UNIVERSIDAD NACIONAL AUTONOMA DE MEXICO

FACULTAD DE CIENCIAS

IMPORTANCIA PREBIOTICA DE COMPUESTOS ORGANICOS EN NUCLEOS DE COMETAS

T E S I S   P R O F E S I O N A L

Que para obtener el Título de:

BIOLOGO

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México, D. F.   198[illegible]

TESIS CON FALLA DE ORIGEN

Habe nun, ach! Philosophie,
Juristerei und Medizin,
Und leider auch Theologie
Durchauss studiert, mit heissem Bemühn.
Da steh'ich nun, ich armer Tor!
Und bin so klug als wie zuvor;
Heisse Magister, heisse Doktor gar,
Und ziehe schon an die zehen Jahr
Herauf, herab und quer und krumm
Meine Schüler and der Nase herum-
Und sehe, dass wir nicht wissen können!

Goethe, *Fausto*

Con ardiente afán ¡ay! estudié a fondo
La Filosofía, Jurisprudencia, Medicina
Y también, por mi mal, la Teología;
Y héme aquí ahora, pobre loco,
Tan sabio como antes.
Me titulan Maestro, me titulan Doctor,
Y por cerca de diez años he llevado
A mis estudiantes de acá para allá,
A diestro y siniestro.
Y ahora veo que nada podemos saber.

A la Dra. Paris Pishmish y a Hernán, Ana y la Pepa Larralde Ridaura, por su constante preocupación en ver concluído éste trabajo.

I. EL SURGIMIENTO DE LA VIDA EN LA TIERRA.

> ... lord Ardilaun has to change his shirt
> four times a day, they say. Skin breeds
> lice or vermin.
>
> James Joyce, *Ulysses*

En 1862 Louis Pasteur, al anunciar ante la Academia de Ciencias francesa los resultados de sus experimentos sobre la generación espontáneo en los que había utilizado los famosos matraces de cuello de cisne, declaró que:

"Jamás se recuperará la doctrina de la generación espontánea del golpe mortal que este simple experimento le ha dado..."

La afirmación de Pasteur, sin embargo, era injustificada, especialmente dado el número tan reducido de experimentos que llevó a -- cabo. Y aún cuando Bastian, Schäffer y otros más se apresuraron a señalar las limitaciones del trabajo de Pasteur, sus opiniones -que por otra parte, no dejaban de presentar serios errores-, fueron ignoradas o rechazadas. Los puntos de vista de Pasteur sobre la inexistencia de la generación espontánea pronto fueron elevados hasta la categoría de un dogma, apoyados por una superestructura política que asociaba a este fenómeno con las ideas de los revolucionarios franceses del siglo XVIII y al darwinismo con los intentos de subversión contra el Estado francés que encabezaba Napoleón III (Farley 1977, 1979).

Sin embargo, algunos años más tarde, hacia 1878, el mismo Pasteur escribió:

"Busco la generación espontánea sin descubrirla desde hace veinte años. No, no la juzgo imposible".

Es cierto que para entonces ya era mucho más seguro adoptar estas posiciones y hablar a favor del evolucionismo sin el temor a ser rechazado por burocracia científica que tanto apoyó a Napoleón el Pequeño; pero también es igualmente cierto que esta última cita de Pasteur corresponde a un momento en el que la aceptación de las ideas de Darwin y Wallace sobre la evolución de la vida por una parte, y por otra, la inexistencia de una explicación sobre el origen de los primeros organismos, habían llevado a las ciencias naturales a una situación crítica de la que no parecía existar salida.

La imposibilidad de obtener vida en el laboratorio, que era como también se podían interpretar las conclusiones de los experimentos de Pasteur, llevó a los científicos y pensadores vitalistas, capitaneados por Driesch en Alemania y por Bergson en Francia, a señalar que se demostraba así que la brecha entre la materia viva y la inerte era insalvable, y más aún, que la esencia misma de la vida poseía un carácter metafísico. Estas conclusiones, por mucho que irritaran a los materialistas de la época, era difícilmonte combatibles. Algunos de estos últimos, como Emile Du Bois Reymond, llegaron a la conclusión de que la aparición primera de la vida era uno de los enigmas del Universo que los científicos jamás podrían resolver; otros, como Richter (1865), Helmholtz (1879) y Arrhenius (1908) sugirieron un origen extraterrestre para los primeros seres vivos en la Tierra, y otros más, como Troland (1914, 1916, 1917) en Estados Unidos y Herrera (1924) en México, intentaron explicar el origen de la vida desde una perspectiva mecanicista (*cf.* Aguilar *et al.*, en prep.).

Con el propósito explícito de combatir a las corrientes neovitalistas que proliferaban en las ciencias naturales, Leonard T. Troland, de la Universidad de Harvard, publicó entre 1914 y 1917 una serie de artículos en los que sugería que la vida había aparecido en los mares primitivos de la Tierra gracias a que una combinación fortuita de -- átomos y substancias disueltas había dado origen, en forma espontánea, a una molécula capaz de autoreplicarse y de regular a su alrededor la síntesis de otros compuestos. Así, al azar, rechazado durante tanto tiempo por los biólogos cartesianos como un elemento importante en el problema del origen y la esencia de la vida (Farley 1977) cobraba en el esquema de Troland --que ya desde su primer trabajo de 1914 se -- autoproclamaba un mecanicista decidido- una importancia singular al ser incorporado como un elemento ontológico, situación que se preserva hasta nuestros días en prácticamente todos los esquemas reduccionistas que existen en la biología contemporánea.

Las ideas de Troland fueron recogidas y modificadas por Hermann J. Muller, el célebre genetista norteamericano, quien propuso por primera vez en 1929 (Muller 1929) que en la hidrósfera de la Tierra primitiva había surgido de manera espontánea y repentina no una enzima, -- como decía Troland, sino un gene aislado, que además de poseer las -- propiedades auto- y heterocatalíticas que Troland asignaba a la molécula primigenia, era capaz de sufrir mutaciones. Influenciado sin -- duda alguna por los postulados de Weissman sobre la naturaleza del genoma, y por sus propios trabajos en genética, Muller buscaba así explicar no solamente el problema del origen de la primera forma de vida sino además su evolución subsequente. Pero tanto Troland como Muller no hacían sino replantear los postulados esenciales de las teorías de la generación espontánea, solo que ahora llevándolos a nivel molecular; en efecto, como bien ha demostrado Keosian (1972, 1974), el problema del origen de los primeros organismos de ninguna manera se puede reducir al origen espontáneo de una sola molécula o substancia a partir de la cual se pueda considerar que la vida se ha iniciado.

Entretanto, influenciados también por las diferentes corrientes del materialista mecanicista que buscaban explicar los fenómenos característicos de los seres vivos a partir de las propiedades de los coloides, las enzimas, o los virus, Alexander I. Oparin, en la Unión Soviética, y John B.S. Haldane, en Inglaterra, intentaron abordar el problema del origen de la vida desde una perspectiva diferente.

En una conferencia sustentada en 1922 ante la Sociedad Botánica de Moscú, Oparin, entonces un jóven bioquímico preocupado por el problema del origen y la evolución de la fotosíntesis aerobia, sugirió que las condiciones del planeta, antes de la aparición de la vida, habían sido radicalmente diferentes a las actuales. En particular, Oparin creía en la existencia de una atmósfera reductora, en donde, gracias a la acción de la energía geotérmica, se habían sintetizado compuestos orgánicos que habían actuado como precursores de moléculas más complejas, de carácter orgánico, y sintetizadas abióticamente. Estas moléculas, disueltas en los mares primitivos de la Tierra, habían dado origen a coloides de cuya evolución gradual surgieron los primeros seres vivos, pequeños micro-organismos heterótrofos y anaerobios. Los puntos de vista de Oparin fueron publicados por primera vez en un pequeño libro que apareció en 1923 (aunque la fecha de publicación que aparece en la portada corresponde a 1924). Es bien sabido que en forma independiente a los trabajos de Oparin, Haldane publicó en 1928 un artículo igualmente significativo, en el que propuso que gracias a la acción de la radiación ultravioleta de origen solar, se formaron en la atmósfera primitiva, en donde el carbono se encontraba bajo la forma de CO_2, compuestos orgánicos que al disolverse en los mares, dieron origen a una solución diluída y caliente de compuestos orgánicos. Aparecieron entonces, según Haldane, los virus, y la vida estuvo representada en el planeta por este tipo de sistemas durante un tiempo considerable, hasta que luego surgieron las primeras células heterótrofas y anaerobias.

