *et al.*, 1978; Srinivasan and Anders, 1978; Yeh and Epstein, 1978; and references therein.) Inability to explain these anomalies with nuclear or nonnuclear processes within the solar system suggests that they are relics of presolar or interstellar matter which were incompletely homogenized in the solar nebula. If comets were samples of presolar matter preserved in bulk form, they would contain clues to the presolar history of this region of the galaxy.

The hypothesis that comets contributed substantial amounts of mass to some of the planets in the solar system appears widely accepted, particularly the idea that Neptune and Uranus were constructed from cometary building blocks. Especially interesting is the possibility that comets supplied the terrestrial planets with a significant proportion of the volatile, atmophilic, organogenic elements (Whipple, 1976). Were this the case, comets may well have played a key role in the origin of life on Earth.

III. CARBONACEOUS METEORITES, COMETS, AND INTERSTELLAR MATTER

This section briefly describes carbonaceous meteorites and compares them with comets and interstellar matter, the emphasis being on organic chemical aspects. For more detailed information on meteorites and comets the reader is referred to Nagy (1975), Wasson (1974), and Delsemme (1977).

Carbonaceous meteorites consist of complex assemblages of relatively fine-grained mineral and organic matter that reflect a broad range of elemental compositions, textures, and petrologies, indicative of wide variations in the environment of origin for the various components. According to one prevailing model for their origins, some of the mineral ingredients were formed primarily by equilibrium condensation from the cooling gaseous solar nebula. Others resulted from alteration of the primary material. Presumably the diverse ingredients were eventually assembled into rocky material on parent bodies, possibly resembling asteroids, where compaction and the environmental conditions further influenced their chemistry, mineralogy, and petrology. Disruption of the parent bodies (perhaps by collison with other bodies) yielded fragments representative of the various parts which, in time, fell under the influence of the Earth's gravitational field. The identification of primary minerals and the elucidation of the possible secondary effects that can account for the observed compositions of meteorites constitute major efforts in meteorite research; the ultimate objective is to reconstruct the physical and chemical environments and early histories of the solar nebula and the parent bodies.

Figure 2 summarizes major and minor phases found in carbonaceous meteorites, gives their probable temperature of formation by equilibrium condensation from the gaseous nebula or by secondary alteration, either in a solar composition gas or on a parent body, and shows their relative abundances and distributions in three types of carbonaceous meteorites. For present purposes, the major differences between the C3, C2, and C1 meteorites are their increasing content of volatile elements and decreasing content of minerals of high-temperature origin. Accordingly, the amount of organic matter increases in the same order from about 0.5 to 5% by weight. High-temperature inclusions containing melilite, spinel, and perovskite occur most abundantly in C3 meteorites, along with metal (iron and nickle) and the mafic silicates, olivine, pyroxene, which comprise the bulk of their mass. These minerals exist only in low to trace amounts in C2 meteorites; all, except for traces of mafic silicates, appear to be absent in the C1 meteorites.

A complex carbonaceous phase, characterized by insolubility in solvents and acids and a carbon-to-hydrogen ratio near 1, occurs as the major carbon component in all three types of meteorites, but is lowest in abundance in the C3 meteorites. Terrestrial sediments contain a material called "kerogen," which has similar characteristics but is of obviously different origin. To distinguish it from terrestrial kerogen, the meteoritic substance is designated as the acid-insoluble carbonaceous (AIC) phase. Figure 2 indicates its temperature of formation occurs at the midpoint of a ±400 K range. Although the production mechanism for this material in meteorites is unknown, carburization reactions used by the steel industry may provide relevant models; in

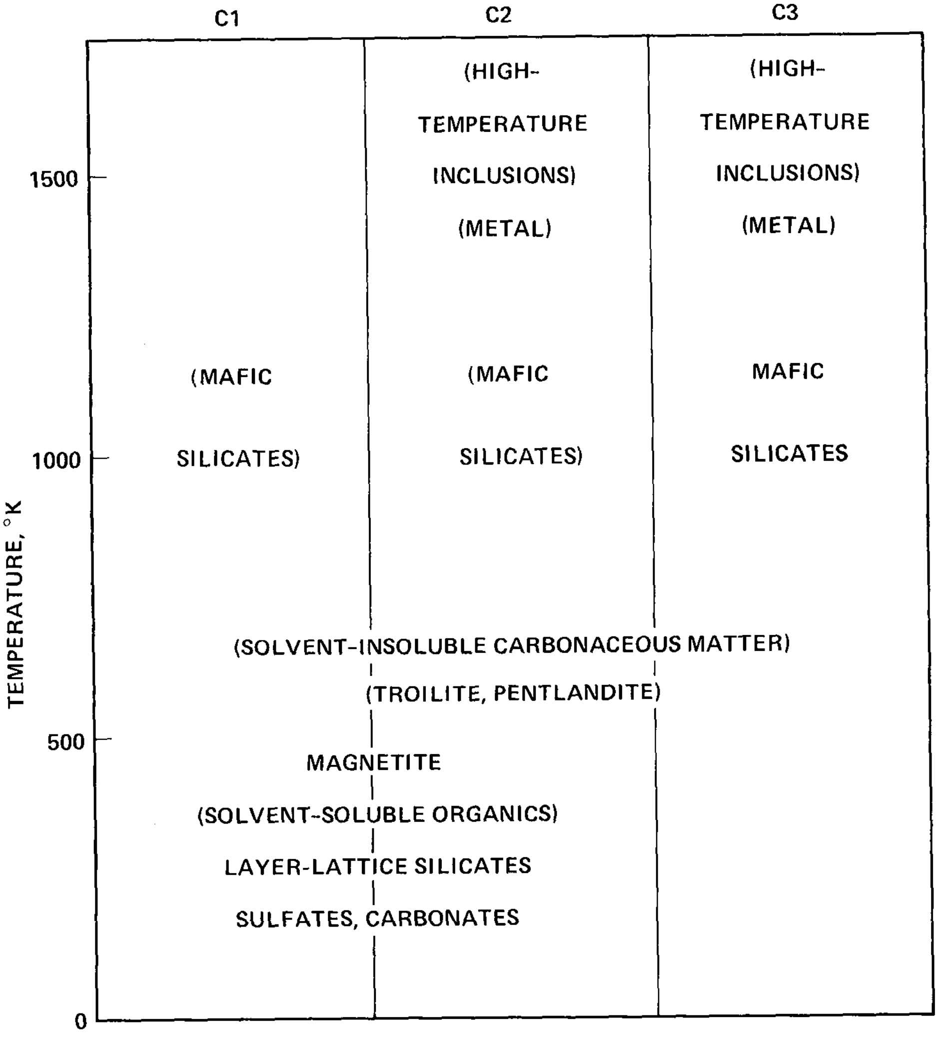

Fig. 2. Distributions and approximate condensation temperatures of minerals in carbonaceous meteorites (adapted from Wood, 1975). Parentheses indicate low to trace amounts.

these reactions, the interaction of carbon monoxide with a metal surface heated to 500 to 1,100 K causes deposition of carbon within and on the surface (Freuhan, 1973; Meroc and Boulle, 1968). At lower temperatures, Fischer-Tropsch-type (FTT) reactions (Anders _et al._, 1973), also catalyzed by minerals, can produce the AIC substances. Organic synthesis promoted by FTT reactions, electric discharges, ultraviolet photochemistry, or other mechanisms must have occurred at temperatures sufficiently low to permit preservation of the variety of volatile and thermally labile organic compounds found in low abundances in C1 and C2 meteorites (see below). Although we are uncertain where these compounds were synthesized, many investigators favor production on a parent body rather than on mineral grains suspended in the solar nebula (Miller _et al._, 1976).