Es igualmente conocido el que en 1925 se publicó la primera edición de la *Dialéctica de la Naturaleza*, de Engels y que en 1935 vió la luz pública la célebre carta que Darwin dirigiera en 1871 a su amigo F.J. Hooker; ambos textos, que constituyen antecedentes de singular importancia a los puntos de vista contemporáneos sobre el origen de la vida en la Tierra, eran, sin embargo, desconocidos tanto para Oparin como para Haldane al momento de publicar sus trabajos. ¿Cuáles fueron, entonces, las influencias a las que estuvieron sujetos tanto Haldane como Oparin para proponer sus primeras hipótesis sobre la aparición de la vida? En el caso de Haldane, el desarrollo de la enzimología, la virología, y los experimentos de Baly (1927) que demostraban la síntesis abiótica de compuestos orgánicos, la aparición de coloides y el surgimiento de los primeros seres vivos. En ambos autores, sin embargo, la influencia fundamental la ejerció el darwinismo, por una parte, y por otra, un clima social que permitía en sus respectivos países, el desarrollo de teorías materialista sobre problemas tan medulares a la concepción del mundo como el del origen y la esencia de la vida.

Aunque Haldane habría de jugar un papel esencial en la construcción del neodarwinismo, y sufrió un proceso de radicalización ideológica que le llevó a convertirse en uno de los científicos de izquierda más lúcidos de Occidente, en todos sus trabajos posteriores sobre el origen de la vida (Haldane 1954, 1964, 1965) siguió manteniendo la idea de un proceso de evolución química en el que sin embargo, el origen repentino de sistemas virales recuerda las ideas de la generación espontánea. Oparin, en cambio, abandonó rápidamente las posturas mecanicistas que había mostrado en su libro de 1924, y en 1936, luego de un largo período en que acumuló evidencias que apoyaban la idea de un proceso de evolución de la materia previo al origen de lo primeros organismos, publicó un segundo libro, también llamado *El Origen de La Vida* (Oparin 1936), en el que la postura materialista y dialéctica es clara, no solamente en el lenguaje utilizado, sino también respecto a la concepción del surgimiento de los primeros seres vivos como el resultado de un proceso gradual de evolución de la materia en el que nuevas formas cualitativamente más complejas, van surgiendo y van abriendo así nuevas posibilidades. Pero no se puede de ninguna manera suponer que el cambio radical que se había operado en Oparin era exclusivamente el resultado de una profundización en los aspectos teóricos o experimentales del problema; el clima político, social e ideológico que vivía la URSS en ese momento, y en particular, el empeño de los científicos soviéticos en construir una ciencia desde la perspectiva del materialismo dialéctico, habría de jugar un papel esencial en la formulación contemporánea de los puntos de vista de Oparin sobre el origen de la vida. Este fenómeno, que ha sido examinado parcialmente por algunos autores (Graham 1976; Farley 1977, 1979; Keosian 1972, 1974), es objeto de un trabajo posterior (Oparin y Lazcano-Araujo, en prep.).

El segundo libro de A.I. Oparin sobre el origen de la vida, pronto fué traducido al inglés, pero no fué sino hasta después de la Segunda Guerra Mundial que su impacto se dejó sentir claramente en la investigación científica sobre el problema del surgimiento de la vida.

Aunque las síntesis abióticas de materia orgánica son conocidas en la literatura científica desde la síntesis clásica de urea, realizada por Woehler en 1828, el primer experimento diseñado con el propósito explícito de mostrar la posibilidad de obtener compuestos orgánicos en condiciones que simularan las de la Tierra primitiva, fué llevado a cabo por Groth y Suess (1938), quienes irradiaron una atmósfera de CO_2 y H_2) con luz ultravioleta de longitud de onda de 1470 Å y obtuvieron así formaldehído. Años después, el grupo de Calvin en la Universidad de California en Berkeley, irradió con partículas alfa obtenidas del ciclotrón de Berkeley una solución acuosa que contenía Fe^{++} en equilibrio con una atmósfera de CO_2 y H_2. Obtuvieron así formaldehído, y ácidos fórmico y succínico (Garrison <u>et al.</u> 1951). Harold C. Urey, entonces en la Universidad de Chicago, al --

examinar el experimento del grupo de Calvin llegó a la conclusión de que las condiciones utilizadas en estas simulaciones de la Tierra primitiva no correspondían ni a las sugeridas por Oparin (1938) ni a las que él mismo había descrito para la atmósfera reductora de la Tierra (Urey 1952), y no fué sino hasta un año más tarde, cuando Miller (1953), utilizando descargas eléctricas sobre una atmósfera de CH_4, NH_3, H_2O y H_2 en su experimento ya clásico, pudo demostrar la síntesis abiótica de aminoácidos proteínicos y no-proteínicos, de ácidos orgánicos y de otras substancias de interés biológico. El impacto de los resultados de Miller y Urey fué inmediato; muchos otros laboratorios repitieron experimentos similares, y la síntesis abiótica de una amplia variedad de compuestos orgánicos utilizando diferentes precursores y diversas fuentes de energía libre es aceptada hoy en día como un modelo experimental válido para simular las condiciones de la Tierra primitiva previa a la aparición de la vida.

El mismo año en que Miller dió a conocer los resultados de su experimento (Miller 1953), sin embargo, coincidió con la publicación del modelo de la doble hélice que Watson y Crick (1953) propusieron para explicar la naturaleza de la molécula del ácido desoxirribonucleico. Dos años más tarde, Muller (1955) sugirió que la vida en la Tierra era el resultado de la aparición espontánea ya no de un gene, sino de una molécula primigenia de ADN. La obtención abiótica de adenina (Oró 1961; Ponnamperuma et al. 1963) y de otros componentes de los ácidos nucleicos llevó a Muller a modificar luego su teoría y sugirió así que en los mares primitivos de la Tierra se habían sintetizado primero nucleótidos, que luego reunidos espontáneamente, había dado origen al ADN ancestral, de donde se derivaron todos los seres vivos (Muller 1966). Para entonces, sin embargo, el reduccionismo de Muller no obedecía tan sólo a motivos científicos, sino a una repulsa visceral a los trabajos soviéticos sobre el origen de la vida (Keosian 1972), actitud que mantuvo hasta el fín de sus días, y que le llevó a afirmar que los puntos de vista de Oparin formaban parte de una conjura comunista que buscaba minar la genética occidental (Muller 1966).

Es innegable que un problema fundamental en el estudio del origen de la vida en la Tierra, es el del origen del código genético; sin embargo, es también evidente que la vida no surgió gracias a la aparición repentina y espontánea de una molécula de ADN, sino como resultado de un proceso gradual de evolución de la materia en el que se puede reconocer la fase de evolución química, que corresponde a la síntesis abiótica de materia orgánica; la llamada evolución prebiológica, que implica la formación de sistemas polimoleculares --- abiertos con separación de fase, en cuyo interior es posible pensar se originó el metabolismo, incluyendo, por supuesto, la relación --- entre códigos genéticos ancestrales y los primeros polipéptidos que fueron codificados; y en tercer lugar, la etapa de evolución biológic que se inicia con la aparición misma de los primeros seres vivos o eubiontes (Oparin 1972).

En este contexto específico, el descubrimiento de compuestos orgánicos extraterrestres en las nubes del medio interestelar, en condritas carbonosas, en asteroides y en cometas (cf. Oró 1972), cobra un significado particular; demuestra, por una parte, la validez de los modelos experimentales sobre la síntesis abiótica de materia orgánica en el laboratorio (Wolman *et al.* 1972), pero al mismo tiempo, comprueba que la fase llamada de evolución química pudo haber ocurrido previamente a la formación de la Tierra misma (Bernal 1965).