According to the equilibrium condensation model, the predominant sulfides (troilite, pyrrhotite, and pentlandite, which occur in minor amounts in all three types of meteorites) were formed at about 700 K by the reaction of hydrogen sulfide in the nebula gas with previously formed metallic iron and its alloys. Similarly, the model also hypothesizes that the magnetite found in C1 and C2 meteorites (5 to 15%) is produced by secondary reactions of metallic iron with water vapor at temperatures ≤400 K. Some of the magnetite, however, exhibits morphological and chemical characteristics suggestive of a primary condensation origin (Nagy, 1975). Magnetite occurs in trace quantities, if at all, in C3 meteorites.

The predominant minerals in C1 and C2 meteorites (50 to 80%) are the layer-lattice silicates or phyllosilicates. These minerals resemble terrestrial clays in crystallographic structure, but exhibit elemental compositions remarkably similar to the pattern of cosmic abundances. This similarity suggests a primary origin for this material (Arrhenius and Alfvén, 1971; McSween and Richardson, 1977), but the likelihood of direct condensation as stable minerals from a solar composition gas has not been quantitatively assessed. A more likely mode of production involves hydrothermal alteration at about 350 K of previously formed silicates in an unknown environment (Bostrom and Fredriksson, 1966; Kerridge, 1977; Bunch and Chang, 1978; and references therein). Also found only in C1 and C2 meteorites are minor amounts of sulfates and carbonates. These too, apparently, have a predominantly secondary origin.

Although the effects of water on the mineralogy of C1 and C2 meteorites are evident, considerable uncertainty exists regarding the amount of free water that they contain. Apparently, the meteorites are easily contaminated with terrestrial water. Kaplan (1971) has critically reviewed the data and estimated upper limits of 10 and 5% for the total water content in C1 and C2 meteorites, including both free water and water bound as water of hydration in minerals, as phyllosilicate lattice hydroxyls, and as hydrogen in organic matter. Thus, a relatively small amount of water remains in these meteorites, despite its apparent major influence in the past.

The column sequence from right to left in Fig. 2 passes from C3 meteorites, which were apparently isolated from the physical and chemical effects of a low-temperature (<500 K) environment, to C2 and C1 meteorites, which contain only trace relics of high-temperature minerals and show abundant signs of exposure to a low-temperature environment containing gaseous and/or liquid water. To accommodate comets as the low-temperature end-member of a condensation sequence, one could construct a fourth column on the left of Fig. 2 in which the rock-forming minerals, sulfates, carbonates, and organic compounds are minor constituents, and water and CO_2 ices constitute the major components (Delsemme, 1977a). Spectra of cometary meteoroids (Millman, 1977) and laboratory analyses of interplanetary dust (Brownlee *et al.*, 1977) indicate that the nonvolatile component of comets bears strong resemblance to that of C1 and C2 meteorites. If the cometary matter condensed at $\leq$300 K, however, the mineralogy would likely bear little resemblance to that of carbonaceous meteorites. Indeed, if comets are formed at a great distance from the inner solar nebula, their mineralogy and chemistry are expected to resemble more closely those of interstellar grains.

Table II lists the atoms, ions, and molecules that have been detected in the interstellar medium, comets, and carbonaceous meteorites. These components are listed under the general class of organic compounds to which they belong or from which they can be produced by partial decomposition. Data for the table were taken from Delsemme (1975), Hayes (1967), Jungclaus *et al.*, (1976, 1976a), Nagy (1975), Zuckerman (1977), and references therein. Repeated entries under the heading *Comets* (e.g., H, C, CO^+) reflect the variety of organic compounds that may serve as precursors. Within each compound class the organics of the meteorite are listed in order of decreasing abundances. Phyllosilicate and carbonate mineral species are also included because they occur in abundance and represent inorganic analogs of organic alcohols and acid derivatives, respectively. Spectroscopic and polarimetric observations and detection of SiO indicate that silicates also exist in the interstellar medium (Greenberg, 1973; Day, 1974). Although the cometary species can be derived from both interstellar and meteoritic compounds, the closer correlation between the molecular structures of cometary and interstellar species does not necessarily show a genetic relationship between the

TABLE II

ATOMS, IONS, AND MOLECULES DETECTED IN THE INTERSTELLAR MEDIUM, COMETS, AND CARBONACEOUS METEORITES

Interstellar molecules	Comets	Carbonaceous meteorites
Hydrocarbons CH, CH^+, HC_2, HC_2H, HC_2CH_3	H, C, CH, CH^+, C_2, C_3	Aliphatics, Alicyclics, aromatics, C_1 to C_{20}
Alcohols OH, H_2O, CH_3OH, C_2H_5OH	H, O, OH, OH^+, H_2O, H_2O^+	Phyllosilicates, H_2O, C_1 to C_4 alcohols
Aldehydes and ketones HCO, HCO^+, H_2CO, CH_2CO CH_3CHO	H, C, CO^+	C_2 - C_5 aldehydes and ketones, H_2CO
Acids and derivatives CO, HCO_2H, HCO_2CH_3	H, C, O, CO^+, CO_2^+	$CO_3^=$, CO_2, C_2-C_8 mono and dicarboxylic acids, CO
Amines and derivatives NH_3, CH_2NH, CH_3NH_2, NH_2CHO, NH_2CN, $HNCO$	H, NH, NH^+, NH_2, N_2^+, CH, HCN, CO^+	Amino acids, C_1-C_4 amines, NH_3, N-heterocycles
Nitriles CN, HCN, HNC, NH_2CN, C_2CN, HC_2CN, H_2C_2HCN, CH_3CN, C_2H_5CN, HC_4CN	H, CN, HCN, CH_3CN	
Miscellaneous H_2, H_2CS, CS, SO, OCS, H_2S, SO_2, NS, SIO, N_2H^+, CH_3OCH_3	N_2^+	O- and S-heterocyclics

two, although it does accord with the view that comets were accreted from interstellar matter. Especially significant is the abundance of interstellar and cometary molecules (nitriles or cyanides) containing the CN fragment, and the apparent lack of similar molecules in meteorites. While the analyses of meteorites have not been directed at seeking nitriles, their presence would have been revealed in the course of many investigations (see below).