Cabría preguntarse, sin embargo, si los compuestos orgánicos extraterrestres solamente son evidencias analógicas de un proceso de evolución química o si también jugaron un papel en la evolución de la Tierra primitiva, y en consecuencia, en los procesos que condujeron a la aparición de la vida. El propósito del siguiente capítulo es precisamente el de discutir el significado prebiótico de los cometas, y más específicamente, de los compuestos orgánicos que existen en estos cuerpos.

Una de las posibilidades que existen para resolver esta pregunta es la caracterización de las condiciones ambientales de la Tierra primitiva que permitieron la síntesis abiótica de compuestos orgánicos, la aparición de sistemas precelulares y la evolución gradual, a partir de estos últimos, hasta llegar a los primeros organismos.

En éste sentido, el descubrimiento de cinco morfotipos y de estromatolitos fósiles en rocas sedimentarias de tres mil quinientos millones de años de edad (Awramik *et al.* 1980) y y los estudios de longitud del fragmento de ácido poliadenflico del mRNA para organismos contemporáneos, que sugiere que la vida pudo haber aparecido en la Tierra hace aproximadamente cuatro mil millones de años (Carlin 1980), colocan a la aparición de los eubiontes en una época de la historia de la Tierra para la cual desafortunamdamente nuestros conocimientos actuales resultan por demás limitados. En todo caso, la presencia de rocas sedimentarias en la formación de Isua, de 3.8 x 10^9 años de edad sugiere la presencia de una hidrósfera, y dada la abundancia de carbonatos que existen en ésta formación, de una cantidad de CO_2 atmosférico comparable a la contemporánea.

Por otra parte, el estudio de las superficies de los cuerpos del Sistema Solar interior, y más especificamente, de la Luna y Mercurio, a mostrado la gran cantidad de cráteres por impacto que fueron formados en un periodo anterior a los cuatro mil millones de años; es decir, la historia temprana de los planetas del Sistema Solar estuvo caracterizada por un gran número de colisiones de meteoritos, asteroides y presumiblemente cometas, que se puede explicar como la parte tardía de los procesos de acreción que dieron origen a los planetas. La antiguedad de la vida en la Tierra sugiere entonces que para caracterizar el medio ambinete prebiótica es necesario reconocer no únicamente la presencia de una atmósfera anóxica y de temperaturas moderadas que hayan permitido la supervivencia de las moléculas sintetizadas abióticamente, sino también la de una gran número de colisiones con cuerpos ricos en volátiles que la chocar contra la Tierra primitiva liberaban grandes cantidades de energía que presumiblemente pudo haber contribuído a la síntesis no biológica de monómeros, oligo-, y polímeros de interés prebiológico.

El propósito de los dos trabajos que forman el capítulo segundo de ést tabajo es precisamente el de establcer la contribución que cuerpos sismilares a los cometas pudieron hacer a éste proceso de colisión, los volátiles aportados y la consecuencias en términos de la sítesis de materia orgánica.

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II. LOS COMETAS Y EL ORIGEN DE LA VIDA*

> Se dice que no sale en vano, que no cae en vano su flechazo: agusana las cosas.
> Y de lo que ha sido flechado se dice: "Está flechado por la estrella; está agusanado". Ya no es comido; es visto con temor; es visto con asco; está peído; da mucho asco.
>
> Y en la noche bien se protegen, se envuelven, se cubren, se envuelven con mantos, se lían. Es temido el flechazo de la estrella.
>
> *La Cauda del Cometa*. Augurios y Abusiones de los Textos de los Informantes de Fray Bernardino de Sahagún.

* Este capítulo está formado por dos manuscritos actualmente en prensa; el primero de ellos, de J. Oró, G. Holzer y A. Lazcano-Araujo (The Contribution of Cometary Volatiles to the Primitive Earth), fué presentado en la XXII COSPAR Plenary Meeting, Bangalore, India (Mayo de 1979), y aparecerá en un volumen editado por R.M.Holmquist y publicado por Pergamon Press (Nueva York). El segundo, de A. Lazcano-Araujo y J. Oró (Cometary Material and the Origins of Life on Earth), fue presentado en el Fifth College Park Colloquium on Chemical Evolution, College Park, MD, EEUU (Octubre de 1980) y aparecerá en un volumen editado por C. Ponnamperuma y B.D. Donn que recoge los trabajos invitados a dicha reunión y que será publicado por Reidel Publ. Co. (Dordrecht)

III. LOS COMETAS Y EL ORIGEN DE LA VIDA*

Se dice que no sale en vano, que no cae en vano su flechazo: aguzana las cosas.
Y de lo que ha sido flechado se dice: "Está flechado por la estrella; está agusanado". Ya no es comido; es visto con asco; es visto con asco; está podrido da mucho asco.

Y en la noche bien se protegen, se envuelven, se cubren, se envuelven en mantas, se lían. Es temido el flechazo de la estrella.

La Cauda del Cometa. Augurios y Abusiones de los Textos de los Informantes de Fray Bernardino de Sahagún.

* [illegible] publicado por [illegible] A. [illegible] "Cometary Material and the Origin of Life" [illegible] (Noviembre de 1981) [illegible] C. Ponnamperuma y [illegible] invitados a dicha [illegible] Reidel Publ. Co. (Dordrecht).

THE CONTRIBUTION OF COMETARY VOLATILES TO THE PRIMITIVE EARTH

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ABSTRACT

It has been estimated that during its early history the Earth captured a mass of cometary material of the order of 10^{23} grams. Since carbon is supposed to be at least three times more abundant in comets than in carbonaceous chondrites (3.5% C in C 1 chondrites), it can be deduced that about 1 x 10^{22} grams of carbon (as carbon compounds) was added by comets to the surface of the prebiotic Earth. This carbon value is of the same order of magnitude as the value of the organic carbon buried in the Earth's sedimentary shell, but approximately one order of magnitude lower than the Earth's surface total carbon (7 x 10^{22} gm). The capture of comets by the Earth would also have contributed to generating the appropriate aqueous and reducing environmental conditions necessary for organic synthesis.

Although it is possible that some of the cometary carbon compounds falling on the Earth survived, most of them were probably decomposed by the heat and shock waves of the cometary collision. Upon quenching to low temperatures, however, the reactive chemical species produced by the impact would have recombined, leading to the synthesis of a great variety of organic molecules. Laboratory experiments with radiation, heat and shock waves have demonstrated that some of the synthesized compounds are biochemical molecules: amino acids, sugars, purines, and pyrimidines. These are essential to all living systems.

INTRODUCTION

There is a long tradition that links cometary phenomena with the appearance of life. For instance, in the seventeenth century, Newton expressed his belief that plants could be generated spontaneously from the emanations arising from cometary tails [1]. In 1871 Hermann von Helmholtz, then an advocate of the theory of panspermia, wrote [2] "Who can say whether the comets and meteors which swarm everywhere through space, may not scatter germs wherever a new world had reached the stage in which it is a suitable place for organic beings".

During the first part of this century the extension and further development of Darwin's concepts by Oparin [3] and Haldane [4] provided a new insight into prebiological phenomena. But comets did not disappear from the new scenario! Indeed, Oparin pointed out in his classical 1924 book that the presence of hydrocarbons, cyanogen, and carbon monoxide in cometary spectra was evidence for the reducing character of the prebiological Earth's environment.

In recent times there has been a reassessment of the role that cometary matter played in prebiotic evolution. Comets have been proposed as a source of volatiles for the primitive Earth [5-22], while cometary collisions have been suggested as an energy source for abiotic organic synthesis [23-29]. Moreover, Hoyle and Wickramasinghe [30,31] and Hoyle [32] have proposed, like von Helmholtz did in 1871, that the earliest forms of life originated in cometary nuclei, from which they arrived on the prebiotic Earth.

The purpose of this paper is to examine some of the previous possibilities. First we review briefly some aspects of cometary phenomena that are relevant to organic cosmochemistry. We then consider in some detail the contribution of cometary matter, especially volatile compounds of the organogenic elements (H, C, N, O, S, P) to the primitive Earth, as well as the role of these simple compounds in the formation of biochemical molecules. Finally, the possibility that life could arise in cometary nuclei and interstellar clouds rich in organic molecules is critically examined.