Using the known distribution of cometary ions, radicals, and molecules, we may be able to reconstruct the chemical composition of comets. The lack of a piece of comet for study makes this reconstruction essential to understanding what comets are. In the "dirty ice" model (Whipple, 1950; Whipple and Huebner, 1976), comets consist of simple and complex organic molecules and meteorite-like dust imbedded within a matrix of frozen H_2O and other gases. Near the sun, the volatile ice constituents evaporate, ejecting volatile compounds (e.g., H_2O, CH_4, CO_2, NH_3) and nonvolatile dust from the nucleus. According to this model, interaction of the parent compounds with solar photons and solar wind particles produces most of the observed cometary species by dissociation and ionization.

Recently, Oppenheimer (1975) questioned the necessity or relevance of some candidate parent molecules because their rates of photodissociation were too slow to account for the observed molecules. In his scheme, starting only with molecular hydrogen or a hydrogen-bearing molecule (such as methane plus atoms of other elements), gas phase ion-molecule reactions, similar to those postulated to account for formation of simple interstellar molecules, can produce the observed species in a comet's coma. The influence of ion-molecule reactions on the ionic species of comet tails has also been discussed by Wyckoff and Wehinger (1976). Ion-molecule reactions also appear able to reshuffle rapidly the constituent atoms of parent molecules. The implication is that the nucleus may have a composition different from the frozen ice model. Clearly, under these circumstances, reconstruction of the physical and chemical state of the nucleus from the identity, abundance, and distribution of observable species poses a formidable task having more complications than originally thought. However, since ion-molecule reactions have not yet been shown to provide promising pathways for formation of the observed CH_3CN (Heubner, 1977), the concept of the parent molecule still retains its relevance to the chemistry of comets. Moreover, interpretations of ultraviolet observations of comets by Keller (1976) show how the production of H and OH can be correlated with the presence of H_2O as a major parent molecule.

Examination in more detail of the organic compounds in carbonaceous meteorites may provide additional insight into the organic chemical composition of comets. Table III shows the distribution of carbon in the Murchison meteorite, the most pristine and carefully examined carbonaceous meteorite. Note that the volatile organic compounds, the hydrocarbons, carboxylic acids, ketones, aldehydes, alcohols, and amines, constitute a small fraction of the total carbon and less than 0.05% of the total mass of the meteorite. The amino acids that have drawn so much attention occur in minute amounts. Since the sum of the listed compounds agrees well with the total amount of carbon, we are confident that no major reservoirs of carbon have been overlooked. While carbonate minerals exist in the Murchison meteorite, their abundance is based on the amount of CO_2 released by acids. Therefore, it is not clear whether or not some fraction of that gas was actually CO_2 trapped in the meteorite matrix.

TABLE III

DISTRIBUTION OF CARBON IN MURCHISON METEORITE[a]

Acid insoluble carbonaceous phase, %	1.3 to 1.8
$CO_3^{=}$, %	0.2 to 0.5
Hydrocarbons and lipids, %	0.07 to 0.11
Carboxylic acids, ppm	~350
Amino acids, ppm	10 to 30
Ketones and aldehydes, ppm	~17
Urea and amides, ppm	<2 to 15
Alcohol, ppm	~6
Amines, ppm	~2 to 3
N-heterocycles, ppm	<2 to 40
Sum: 1.81 to 2.45%	
Total carbon: 2.0 to 2.58%	

[a] Estimates are based on data provided by Kvenvolden et al. (1970), Folsome et al. (1971), Cronin and Moore (1971), Yuen and Kvenvolden (1973), Lawless et al. (1974), Pereira et al. (1975), Hayatsu et al. (1975), Jungclaus et al. (1976, 1976a), Chang et al. (1978), Van Der Velden and Schwartz (1978), Bada and Peltzer (1978).

Table IV shows the volatilization characteristics of carbonaceous meteoritic material. The data correspond to abundances of the indicated ions (relative to CH_4 at 423 K) obtained from mass spectra of the gases volatilized under vacuum over the temperature range 325 to 1,500 K. The sample is a C2 inclusion removed from Jodzie, a howardite meteorite (Bunch *et al.*, 1976). However, the C2 meteorites, Murchison and Murray, give essentially similar results (Simoneit *et al.*, 1973; Wszolek *et al.*, 1973). Below 423 K, adsorbed terrestrial H_2O is mostly evolved; at 423 K, molecules of H_2O, CO_2, and CH_4 are released. The H_2O is derived predominantly from dehydration of phyllosilicate minerals; the CO_2 probably results from decomposition of carbonates and organic matter and release of trapped gas; the CO appears to be produced in the mass spectrometer as a fragmentation product of the CO_2^+ ion. Neither HCN nor CH_3CN evolved in significant amounts at 423 K. At 673 K, traces of HCN are released as a thermal decomposition product of other substances, as are all the other indicated species. Volatilization of meteoritic compounds into a mass spectrometer in which the compounds are ionized and fragmented into primary and secondary ions is a process analogous to a putative cometary process. Comparison of data in Table IV with the production rates in Table V shows that the major meteoritic volatiles, and fragments derived from them, can account qualitatively for the predominant cometary species; but the parent molecules involved and the temperatures required may differ greatly. Nonetheless, this agreement does not conflict with the view that comets and carbonaceous meteorites represent nebula condensates formed at different temperatures or with the view that comets were assembled in the interstellar medium. Obviously, the suite of volatile and organic components in comets and C2 (and C1) meteorites may overlap somewhat. The absence of HCN

TABLE IV

RELATIVE ABUNDANCES OF IONS CORRESPONDING TO VOLATILES RELEASED BY VACUUM PYROLYSIS FROM CM2 CHONDRITES AT 423 AND 673 K

Ion species	423 K	673 K
H_2O	36	60
CO_2	5.0	200
CO	2.0	10
CH_4	1.0	4.0
N_2	0.2	0.2
SO_2	0.04	0.8
C_3H_6	0.03	0.4
C_2H_4O	0.02	0.2
HCN	<0.01	0.1

TABLE V

PRODUCTION RATES OF COMETARY SPECIES

(In 10^{28} sec $^{-1}$, reduced to R = 1 AU;
adapted from Delsemme, 1977a)

Species	1970 II Bennett	1973 VII Kohoutek	1976 VI West
H	54 to 65	34	46
OH	30	20	20
O	18	3.8 to 8.0	23
C		0.6 to 1.6	9.0
CO			8.5
C_2		0.1 to 0.04[a]	
CN		0.04 to 0.01[a]	
HCN		0.01 to 0.1	
CH_3CN		0.01 to 0.1	

[a] Production rate before perihelion to after perihelion.

and CH_3CN in meteorites, coupled with a relatively low water content when compared to comets, points to differences in volatiles content and organic chemistry that relates to differences that prevailed in the respective environments of formation. Note that the organic compounds observed in meteorites, comets, and the interstellar medium represent the products of kinetic rather than equilibrium thermodynamic processes (Barshay and Lewis, 1976). Elucidation of their formation will provide both insight into the dynamics of the environments in which they formed and constraints on models that purport to describe these environments.