COMETS AND ORGANIC COSMOCHEMISTRY

Cometary nuclei are small bodies with diameters of ~1 to a few tens of kilometers, a mass ranging approximately from 10^{15} to 10^{18} grams and a typical density of about 1 to 1.5 gm cm^{-3}. They consist of ices and clathrates of simple compounds of H, C, N and O, and other elements. In addition refractory components such as metals and silicates have been detected (Table 1).

TABLE 1. Chemical Species Detected in Comets and Other Cometary Data

Composition	
Head	H, C, C_2, ^{12}C, ^{13}C, C_3, CH, CN, NH, NH_2, CS, CO, O, H, H_2O, Na, K, Cr, V, Mn, Fe Co, Ni, Cu, S
Tail	CH^+, CO^+, CO_2^+, N_2^+, OH^+, H_2O^+, Ca^+
Head-tail continuum	Including silicate particles (10 and 18 μm bands)
Parameters of Cometary Nuclei	
Average mass	$10^{18\pm3}$ grams (10^{18} gm minimum mass for Halley's comet)
Diameter	~1 to a few tens of km
Density	~1 gm cm^{-3} to 1.5 gm cm^{-3}
Internal compressive strenth	~10^4 - 10^6 dyne cm^{-3}
Present Mass of the Oort's Cloud	~10^{27} grams.

Delsemme [33] has shown from analysis of the dust-to-gas mass ratio of Comet Bennet 1970 II and Comet Arend-Roland 1957 III, that comparable amounts of dust and gas are present in the material emitted by a comet, therefore suggesting that a large fraction of a comet may consist of nonvolatile dust and rocky material [34].

The overall cometary population extends out to a great distance from the Sun, and includes two major systems: a central planetary system of short-period (less than 200 years) comets, and the general circumsolar system of long-period comets, the latter forming the Öpik-Oort cloud out to solar distances of 10^4 to 10^5 AU [35, 36] where, as Oort suggested, $\sim 10^{11}$ comets with a total mass of $\sim 10^{27}$ grams may still remain. Most, and probably all present comets come from the Öpik-Oort cloud system [37]. The interaction of this system with the interstellar environment may send some cometary nuclei into the inner solar system, where some of the long-period comets are later perturbed by Jupiter and evevtually acquire a short-period orbit. Marsden and Sekanina [38] found no evidence for orbits of interstellar origin, a conclusion supported by the carbon isotopic measurements of cometary chemical species which show that the $^{12}C/^{13}C$ values (100) for comets is higher than that for interstellar clouds [39].

The spherical distribution of comets' orbits supports the assumption that they reflect an early formation from the solar nebula. The activity of new comets at large solar distances shows that comets were formed at a region of low temperature, probably below 100°K [17]. Because of these low temperatures, chemical reactions are slow and we are therefore provided with the opportunity for studying the most primitive material in the solar system. Indirectly this research would also be of value in determining, because of similar conditions, some aspects of the chemistry of the interstellar medium.

From the determination of cosmic elementary abundances it was known [40,41] that, with the exception of the noble gases, six of the most abundant elements in the universe (H, C, N, O, S, P) were precisely the ones necessary for the formation of the organic compounds present in living systems. It was therefore logical to conclude [42] that the molecules formed from these elements would also be the most abundant compounds in the universe. Indeed such a conclusion has been confirmed with the detection of a large number of organic and inorganic molecules of prebiological and biological relevance in the Milky Way and in other galaxies. These molecules range in complexity from formaldehyde and hydrogen cyanide to cyanooligo-acetylenes [43]. One of the more remarkable surprises which has emerged is that the molecules identified in interstellar space are precisely the ones that had been used in terrestrial laboratories for simulations of prebiotic organic synthesis, such as, in Miller's experiment [44]. In fact, ten of these molecules can be considered as the prebiological precursors of essentially all the biochemical compounds present in living systems. These are: hydrogen, water, ammonia, carbon monoxide, formaldehyde, acetaldehyde, thioformaldehyde, hydrogen cyanide, cyanoacetylene and cyanamide. These ten molecules, plus phosphine and aldehydes, are listed in Table 2. It is quite probable that all these molecules or their immediate derivatives, may be present in cometary nuclei. Phosphine, which has only been detected in the atmosphere of Jupiter, may also be present in small amounts in the interstellar space and in comets.

COMETARY COLLISIONS IN THE PRIMITIVE EARTH

Though impact craters are a common feature [45] in the inner solar system, only three probable impact craters dating from Precambrian times are known [46] to exist on the Earth's surface: Vredefort, S. Africa (1970 ± 100 million years old), Sudbury, Canada (1940 ± 150 million years old) and Janisjarvi, U.S.S.R. (700 million years old). There can be little doubt that the primitive Earth, when it had grown close to its final mass, suffered an intense bombardment by interplaneplanetary debris, as indicated by models of planetary accretion [47], and data on ancient lunar cataclysms [48]. There is ground to suspect that comet-like bodies and related meteoritic material participated in this process. Comets are associated with the interplanetary flux of material that impacts on the Earth [49]. Moreover, the orbits of some comets bring them quite close to our planet, and may even cross its orbit during their approach to perihelion. Though the present cometary contribution is negligible, during its past history the Earth must have acquired a significant amount of cometary matter [17].

TABLE 2. Biochemical Monomers and Properties Which Can be Derived from Interstellar Molecules [77]

Interstellar molecules	Formulae	Biochemical monomers and properties
1. Hydrogen	H_2	Reducing agent, protonation
2. Water	H_2O	Universal solvent, hydroxylation
3. Ammonia	NH_3	Base catalysis, amination
4. Carbon monoxide (+H_2)	CO	Hydrocarbons and fatty acids
5. Formaldehyde	CH_2O	Monosaccharides (ribose) and glycerol
6. Acetaldehyde	CH_3CHO	Deoxypentoses (deoxyribose)
7. Aldehydes (HCN)	RCHO	Amino acids
8. Thioformaldehyde	CH_2S	Cysteine and methionine
9. Hydrogen cyanide	HCN	Purines (adenine, guanine) and amino acids
10. Cyanacetylene	HC_3N	Pyrimidines (cytosine, uracil, thymine)
11. Cyanamide	H_2NCN	Polypeptides, polynucleotides and lipids
12. Phosphine (Jupiter)	PH_3	Phosphates and polyphosphates

Collision with comet-like bodies must have been particularly important in the last stages of accretion of the solar system, when large numbers of residual bodies left over after the formation of the planets must have moved in heliocentric orbits colliding with the terrestrial planets [34]. Wetherill [50] has shown that although ~99% of such interplanetary debris was ejected out of the solar system by Jupiter, perturbations by the giant planets sent cold, volatile-rich, small bodies from the Uranus-Neptune region into the inner solar system.

There is conclusive evidence [48] that the Moon's surface was subjected to such heavy late-bombardment culminating ~3.9 x 10^9 years ago, and according to Wetherill's calculations [50], the influx of infalling cometary material on the lunar surface was ~2 x 10^{20} grams (Table 3).

TABLE 3 Cometary Matter Trapped By Solar System Bodies

	Cometary matter trapped (grams)	Time	Reference
Sun	~10^{26}	main-sequence stage	Joss [52]
Venus*	4 x 10^{20}	2 x 10^9 years	Lewis [56]
Moon	2 x 10^{20}	late-accretion period	Wetherill [50]
Earth	2 x 10^{14} to 10^{18}	first 2 x 10^9 years	Oro [5]
	10^{25} to 10^{26}	late-accretion period	Whipple [17]
	(3-4) x 10^{21}	late-accretion period	Sill and Wilkening [22]
	~10^{23}	first 2 x 10^9 years	this paper

*Estimated from the influx of 2 x 10^8 kg yr^{-1} of cometary material on Venus given by Lewis [56].

The primitive Earth must have experienced simultaneously such heavy-bombardment, but due to its larger gravitational field, a greater amount of interplanetary debris of cometary nature was captured. As this collisional process took place during the time of prebiological and early-biological evolution, it must have played a significant role in shaping the environmental conditions under which life arose and evolved.

The first suggestion that the capture of comets by the primitive Earth could be of prebiological significance was made by Oro [5], who from Urey's [51] collisional probabilities estimated that during its first 2 x 10^9 years the primitive Earth captured from interplanetary space 2 x 10^{14} to 1 x 10^{18} grams of cometary material. Under the oxygen-free conditions then prevailing, substantial amounts of precursors (HCN, NH_3, H_2O, etc.) of monomers and polymers of prebiological and biological significance accumulated on the primitive Earth. Other estimates of cometary material trapped by the Earth have been made for different periods of time (Table 3). Whipple has suggested [17] that if 10^{29} grams of ice-conglomerate material was formed in the Uranus-Neptune region, a large fraction of these bodies would be transferred into Jupiter crossing orbits, thus forming a short-lived (~10^8 years) "cometary nebula" within Jupiter's orbit. The collisions between such comets and the Earth would accumulate in the latter ~10^{25} to 10^{26} grams of volatiles, a figure comparable to Joss' estimate [52] of cometary material accreted by the Sun during its main-sequence stage.

Thus, according to Whipple [17] the secondary atmospheres of Mars, Venus, and the Earth may have accumulated entirely from comets that replenished the gases and volatile compounds that were lost during the accretion period of these planets. For the late-accretion period of our planet a more conservative estimate was given by Sill and Wilkening [22], who suggested that during the heavy-bombardment phase of the solar system the Earth acquired (3-4) x 10^{21} grams of cometary material rich in clathrates and other volatiles.

From Everhart's [53] paper, "Close Encounters of Comets and Planets", that considers the interaction between 10^9 random parabolic comets and the planets, we have estimated that the Earth captured during its first 2 x 10^9 years ~10^{21} grams of cometary material, by assuming that all the colliding comets would follow the absolute magnitue-mass relationship of Allen [54],

$$\log_{10} (M \text{ in gm}) \sim 21-0.4\, M_\circ$$

where $M_\circ$ is the absolute magnitude. It is clear, however, that this figure is an underestimate, since Everhart [53] does not take into account the collisional history for the early solar system. Therefore, we have used Wetherill's [50] collisional probability tables to estimate the mass contributed by bodies of cometary-type orbits to the Earth during its first 2 x 10^9 years, a period when according to geochemical and paleontological evidence the value of the free-oxygen partial pressure was negligible [55]. Table 3, above, summarizes our results.

Cometary collisions probably deposited large amounts of volatiles on the other planets of the inner solar system, all of which still bear the scars of the intense bombardment suffered in the past. However, the weak gravitational fields of Mercury and the Moon were not able to retain the volatiles of cometary origin, while on Mars corpuscular radiation and large UV fluxes must have decomposed large amounts of these volatiles [20]. On Venus the captured cometary and associated meteoritic material must have contributed to the present abundances of volatiles. Lewis [56] has estimated that ~2 x 10^{11} grams of cometary material--of which 50% is water--fall annually on Venus. From this figure we derived a value of 4 x 10^{20} grams for the total cometary infall on Venus during 2 x 10^9 years (Table 3), though this value is an underestimate since Venus must have had an accretional history comparable to that of the Earth. It is likely that comparable amounts of cometary material accumulated on these two planets, Venus and Earth, though differences in chemical composition could be expected from kinetic and temperature effects due to the different distances from the Sun [17].

On the other hand, since carbon is supposed to be at least three times more abundant in comets than in carbonaceous chondrites (3.5% of C in C 1 chondrites) (Table 4), it can be deduced that about 1 x 10^{22} grams of carbon, in several forms were added by comets to the primitive Earth. This figure is of the same order of magnitude as the value of the organic carbon buried in the Earth's sedimentary shell, but approximately one order of magnitude lower than the 7 x 10^{22} grams of carbon that constitute the Earth's surface total carbon (Table 5).

In addition to carbon, comets contain substantial amounts of water, either free or bound in clathrates (such as $CH_4 \cdot 6H_2O$). They also contain hydrogen-bearing compounds (NH_3, CH_4, HCN) and free hydrogen (Table 1 above). It appears therefore that the capture of comets must have contributed towards generating the appropriate aqueous and reducing environmental conditions necessary for organic prebiotic synthesis and the early evolution of life.

TABLE 4 Some Atomic Abundances in the Solar System*
(Numbers Normalized to Silicon = 1)

	Sun	C I Chondrites	Comets	Comet/C.I. ratio
H	30,000	1.5	15	10
C	12	0.7	3 to 6	4 to 8
N	3	>0.05	0.1	Larger than 2
O	21	7.5	21	3
Si	1	1.0	1	1
H/O	14,000	0.2	0.7	3.5

*from Delsemme [73]

TABLE 5 Carbon Abundances in the Earth

	Dominant form of carbon	Mass in carbon (in grams)	Reference
Biosphere (living matter)	biomass	10^{18}	Garrels and MacKenzie [78]
	biomass	8.3×10^{17}	Abelson [79]
Crust			
Sedimentary shell (total mass)	several forms	2.4×10^{24}	Garrels and Lerman [80]
Sedimentary organic	organic carbon	1.2×10^{22}	Schidlowski [81]
	organic carbon	1.9×10^{22}	Hunt [82,83]
Carbon added to Earth by cometary collisions		1×10^{22}	this paper

It is unlikely that the organic compounds present in cometary nuclei would survive planetary collision [23]. Cometary nuclei, being fragile bodies of low density probably never reached the surface of the primitive Earth, but exploded on reaching the outer limit of the paleotroposphere, causing a substantial change and diffusion of their organic and inorganic constituents. Thus, in addition to the major components (CO_2, CO, N_2, H_2O, H_2) of the primitive terrestrial atmosphere which were liberated in an early degassing period [57], this atmosphere also contained smaller amounts of noble gases and other volatile compounds, such as NH_3, HCN, CH_4, and H_2S, derived from accreted cometary material.

Under the anoxigenic conditions then prevailing and upon a subsequent quenching to low temperature, the reactive chemical species produced by the heat and shock wave of the cometary impact would recombine, leading to a great variety of organic compounds. These compounds would reach the Earth's surface and hydrosphere only if they were quickly transported from the upper atmosphere to zones where the UV solar flux would not destroy them. This should in fact be the case considering the turbulent nature of planetary atmospheres (e.g. Jupiter, Venus, Earth).

Cometary collisions may be considered an important free-energy source. This energy could be released as heat and shock waves. Very high yields in the synthesis of amino acids have been obtained [24,25] in laboratory simulations with shock tubes containing mixtures of CH_4, NH_3 and H_2O. If such yields were obtained in the primitive environment in naturally occurring shock waves then this source of energy must have been very important in prebiological synthesis [27, 28], and in modulating the chemical kinetics of primitive atmospheres [29].

The best contemporary example of such a cataclysmic event is provided by the Tunguska explosion, that was probably caused by a small comet or, as suggested recently [58] by a fragment of the Encke comet. This cometary material, with a mass of 5×10^{10} grams exploded at a height of ~ 8.5 km above the surface with an associated energy of $(5 \pm 1) \times 10^{23}$ erg [59], enough to destroy most, if not all, of the compounds present in it (Table 6).

TABLE 6 The Tunguska Explosion

Energy of the main explosion (at a height of 8.5 km)	$5 \pm 1 \times 10^{23}$ erg	Ben-Menahem [84]
Absolute visual magnitude	+26.0	Brown and Hughes [59]
Geocentric velocity	28 to 50 km seg^{-}	Krinov [85]
	47 km seg^{-}	Levin [86]
Mass (estimated from the geocentric velocity given by Levin, 1954)	5×10^{10} gm	Brown and Hughes [59]
Diameter	40 m	Brown and Hughes [59]
Collisional probability	1/2000 yr	Brown and Hughes [59]

A comet hitting the Earth would liberate a high amount of energy, according to the kinetic equation $E = 1/2\ MV^2$ where V^2 is the velocity of the comet's nucleus at 1 AU. The velocity of a comet for any point of its orbit can be calculated from $V^2 = GM_\odot\ (2/r - 1/a)$, where G is the universal constant of gravitation, $M_\odot$ is the solar mass = 1.99×10^{33} grams and r is the semi-major axis of the elliptical orbit. We have estimated the velocity for typical short-period comets when r = 1 AU (Table 7). By assuming that 40 km sec^{-1} would be the velocity of all the cometary nuclei impacting the Earth in its first 2×10^9 years, these nuclei would liberate ~ 2 cal cm^{-2} yr^{-1}.