What evidence can be brought to bear on the question of where comets were formed? One approach compares the isotope ratios of ^{12}C to ^{13}C for cometary carbon with carbon in the solar system, in other stars, and in the interstellar medium. Since the isotopic ratios of elements reflect the nucleosynthetic pathways of formation, we may be able to tell whether comets originated in the solar system or in the interstellar medium.

As expected, the data in Table VI show a common value of about 90 for the ratios of ^{12}C to ^{13}C in solar system bodies. Comets exhibit both higher and lower ratios; but the differences appear insignificant in light of uncertainties in the measurements. Red giant stars cover a fairly narrow range from 12 to 51. Carbon stars and the interstellar medium exhibit rather wider ranges of isotopic composition. Vanysek (1977), however, argues that the most reliable interstellar values center around 40; he concludes that the difference between this value and the factor-of-two larger ratios for comets precludes an interstellar origin for comets. While this appears a reasonable conclusion, laboratory studies and model calculations of ion-molecule reactions involving C^+ and CO indicate that kinetic isotope effects can yield

TABLE VI

RATIOS OF ^{12}C TO ^{13}C IN THE COSMOS

Object	Diagnostic Species	$^{12}C/^{13}C$	LITERATURE
Sol	CO	90 ± 14	*a*
Venus	CO_2	~100	*b*
Earth	Various	89 (+7, -1)	*c*
Moon	Various	89 ± 2	*d*
Mars	CO_2	87 ± 2	*e*
Meteorites	Various	89 (+3, -6)	*d*
Jupiter	CH_4	89 (+12, -10)	*f*
Saturn	CH_4	89 (+25, -18)	*f*
Interstellar medium	CH^+, CO, H_2CO	>13 to 105	*g*
Red giant stars	CN	12 to 51	*h*
Carbon stars	C_2, CN	2 to ≥100	*i*
Comets:			
Ikeya (1963 I)	C_2	70 ± 15	*j*
Tago-Sato-Kosaka (1969 IX)	C_2	100 ± 20	*j*
Bennett (1970 II)	C_2	≥50	*j*
Kohoutek (1973 VII)	C_2	115 (+30, -20)	*j*
		135 (+65, -45)	*j*
Kobayashi-Berger-Milon (1975 IX)	C_2	110 (+20, -30)	*j*

[a] Hall et al. (1972)

[b] Connes et al. (1968).

[c] Wedepohl (1969).

[d] Kaplan (1975).

[e] Nier et al. (1976)

[f] Combes et al. (1977).

[g] Bertojo et al. (1974); Matsakis et al. (1976), and references therein.

[h] Lambert and Sneden (1977) and references therein.

[i] Scalo (1977) and references therein.

[j] Vanysek (1977) and references therein.

rather large isotopic fractionations, which may obscure the true ratio of ^{12}C to ^{13}C in the interstellar medium (Watson et al., 1976; Langer, 1977). Since the same ion-molecule reactions may play important roles in comet chemistry, the observed isotope ratios of comets may be similarly influenced. These ambiguities surrounding the interpretation of carbon isotope ratio measurements make them unsuitable at this time for clearly distinguishing between a solar system or interstellar origin for comets.

If it is assumed that comets, like meteorites, did form in the solar system, a more detailed look at the carbon isotope ratios in meteorites may be instructive. Figure 3 plots the isotopic composition of carbon versus total carbon content of meteorites. The precision of these laboratory analyses permits distinction of part per thousand variations in the isotope ratios, whereas the astronomical measurements of Table V allow precision of only tens of percent. Increasingly negative values for $\delta^{13}C_{PDB}$ signify increasingly higher ratios of ^{12}C to ^{13}C relative to a standard. The C1 and C2 meteorites occupy a part of the field in the figure that is quite distinct from the C3 and other meteorites. While the reasons for the isotopic variations between types of meteorites are not understood, the data indicate a high degree of carbon isotopic heterogeneity in the early solar system (see also Kung and Clayton, 1978). When the isotopic composition of various carbonaceous phases is displayed as in Fig. 4, the extensive isotopic heterogeneity within single meteorites becomes apparent. This heterogeneity cannot be readily explained simply as resulting from kinetic isotopic fractionation associated with the synthesis of the various phases in Fischer-Tropsch-type reactions, as postulated by Lancet and Anders (1970). The various forms of meteoritic carbon, which have various ranges of isotopic composition, may represent at least two

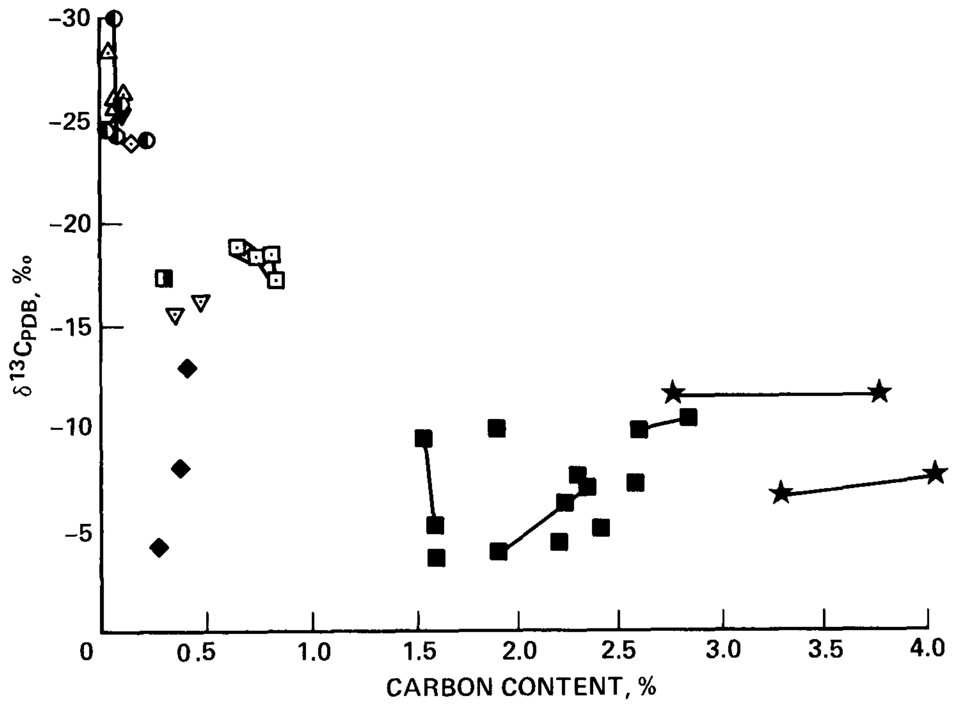

Fig. 3. Plot of carbon isotope ratio versus total carbon abundance for various meteorites. The lines connect independent analyses of the same meteorite. ★ = C1; ■ = C2; □, ◧, ▽ = C3; ▼ = C4; △, ◐ ordinary chondrites; ◆ = enstatite chondrites (see Wasson, 1974, for descriptions of the various types of meteorites not discussed here). The isotopic compositions are given as δ-values relative to the Peedee belemnite limestone standard and are defined in the following fashion:

$$\delta^{13}C_{PDB} = [(R_{Sample}/R_{Standard}) - 1] \times 10^3, \quad R = {}^{13}C/{}^{12}C.$$

Data are taken from Boato (1954), Belsky and Kaplan (1970), Smith and Kaplan (1970), Kvenvolden *et al.* (1970), and Chang *et al.* (1978).