TABLE 7 Short-period Comets

Comet	Absolute magnitude* m_o	Mass (in grams)	Veolcity at 1 AU (km s^{-1})
Encke	12	1.58×10^{16}	37.05
Temple 2	13	6.31×10^{15}	38.45
Finlay	14	2.51×10^{15}	39.08
Whipple	11	3.98×10^{16}	39.25
Comas Solá	10	$1.0 \times 10^{[illegible]}$	39.52
Olbers	5	1.0×10^{19}	41.48
Halley	4	2.51×10^{19}	41.52
Schaumasse	12	1.58×10^{16}	39.43
Vhisala	14	2.51×10^{15}	39.86
Tunguska object †	26	5.0×10^{10}	50.0

*Allen, C. S., 1973 Astrophysical Quantities (the Athlone Press, London) 3rd. ed., p. 153. [54]

†Brown, J. C. and D. W. Hughes [59].

Other sources of interplanetary debris-like nonvolatile dust of cometary origin may also be accreted by the Earth. Particularly significant, however, must be the capture by the primitive Earth of "Apollo objects", which have been suggested to be the nonvolatile remnants of the nuclei of extinct comets, and appear to be related to chondritic meteorites, as indicated by photometric measurements [49, 60]. The atmospheric studies of Mars, Venus and the Earth suggest that substantial amounts of carbonaceous chondritic material was acquired by our planet in the late-accretion period [61], an assumption supported by the carbonaceous chondritic nature of Phobos [62], which is either a remnant of the primeval accretion that led to the formation of Mars, or was captured later by this planet.

THE APPEARANCE OF LIFE

Our knowledge of the formation of interstellar molecules and of the evolutionary development of interstellar gas and dust clouds is so inadequate that it would be premature to make any major generalizations about the significance of these findings for prebiological organic chemistry and the possibilities of extraterrestrial biology [7]. We have already pointed out that many of the organic molecules detected in space are those found in laboratory experiments that attempt to reconstruct the environmental conditions of the prebiotic Earth, and that in the group of identified interstellar molecules are ten of the prebiological precursors of biochemical compounds present in living systems (Table 2, above).

It has been suggested that interstellar grains are rich in polysaccharides (Hoyle and Wickramasinghe [30, 31] and other organic polymers that could contain amino acids [62, 63]. According to Hoyle and Wickramasinghe [63] and Wickramasinghe et al. [64], primitive life forms resulting from the formation and destruction of clumps of grains rich in organic polymers, could evolve in the interstellar environment. However, the presence of organic molecules is not in itself indicative of the presence of an interstellar biota. Sagan [65] has argued that due to the low densities, the rate of growth and reproduction for an organism would be very slow, making its appearance quite unlikely. In fact, the interstellar environment with its high values of ultraviolet and corpuscular radiation and lack of liquid water seems to preclude the existence of life [66].

Thus, although the initial stages of evolution of carbon compounds which gave rise to life on Earth are widely represented in the universe; the nature of the processes of chemical evolution in the interstellar clouds differs essentially from all of what is required for the origin and development of life on Earth.

The development of matter on Earth that led to the appearance of life can be briefly summarized as follows: As a result of various kinds of energy and catalytic effects (electric discharges, ultraviolet light, heat, Fischer-Tropsch-type catalyses), the simple molecules from the atmosphere, hydrosphere and lithosphere of the primitive Earth reacted to form a wide variety of low molecular weight compounds, among which also were formed the monomers of biochemical significance--amino acids, fatty acids, sugars and the purine and pyrimidine bases. With the accumulation of these biochemical monomers in the shallow lakes and ponds of the primitive Earth further condensation and polymerization reactions occurred yielding higher molecular weight compounds and polymeric products. These included oligomers, polymers and catalytic molecules. This is the stage of biopoesis that is usually identified as chemical evolution.

However, in the transition of chemical evolution to biological evolution, an intermediate stage can be distinguished, i.e., a different developmental stage termed prebiological evolution, during which the oligomers having some of the essential attributes of biological molecules (oligodeoxynucleotides, catalytic oligopeptides and aminoacyloligoribonucleotides) selectively associated and interacted within microvesicles created by the self-assembly of phospholipids or other amphiphilic molecules into a protomembrane that provided a microenvironment and protocellular organization from which, by a process of molecular association or "protoselection" [10, 11, 67, 68] the first living cells eventually emerged.

Recently Hoyle and Wickramasinghe [30, 31] and Hoyle [32] have brought forward the suggestion that life did not arise on Earth but originated in cometary nuclei, reaching our planet at a later time on comets that collided with the Earth or on cometary debris that deposited anaerobic, fermentative prokaryotic cells on our planet. Assuming that polymerization processes that take place in the interstellar medium will eventually result in cometary nuclei rich in polysaccharides, polypeptides and other organic polymers, they propose that during approach to perihelion liquid water located in the interior of the comet's nucleus provides a Darwinian "little warm pond" in which life would originate.

Just how far has chemical evolution proceeded in a cometary nucleus is still an open question, for which a detailed answer will perhaps be provided by fly-by missions, detailed gas chromatographic and mass spectrometric analysis and the eventual recovery of a sample of cometary nuclei material [69]. However, an idea of the chemical species present in a comet may be obtained from simulations in added to the primitive Earth substantial amounts of water and other hydrogen-bearing compounds (CH_4, NH_3, HCN) that contributed to generate the appropriate aqueous and reducing environmental conditions necessary for the organic synthetic processes that preceded the appearance of life.

Since cometary nuclei are fragile bodies of low density and high mass, they probably never reached the surface of the Earth, but would explode on reaching the outer limit of the paleotroposphere. In this explosion many of the cometary compounds were probably destroyed, decomposed by the heat and shock waves of the cometary collision. Thus, in addition to its major components (CO_2, CO, N_2, H_2O, H_2) the primitive atmosphere of our planet contained smaller amounts of noble gases and other voltile compounds, such as NH_3, HCN, CH_4, and H_2S, derived from the accreted cometary material. However, upon quenching to low temperatures, many of the highly reactive chemical species produced by the impact would have recombined, leading to a great variety of organic compounds. The enormous amount of energy liberated during cometary collisions probably played an important role, up to now largely ignored, on the chemical kinetics of the early atmosphere. Further models of the evolution of the primitive Earth's atmosphere should consider the continuous influx of extraterrestrial material and associated collisions as an important free-energy source.

Although ten of the interstellar molecules identified up to now--hydrogen, water, ammonia, carbon monoxide, formaldehyde, acetaldehyde, thioformaldehyde, hydrogen cyanide, cyanoacetylene and cyanamide can be considered as the prebiological precursors of most of the biochemical compounds present in living systems, their mere presence certainly does not indicate the existence of an interstellar biota. Life is the result not only of chemical evolution but was preceded as well by prebiological evolution--the stage during which, in the liquid phase environment of the primitive Earth, oligomers--proto-DNA, protoenzymes and proto-RNA--interacted and associated themselves into polymolecular, open phase-separated microsystems from which the first cells evolved.

The lack of liquid water at moderate temperatures (0 to 100°C) in the interstellar clouds precludes the presence of life in such an environment, a conclusion that also applies to cometary nuclei.

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which condensed gases are irradiated [70, 71]. Experiments by Oro [42] in which an icy mixture of water, ammonia, and methane was irradiated by 5 MeV electrons yielded 20% of nonvolatile organic matter, including simple amino acids. Polymerization probably takes place in the surface of a cometary nucleus, but the observed abundances of oxygen (Table 4) exclude the possibility of large amounts of oxygen trapped in polymeric material. Moreover, Bar-Nun et al., (in preparation) have argued on the basis of irradiation experiments carried out by Kajmakov [72], that liquid water and the other conditions necessary for the appearance of life do not appear to exist in the cometary nuclei environment. The temperatures and surrounding pressures are so low that sublimation is the only conceivable process for the volatilization of cometary ices [73]. Furthermore, it is unlikely that any hypothetical cometary-life forms could reach the Earth undamaged. Particles of assumed cometary origin apparently survive passage through the Earth's atmosphere without suffering any damage, but as they were probably melted at the time of their formation [74] such cometary debris would be sterilized. The supposed organisms on board a cometary nucleus would have even less chance of survival. The nuclei on colliding with the atmosphere would explode.

It is equally improbable that an unknown substance essential to the origins of life on Earth was formed only in an interstellar cloud or was present in a cometary nucleus, and that when such a compound reached the Earth it triggered the appearance of life.

We would like to emphasize that although it has been suggested that the infall of extraterrestrial organic compounds to the primitive Earth is in fact a reassessment of the theory of panspermia [75], the ultimate cometary origin of biochemical compounds should be considered as playing a complementary role in the processes of chemical evolution that according to the Oparin-Haldane theory preceeded the appearance of life on the Earth.

Although our knowledge of cometary phenomena has certainly improved it seems still appropriate to quote the words of Seneca [76], the Spanish philosopher who wrote about the appearance in the sky of "fiery" comets:

> "When this rare and strangely shaped fire appears everyone wants to know what it is and, forgetting everything else, seeks information about the strange visitor, uncertain whether it is to be marveled at or feared".

CONCLUSION

Recent radioastronomical observations have detected the presence in the interstellar clouds of our galaxy and in extragalactic regions an ample variety of molecules, mostly organic, giving direct support to the universality of organic cosmochemistry. Many of these molecules, that are known to be precursors or intermediates in experiments simulating the prebiological organic synthesis, are probably present in cometary nuclei. Since comets are considered to be similar in composition to the primordial material of the solar nebula, we have evidence of the presence of organic matter in the environment from which the solar system originated.

There is considerable evidence that the Earth lost a substantial fraction of its gases and volatile compounds during its early accretionary phase. Part of the volatiles appear to have been added later by the infall of cometary, asteroidal, and related chondritic material. Indeed, we have estimated that during its first 2×10^9 years the Earth captured approximately 10^{23} grams of cometary matter, thus acquiring about 10^{22} grams of carbon. In addition to carbon, cometary collisions

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COMETARY MATERIAL AND THE ORIGINS OF LIFE ON EARTH*

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Dedicated to the memory of H. C. Urey.

ABSTRACT

Comets are the most pristine minor bodies in the Solar System. With the exception of phosphorus, all the organogenic elements (H, C, N, O, S, P) which are necessary for life have been found in comets. By comparing their carbon abundances with those of carbonaceous chondrites it has been estimated that 10% or more of the cometary matter is made of organic compounds. The nature of the chemical species detected in comets suggests that the complexity of their parent molecules is at least comparable to that of interstellar molecules.

The possible sources and origins of cometary organic molecules are: (1) the primordial solar nebula, which must have been the primary source of all the organic and inorganic compounds in comets; (2) the organic molecules formed by the ionized radiation resulting from the decay of ^{26}Al and other short-lived presolar isotopes during the early stages of differentiation of the solar nebula; (3) organic compounds produced by the cosmic-ray heating of the matter in the Öpik-Oort cloud during its lifetime, and (4) the more complex organic compounds synthesized in the icy surface layers of the cometary nuclei by the action of the solar wind, UV radiation and induced exothermic reactions as comets approach perihelion.

The reactivity of some of the chemical species detected in comets (H, OH, NH_2, CO, CS, C_2, C_3, HCN, CH_3CN, H_2O) indicate that a number of biochemical compounds, such as amino acids, purines, pyrimidines, etc., may be present in cometary nuclei. However, due to the small mass (~10^{18}g), low temperatures (<200°K) and other environmental conditions, such as the absence of a proper atmosphere, hydrosphere and lithosphere as on the Earth, it is not likely that the processes of organic synthesis in comets have proceeded beyond the stage of chemical evolution of the organic matter in carbonaceous chondrites.

Although it is highly improbable that life could have appeared in comets, the antiquity of terrestrial life, as is indicated by the presence of a complex fossil microbiota of 3.5 x 10^9 years old suggests that life emerged on Earth during the time in which the influx of cometary material was considerably higher than the present values. Different estimates have shown that the Earth acquired about 10^{22} grams of carbon by accretion of cometary nuclei during its early history. It is likely that most of the cometary carbon compounds were decomposed into highly reactive chemical species by the heat and

shock waves of cometary collisions, thus creating transient, relatively reducing atmospheric environments in which abiotic organic synthesis occurred by quenching and recombination of the reactive species. Furthermore, upon settling to the Earth's surface, some of these compounds must have given rise through different condensation reactions to the formation of the more complex biochemical monomers and polymers essential to living systems. Therefore, we can conclude that comets contributed significantly to the processes of chemical evolution necessary for the emergence of life on the Earth.

INTRODUCTION

The problem of the prebiological significance of cometary material is only part of the more general question of the evolution of organic compounds in space, and ultimately, of the appearance of life in the Universe.

Even through the existence of extraterrestrial organic molecules has been known since the early analytical efforts of Berzelius, Berthelot, Wöhler and other chemists of the XIX century, who demonstrated the presence of hydrocarbons in carbonaceous chondrites (cf. Nagy 1975), modern developments in radioastronomical and other techniques of space exploration have been able to show the presence of an ample array of relatively complex organic molecules in dense interstellar molecular clouds, in cometary spectra, in carbonaceous chondrites, (and presumably in the parent bodies of these meteorites), and in the atmospheres of the Jovian planets and some of their satellites (cf. Oró, 1972). All these discoveries reinforce the hypothesis of organic cosmochemistry (Oró, 1963), and confirm Bernal's (1965) suggestion that the primordial organic synthesis which according to Oparin (1924 et seq.) and Haldane (1928) preceded the emergence of life, may have taken place even before the formation of Earth itself.

But did these extraterrestrial organic molecules play any essential role in the appearence of terrestrial life? Although it is extremely unlikely that life could have evolved in the galactic molecular clouds or in cometary nuclei, as has been recently suggested, the recent discovery of complex ~3.5 x 10^9 year old microfossils in Western Australia (Awramik et al. 1980) shows that life must have appeared on the Earth at a time in which the influx of cometary and related meteoritic material was significantly larger than the contemporary value. It is therefore logical to conclude that comets may have had a role in shaping the environmental conditions of the prebiotic Earth.

The purpose of this paper is to review critically this possibility. First the organic synthetic pathways that occur in dense interstellar clouds of our galaxy and in comets are examined, together with the possibility that more complex organic molecules than those detected up to now may exist in these environments. We then review the different estimates of the amount of terrestrial volatiles that may be of cometary origin, and compare them to other extraterrestrial sources of organogenic elements. We also discuss the prebiological events that might have followed the collision of cometary nuclei accreted by the primitive Earth. Finally, some of the current ideas on prebiological organic synthesis of biochemical monomers and their polymers on the primitive Earth are discussed, together with the emergence of precellular systems and their further evolution, which lead to the appearance of terrestrial life.

INTERSTELLAR ORGANIC COMPOUNDS

Although the presence of simple diatomic combinations (C_2, CN, CH, CO) in the atmosphere of cool stars (cf. Wallerstein, 1973) and in interstellar space (Adams, 1943) has been known for a long time, it was not until the past fifteen years when the development of radioastronomical techniques led to the discovery, in the gas and dust clouds of the Milky Way and other galaxies, of a larger number of predominantly organic molecules (Table 1), thus confirming previous suggestions about the universality of organic chemistry (Oró, 1961, 1963a; Wald, 1964). A discussion on the distribution, and the mechanisms responsible for the formation and destruction of interstellar molecules may be found elsewhere (Turner, 1980).

Quite remarkably, among the identified interstellar compounds are precisely the ones which have been used or produced in laboratory simulations of prebiotic organic synthesis. In fact, nine of the interstellar molecules (molecular hydrogen, water, ammonia, carbon monoxide, thioformaldehyde, aldehydes, hydrogen cyanide, cyanoacetylene, and cyanamide, plus phosphine, which has only been detected in the atmosphere of Jupiter but is probably present in interstellar space), can be considered as the prebiological precursors of essentially all the biochemical compounds present in living systems (Table 2) (Oró et al., 1978a; Oró and Lazcano-Araujo, 1981).