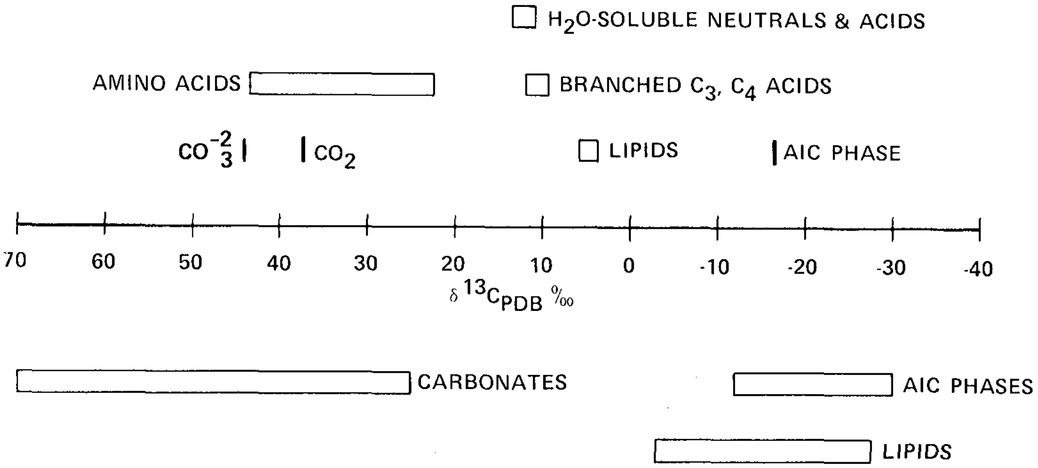

Fig. 4. Isotopic composition of carbon phases in Murchison (above the scale line) and in other carbonaceous meteorites. AIC phase corresponds to acid insoluble carbonaceous phase. Data are taken from references given in the caption of Fig. 3. The data from lipids in Murchison are judged to be least influenced by exposure to terrestrial contamination.

stages of carbon condensation in the early nebula, each of which occurred in a different environment separated in space and in time. Presumably, accretion of the meteorite parent bodies brought together carbonaceous as well as other mineral phases from isotopically different regions of the solar nebula. In particular, the large isotopic separation between the relatively reduced acid-insoluble carbonaceous phase and the oxidized carbonate and amino acid phases may reflect different origins. This view agrees with the concept that an incompletely homogenized solar nebula seems required to rationalize the isotopic anomalies associated with other elements (see Section II).

C3 meteorites exhibit a high-temperature history and a relatively reduced state; acid-insoluble carbonaceous matter relatively enriched in ^{12}C (negative $\delta^{13}C$ value) comprises the only significant carbon phase. C2 meteorites reflect extensive exposure to a low-temperature environment; they contain both the acid-insoluble carbonaceous matter and the oxidized carbon phases relatively enriched in ^{13}C (positive $\delta^{13}C$ values). C1 meteorites are the most highly oxidized, and they contain the most carbonate with the highest ^{13}C abundances. For these meteorites, an isotopic trend is suggested that correlates ^{13}C enrichment with high carbon oxidation state and low-temperature environments. If the trend is real, then the low-temperature origin of comets and the relatively oxidized state required by postulated high abundances of H_2O and CO_2 would point to levels of ^{13}C enrichment in cometary carbon that exceed that of C2 and C1 meteorites. It is interesting to speculate that the ^{13}C-enriched phases in carbonaceous meteorites may have a cometary origin. This possibility could result if the low-temperature environment of the parent body acquired the C- and H-bearing species through the infall of comets (cf. next section). While the majority of the carbon isotopic measurements (Table V) hint that cometary ^{13}C abundances may be lower than those of C1 and C2 meteorites, the measurements are too imprecise to be meaningful.

While a number of aspects of the chemistry of comets, meteorites, and interstellar matter have been examined in this section, we are no more certain about the nature and origin of comets than when we started. Clearly, this stage of affairs emphasizes the need for a quantum jump in knowledge.

IV. COMETS, CARBONACEOUS METEORITES, AND THE ORIGIN OF LIFE

According to the Oparin-Haldane-Miller-Urey paradigm, a highly reducing atmosphere consisting of methane, ammonia, and water prevailed on the primitive Earth. Passage of energy in various forms through this hypothetical atmosphere produced the reservoir of organic molecules from which life evolved. The existence of this atmosphere required the presence of metallic iron in the upper mantle (Holland, 1962), which Walker (1976) pointed out appears incompatible with geochemical observations. Walker (1976) proceeded to develop a case in favor of a primitive atmosphere composed predominantly of CO_2 and N_2. His arguments derive from implications of the inhomogeneous accretion model of the Earth's origin as formulated and developed by Turekian and Clark (1969) and others (Walker, 1976). The relationships between meteorites and comets and the origin of life will be viewed in the context of this model.

The basic features of the model are depicted schematically in Fig. 5 and briefly summarized below. (The reader is referred to Walker (1976) and other references therein for a more detailed description.) In this model, refractory minerals condensing early from the cooling nebula accreted to form the protoplanet. Rapid accretion was accompanied by melting and segregation into molten metallic core and fluid silicate mantle. The initial inventory of

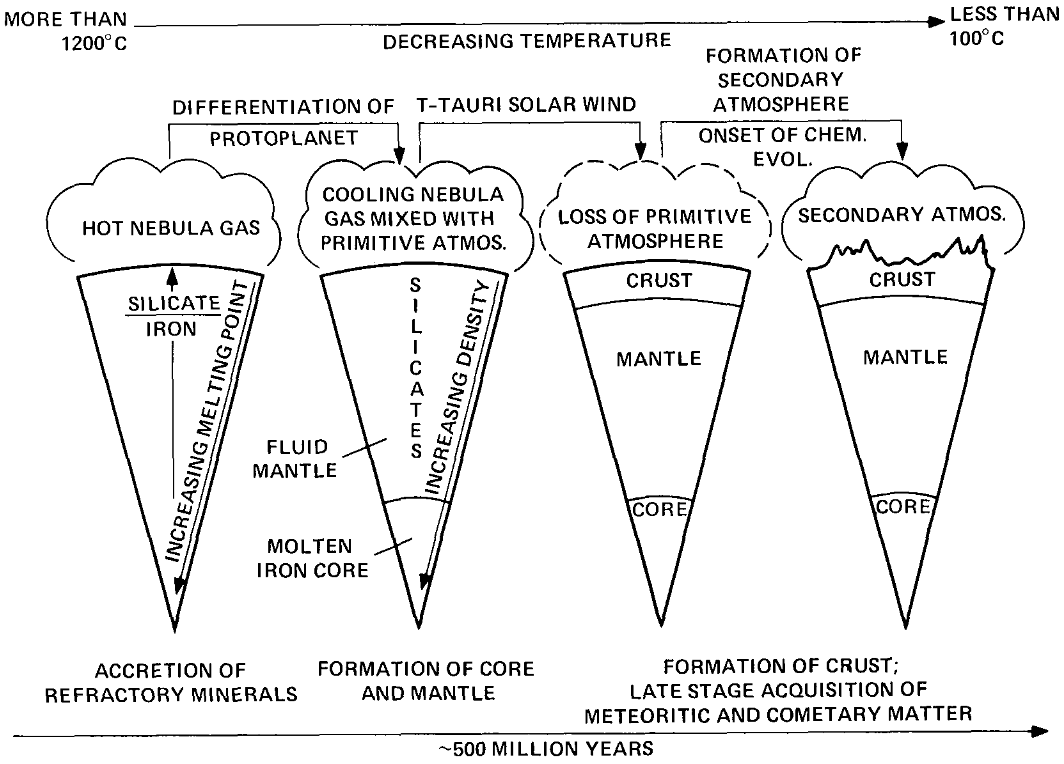

Fig. 5. Stages in the Earth's early evolution.

volatiles was driven to the surface. As the nebula gas continued to cool, metallic iron was converted to the ferrous state. Presumably, when the sun passed through its T-Tauri stage, the powerful solar wind blew the remaining nebular gas out of the inner solar system, carrying the Earth's primitive atmosphere with it. Because doubt exists about the efficacy of the T-Tauri wind, it is significant that another mechanism has been identified that could have achieved the same result. In his recent discussion of a physical model of the primitive solar nebula, Cameron (1978) suggested that tidal stripping of the atmospheric envelope of a giant, gaseous, inner protoplanet by the sun could have occurred early, leaving behind a core of condensed matter. Debris from the nebula condensation was accumulated by the primitive Earth. This debris provided both refractory and volatile-rich material to form the thin crustal veneer of the Earth. Heating of this late-accreted debris either during passage through the atmosphere, during impact with the surface, or while imbedded in a hot surface, released the volatiles to form the secondary atmosphere. As a result of the Earth's continued cooling, a thin, solid, but still hot, crust probably existed about 4.1 to 4.0 Gyr ago. The crust must have formed by about 3.9 Gyr because shortly thereafter aqueous environments and sedimentary processes had begun, as evidenced by the 3.8-Gyr-old metasedimentary rocks of Greenland. (See Allaart, 1976, and references therein.) About 3.3 Gyr ago, life was already depositing evidence of its existence in sediments now located in South Africa (Eichmann and Schidlowski, 1975; Schopf, 1975). The span between about 4.0 and 3.3 Gyr ago, therefore, represents the time within which chemical evolution proceeded to the origin of life.

An important outcome of the study of lunar rocks was the discovery that a late period of intense bombardment of the lunar surface ended about 3.9 Gyr ago (Tera *et al*., 1974). This finding supported the idea that the initial geomorphology of the crustal veneer and the composition of secondary atmospheres of all the terrestrial planets were produced by late-stage impacts. Computer modeling of the late-stage accretion by Benlow and Meadows (1977) yielded an amount of volatiles derived from vaporization of C1 meteorites that was of the same order of magnitude as the present terrestrial inventory. Dynamic considerations indicate that both comets and meteorites could have been the impacting bodies (Wetherill, 1975, 1976, 1977; Whipple, 1976).

According to Walker (1976), H_2O and CO_2 dominated the secondary atmosphere; N_2 occurred in minor amounts; and H_2 and CO were present only in traces, if at all (_cf_. Table IV). Traces of CH_4 and other hydrocarbons were presumed to have been oxidized readily in CO_2 by iron oxides. The composition of this steam atmosphere was determined by the redox potential of the silicate crust and upper mantle and would have strongly resembled contemporary volcanic exhalations. The subsequent evolution of Walker's secondary atmosphere is depicted in stepwise fashion in Fig. 6. Once the temperature of the Earth dropped below 373 K, water condensed to begin formation of the oceans and weathering of basic igneous rocks by CO_2 afforded carbonates. The prebiotic atmosphere that resulted closely resembled the present atmosphere minus oxygen.

Although production of the organic compounds necessary for chemical evolution would have proceeded readily in a highly reducing atmosphere, the possibilities in a CO_2-N_2-H_2O atmosphere with traces of H_2, CO, and/or CH_4 remain essentially unexplored. Of the various energy sources on the Earth today (Table VII), ultraviolet light (>1500 Å) and electric discharges are the only significant ones available on a global scale; there appears to be no compelling reason to assume a different situation for the primitive Earth. The difficulties in synthesizing key compounds such as amino acids in a

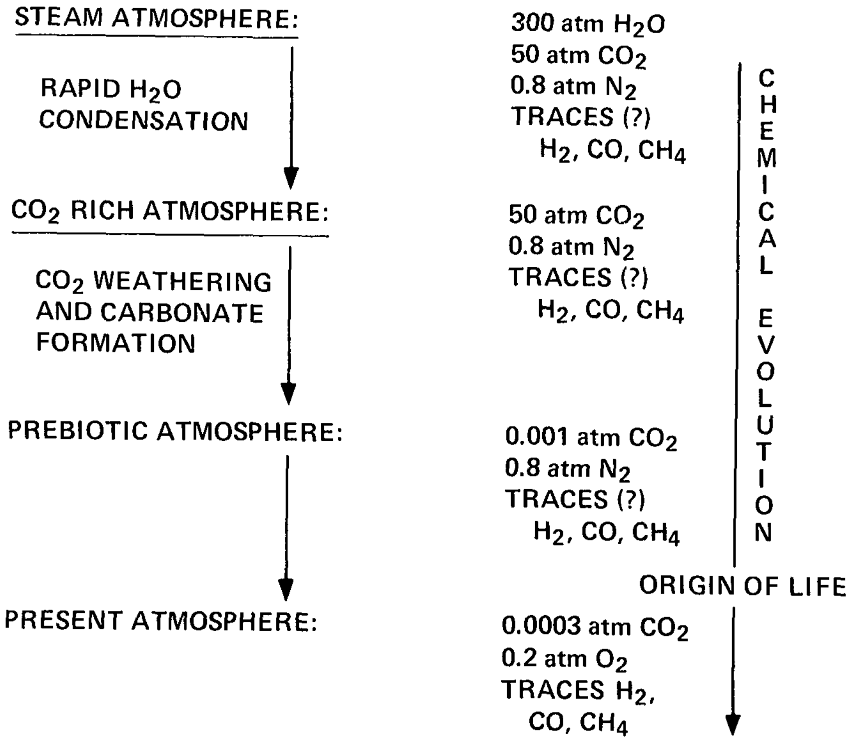

Fig. 6. Stages in the evolution of the secondary atmosphere.

TABLE VII

ENERGY SOURCES ON THE CONTEMPORARY EARTH

(Adapted from Miller and Urey, 1959)

Source	Energy, cal/cm^2 yr
Total solar radiation	260,000
Ultraviolet light	
Less than 2500 Å	570
Less than 2000 Å	85
Less than 1500 Å	3.5
Electrical discharges	4.0
Radioactivity (to 1 km depth)	0.8
Volcanoes	0.13
Cosmic rays	0.0015

CO_2-N_2-H_2O atmosphere have been pointed out by Gabel (1977). Even with CH_4 replacing CO_2, Ferris and Chen (1975) were unable to produce amino acids by ultraviolet photochemistry. In our own laboratory, electric discharges through CO_2-N_2-H_2O mixtures afforded nitric acid as the major product rather than organic compounds. Clearly, the presence of a reducing gas (H_2, CH_4, or CO) is required if organic synthesis occurred in the atmosphere. Walker (1976) offered the possibility that H_2 produced volcanically through decomposition of H_2O in early tectonic processes and amounting to about 1% of the atmosphere could have persisted for about 0.5 Gyr on the early Earth. Whether or not this amount would have been sufficient to permit organic synthesis remains to be evaluated. If not, how were the basic chemical building blocks of life made available? Hartman (1975) and Gabel (1977) offer some schemes that require reactions in the oceans and on clays, but none has been assessed in a critical or quantitative experimental fashion. Especially noteworthy, however, are Baur's (1978) thermodynamic calculations which indicate that spontaneous formation of reduced organic matter, including amino acids, can occur in heterogeneous systems containing N_2 and CO_2 in the presence of Fe(II)-containing minerals and H_2O. Investigations of the potential pathways for organic synthesis in such heterogeneous systems are highly desirable.

Let us consider the possibility that organic compounds were directly supplied by the leaching and weathering of carbonaceous meteorites that reached the surface of the Earth intact without significant heating. A simple model-dependent calculation can set upper limits on the amounts of amino acids supplied by this mechanism. Evidence from lunar studies points to termination of the late accretion stage at about 3.9 Gyr. Data of Wetherill (1977) indicate that the impact rate probably decreased exponentially over the period 4.5 to 3.9 Gyr ago from values of about 50×10^4 to 10^4

times the present infall rate of 10^3 g s^{-1} (Dohnanyi, 1971). We can assume that a solid crust sufficiently thick to support impacting bodies existed by 4.1 Gyr ago. High surface temperatures, which would lead to amino acid destruction, probably prevailed prior to this point in time. These considerations provide the basis for estimating that the mass of material delivered between 4.1 and 3.9 Gyr ago would amount to about 10^{23} g. If (a) 50% of the mass had C1 or C2 meteorite composition, (b) 10% of it arrived at the Earth's surface intact, (c) the early oceans were as large as they are today (1.3×10^{21} ℓ), and (d) the 30 ppm C abundance as amino acids (see Table III) was all leached out by weathering and transferred to the oceans without loss, then the amino acids would form a highly dilute 5×10^{-7} molar solution. Assumptions (a), (b), and (d) are greatly optimistic (each by factors of 10 or more) in light of contemporary experience; they should more than balance the assumption of present day ocean volume. Given this dilute solution, it is difficult to formulate a geologically reasonable scenario to concentrate the amino acids and continue the course of chemical evolution to more complex molecules. Either a richer source of organic matter was also involved or some undiscovered synthesis and accumulation mechanisms operated on the primitive Earth, or both. If, on the other hand, we assume for carbonaceous meteorites a maximum of 10% H_2O (Kaplan, 1971) and 30 ppm amino acid concentration (with average molecular weight of 100), simultaneous release of all H_2O and amino acids would yield a 0.003 molar solution. To release the hydrogen as H_2O, however, would require heating to temperatures in excess of 100°C, which would destroy the amino acids.

If the secondary atmosphere also contained a cometary contribution, comets could have supplied part or all of the initial inventory of organic matter for chemical evolution, a suggestion first made by Oró (1961). Since we have no clear knowledge of the content of organic compounds or of all the percursors such as HCN in comets, we cannot make an estimate as we did for carbonaceous meteorites. Comparison of the scanty data on production rates in Table V and estimates of the dust-to-gas mass ratio in comets (<2; Delsemme, 1977a) with the abundances of organic compounds in meteorites (Table III) leads one to expect considerably higher abundances of volatile and extractable organic compounds in comets.

Even if comets did not directly supply organic matter, they may well have provided the early atmosphere with the reduced gases CH_4 and CO or HCN and other intermediates that seem to be required for organic synthesis. After H_2O and CO_2, CH_4 and CO may be the most abundant molecules in comets (Delsemme and Rud, 1977). Evaporation of these and other volatiles from an icy matrix rapidly and <u>directly</u> into the atmosphere during entry and impact would free them for atmospheric chemical transformations and lengthen their lifetime against conversion to CO_2 by minimizing contact with a hot silicate impact melt. In contrast, as was shown in Table IV, the volatiles in meteorites require relatively high temperatures to release them from the meteorite matrix; thus, the compounds obtained from meteorites must have been released largely by pyrolytic-oxidative reactions of precursive organic matter with the matrix and/or slow inefficient extraction by rain or other water reservoirs.

Although ignorance about compositions precludes a meaningful estimate of cometary organic compounds and reducing gases, it seems highly desirable to try to estimate how much of the Earth's volatile inventory may have been supplied by comets. The approach we take considers the hydrogen/carbon, nitrogen/carbon, sulfur/carbon and argon/carbon ratios in comets, meteorites, and the Earth. Since all of these ratios are associated with rather large uncertainties, the quantitative significance of the estimate should be viewed with caution. The qualitative implications, however, should be seriously considered. Data needed for this estimate are given in Table VIII. Estimates of the ratios for the Earth's crust originate from three different sources and these supply limits for consideration. Note that Walker's model for the secondary atmosphere (Fig. 6) calls for hydrogen/carbon and nitrogen/carbon ratios of 12 and 0.03, respectively, comparable to the lowest values in Table VIII. The lack of correlation in hydrogen/carbon, sulfur/carbon, and ^{36}argon/carbon ratios between Earth and carbonaceous meteorites is striking. Relative to carbon, the Earth's crust contains more hydrogen and rare gases, and less sulfur than does any class of carbonaceous meteorite. Similar conclusions have been reported by Bogard and Gibson (1978). Some other source of volatiles must have contributed to the crust, and comets would appear to be reasonable alternatives (see also Bogard and Gibson, 1978; and Sill and Wilkening, 1978). Anders and Owens (1977), however, attribute the volatiles to a mixture of ordinary and carbonaceous meteorites dominated by the latter.

Table V supplies the appropriate data for comets. Upper and lower limits for the hydrogen/carbon ratio can be set at 90 and 4, respectively. Two mass balance equations for carbon and hydrogen are given below with the subscripts E, c, and M signifying the Earth's crustal content, the comet contribution and the meteorite contribution, respectively. Next, each term

$$C_E = C_c + C_M \tag{1}$$

$$H_E = H_c + H_M \tag{2}$$

in Eqs. (1) and (2) is divided by the quantity $(H + C)_E$. In the resulting

TABLE VIII

ESTIMATES OF THE ATOMIC ABUNDANCES (RELATIVE TO CARBON) OF VOLATILE ELEMENTS IN THE EARTH'S ATMOSPHERE, OCEANS, AND CRUST AND IN CARBONACEOUS METEORITES

	Hydrogen/ carbon	Nitrogen/ carbon	Sulfur/ carbon	^{36}Argon/carbon ($\times 10^{-6}$)
Earth[a]	87	0.14	0.03	-
Earth[b]	24	0.08	-	0.76
Earth[c]	16	0.03	0.07	0.49
C1 meteorites[d]	<4.2[e]	0.05[f]	0.64	0.013
C2 meteorites[d]	<3.1[e]	0.04[f]	0.63	0.014
C3 meteorites[d]	<2.5[e]	0.007[f]	1.5[g]	0.10[h]

[a] Rubey (1951).

[b] Turekian and Clark (1975).

[c] Anders and Owen (1977).

[d] Ratios are calculated as averages from data of Van Schmus and Hayes (1974), unless otherwise indicated.

[e] Calculated from upper limits for hydrogen, estimated by Kaplan (1971) and median carbon values of Vdovykin and Moore (1971).

[f] Calculated from averaged nitrogen data of Injerd and Kaplan (1974), Kothari and Goel (1974), and Kung and Clayton (1978) and median carbon values of Vdovykin and Moore (1971).

[g] Average value from a range of 0.34 to 2.86 for 16 meteorites.

[h] Average value from a wide range of 0.002 to 0.225 for 16 meteorites.

equations, the comet and meteorite components, respectively, are multiplied by the ratios $(H + C)_c/(H + C)_c$ and $(H + C)_M/(H + C)_M$. Rearrangement of the terms gives Eqs. (3) and (4)

$$C_E/(H+C)_E = C_c/(H+C)_c \cdot (H+C)_c/(H+C)_E + C_M/(H+C)_M \cdot (H+C)_M/(H+C)_E \qquad (3)$$

$$H_E/(H+C)_E = H_c/(H+C)_c \cdot (H+C)_c/(H+C)_E + H_M/(H+C)_M \cdot (H+C)_M/(H+C)_E \qquad (4)$$

Next, allow $X = (H + C)_c/(H + C)_E$ to represent the fraction of the Earth's total hydrogen and carbon that was contributed by comets. Thus $(1 - X) = (H + C)_M/(H + C)_E$ corresponds to the fraction supplied by meteorites. Division of Eq. (4) by (3) produces Eq. (5), which can be solved with the estimated hydrogen/carbon ratios. To calculate the

$$(H/C)_E = \frac{X[H/(H+C)]_c + (1 - X)[H/(H + C)]_M}{X[C/(H+C)]_c + (1 - X)[C/(H + C)]_M} \qquad (5)$$

smallest value for X, we use the representative $(H/C)_M$ value of 3.1, the lowest $(H/C)_E$ ratio of 16, and the highest $(H/C)_c$ ratio of 90. Surprisingly, the lower limit for the fraction of comet-derived volatiles turns out to be 0.79! All other combinations of hydrogen/carbon ratios yield $X > 1$. Even when the carbon in the Earth's upper mantle is included to yield a hydrogen/carbon ratio of 8 (Turekian and Clark, 1975), X takes a minimum value of 0.56. Unless the hydrogen/carbon ratio for the Earth is an order of magnitude lower, or the cometary hydrogen/carbon ratio is an order of magnitude higher, we are led inescapably to the conclusion that comets provided a major fraction of the volatiles that are now in the atmosphere and oceans and bound in the biosphere and the crust. Implications for the sources of the volatiles inventories of other terrestrial planets are clear.

Organic chemical evolution and the origin of life must be bound to the origin and evolution of the atmosphere of the planet that spawns it. If comets supplied as much of the Earth's volatiles as is suggested by these simple calculations, then comets must have made a primary contribution to the set of conditions necessary for life's origin.

IV. CONCLUDING REMARKS

Whether comets represent accreted interstellar matter or bodies condensed in the outer regions of the nascent solar system, or both, cannot be resolved at this time. Surely, however, comets contain the information that will tie them to their source region. The observable chemistry of comets suggests affinities to the chemistries of carbonaceous meteorites and interstellar matter. These similarities hint of fundamental cosmogonic relationships that remain obscured in the current state of ignorance. Thus, comets represent a poorly understood but integral link in the chain of chemical evolution of primitive matter in this part of the galaxy. They may provide the connection between solar system bodies and the interstellar environment from which all were derived.

Comets and carbonaceous meteorites are plausible sources for the Earth's atmophilic and organogenic elements. The relative abundances of these volatile elements, however, are difficult to reconcile with an origin solely from meteorite matter. Although the connection between comets and the origin of life may seem at first tenuous, the probability that they contributed significantly to the Earth's volatiles inventory suggests an essential chemical evolutionary link between comets and life. In this context, it is possible to view the cosmic "accidents" that produced a solar nebula, led to formation of Earth, meteorites, and comets, and perturbed comets into primordial Earth-crossing orbits as the earliest in the series of "chance" occurrences that led to the origin of life in this solar system.

Existing knowledge of comets is unlikely to yield further insights into the role of comets in early solar system history. More substantive chemical, isotopic, mineralogic and chronologic data having direct bearing on the issues of cosmogonic and cosmochemical importance are needed. They can be best obtained through detailed study of the physical and chemical composition of comets in a cohesive program of cometary exploration that involves remote observations from Earth and in space, in situ measurements, and study of matter collected directly from a comet and returned to Earth. Although Halley's comet offers a unique opportunity for generating widespread public interest in and support for a space mission to a comet, other comets may prove equally or more amenable to scientific study. Regardless of the ultimate choices of comets and types of comet mission, this seems an appropriate time to acknowledge again our ignorance about early solar system history and to point out areas where new knowledge about comets can give new insights into our origins.

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