However, as of November, 1980, no interstellar biochemical monomer had been reported. The search for interstellar heterocyclic carbon ring molecules of furan and imidazole (Dezafra et al., 1971), and for pyrimidines and pyridines (Simon and Simon, 1973), has yielded negative results, and Dohn and Khana (1980) have found no experimental support to Johnson's (1972, 1977) claims that the diffuse absorption bands in the visible region of the interstellar sprectrum are Soret band-types produced by a complex metalloporphyrin, bis-pyridyl-magnesium-tetrabenz-porphyrin ($MgC_{46}H_{30}N_8$). Glycine, the simplest amino acid and a major product of abiotic synthesis and the most abundant meteoritic amino acid (Ring et al. 1972; Miller et al., 1976), has been looked for unsuccesfully in nine galactic molecular clouds, including Sgr B2 and Ori A (Brown et al., 1979), although recently Hollis et al., (1980) have detected in SgrB2 one single emission line with a frequency of 84.22 GHz which is coincident with the transition of the lowest energy conformer of glycine.

It should be noted, however, that more than 130 unidentified emission lines have been observed in the 3-6 mm-wavelength region of two molecular clouds in Orion and Sagitarius (Turner, 1978). It is possible that some of these lines could correspond to organic molecules of greater structural complexity than those in Table 1. This possibility is supported not only by theoretical considerations on the existence of interstellar polymers (Wickramasinghe 1974, 1975; Salpeter, 1975; Goldanskii, 1977) but also by a number of laboratory simulations in which icy mixtures of simple molecules (H_2O, CH_4, NH_3, CO_2, etc.) have been irradiated by UV photons (Ausloos et al., 1965; Greenberg et al., 1972; see also Greenberg, this volume) and by ionizing radiation (Table 3). These experiments have yielded non-volatile organic material, including amino acids, purines and pyrimidines, and low molecular weight hydrocarbons, therefore suggesting that these types of compounds may exist as components of interstellar grains.

Recently it has been proposed by Hoyle and Wickramasinghe (1979 a,b, 1980) that the interstellar absorption features in the ultraviolet region (λ < 1900 Å and in the waveband 1900-2800 Å), and the 3μ extinction feature in galactic infrared sources are due to the presence of a large mass of $\sim 10^{40}$ grams of frozen bacteria, algae and viral particles. It is extremely difficult, however, to visualize any possible mechanisms by which such hypothetical organisms could originate, survive and evolve under the harsh environmental conditions of the interstellar medium. In fact, since Hoyle and Wickramasinghe argue that these interstellar cells would have a carbon chemistry, they would therefore be under the same environmental constraints of terrestrial life, which can not survive under the low densities ($10^3 \leq \rho \leq 10^6$ H_2 molecules/cm^3), low temperatures ($10^0 \leq T \leq 100^0$K), high radiation level ($F \simeq 1.0 \times 10^{10}$ particles/cm^3, with a typical energy $E \geq 100$ MeV nucleon) and lack of liquid water which prevail even in the densest molecular clouds, and which appear to preclude the existence of an interstellar biota (Ponnamperuma, 1971; Sagan 1973; Lazcano-Araujo, 1978; Oró et al., 1980).

The presence of organic molecules in the solar nebula is not only indicated by the excellent correlation between the cometary spectra and the molecular composition of dense interstellar clouds, but also indirectly by the large array of amino acids, carboxylic acids, purines, pyrimidines and hydrocarbons which have been found in carbonaceous chondrites (Oró 1972; Nagy, 1976). These compounds, which are condensation and hydrolysis products of several of the compounds detected in interstellar space (Table 2), are evidence that their precursors were part of the material from which the parent bodies of the meteorites and the planets were formed. However, it is likely that the harsh conditions that prevailed during the formation and accumulation of the terrestrial planets led to the destruction or change of most of the compounds present in the solar nebula, therefore precluding an direct relation between interstellar organic compounds and life on Earth.

CHEMICAL EVOLUTION OF COMETARY NUCLEI

Comets are relatively minor bodies with a diameter of a few tens of kilometers at the most, and a small mass ranging aproximately from 10^{15} to 10^{18} grams. They are known to consist mainly of ices (CO_2, NH_3, H_2O, etc.) and clathrates of simple compounds. By comparing comets with CI carbonaceous chondrites, which appear to be the most primitive meteorites, Delsemme (1977) has shown that comets are several times less depleted in H,C,N and O than these meteorites. Therefore, if we exclude hydrogen which is less abundant by a factor of 5×10^{-4} with respect to solar abundances, comets appear to be relatively similar to the primordial solar nebula and can thus be considered the most pristine bodies in the Solar System (Delsemme, 1977).

The observations of cometary spectra have firmly stablished the presence of a number of organic molecules and radicals (C_2, C, CH, CN, CO, CS, HCN, CH_3CN) and other simple chemical species (NH, NH_2, OH, H_2O), all of which have also been identified in the interstellar medium (Table 1); although microwave and infrared techniques have failed to identify more complex organic molecules such as CH_2CO, CH_3OH, $CN{-}CH_2{-}CN$, $CH{\equiv}C{-}CN$, which would be expected to exist in cometary nuclei (Simon et al., 1974; Delsemme, 1979).

In addition to the volatile components, refractory elements (Na, K, Cr, Mn, Fe) and silicate particles are also known to be important components of the nucleus. Delsemme (1977) has shown that from the gas-to-dust ratio of Comet Bennet 1970 II and Comet Arend-Roland 1957 III that comparable amounts of dust and gas are present in the material ejected by a comet, therefore suggesting that a large fraction of the nucleus' mass may consist of non-volatile dust and rocky material. The presence of this refractory component suggests that some volatile-rich meteorites may, in fact, be related to comets, a possibility strenthened by the probable CI and CM chondritic nature of Brownlee particles which may be of cometary origin (Brownlee 1978, 1980). However, it should be emphasized that the comparison and determinations of preterrestrial orbits for the Pribram, Lost City and Innisfree chondritic meteorites (Nagy 1975) support an asteroidal origin for these objects.

There are several possible sources of cometary organic compounds, which according to Kajmakov and Matvejev (1979) may represent up to 65% of the nucleus' mass. These sources include complex organic molecules inherited from the solar nebula (Greenberg 1977, 1978, 1980), the early production of biologically significant macromolecules synthesized by the decay of ^{26}Al and other presolar isotopes (Irvine et al., 1980 a,b), and cosmic ray heating in the Öpik-Oort cloud (Donn, 1976) which has been shown to produce hydrocarbons and other organic compounds (Moore et al., 1980). Furthermore, solid-phase experiments (Figure 1) in which icy mixtures of relatively simple compounds (CH_4, C_2H_6, N_2, NH_3, H_2O, H_2CO) have been irradiated by high-energy electrons, protons and ions are known to produce significant amounts of non-volatile organic compounds, including biochemical monomers such as amino acids, purines, pyrimidines and carboxylic acids (Table 3). These experiments support, therefore, the possibility that similar reactions may take place in the icy surface layers of the cometary nuclei by the action of the solar wind, UV radiation and induced exothermic reactions as comets approach perihelion.

Table 3

However, since a large layer of cometary ices is ablated from the nucleus' surface each time the comet passes through perihelion, it is likely that most of the organic products on the surface would be sublimed, blown off or polymerized (Bar-Nun et al., 1981). It is, therefore, unlikely that these organic compounds or their derivatives could undergo further chemical evolution in the periodically liquid cometary environments which Hoyle and Wickramasinghe (1977) propose as the place for the origin of life, including viruses. In fact, as Kajmakov and Sharkov (1972) have shown, at 1 AU from the Sun the equilibrium temperature of H_2O ice is about -75°C and no liquid water could exist. This conclusion is further confirmed by a number of experiments in which D_2O (Glasel, 1962), H_2O (Kajmakov, 1974) and frozen solutions with metallic inclusions, Al_2O_3, SiO_2, salts, carbamide or phenylalanine (Dobrovolsky and Kajmakov, 1977) have been irradiated, yielding equilibrium temperatures below 213°C and no liquid water. Under such conditions it is difficult to visualize the abiotic synthesis of key life macromolecules and the emergence of life.

However, as Irvine et al. (1980 a,b) and Wallis (1980) have argued, for typical comets with radii of the order of 10 km, the decay of ^{26}Al and other short-lived presolar isotopes could have led to the existence of liquid environments within the cometary nuclei for at least the first 10^7 years of the Solar System. Such transient environments, which would only be possible if accrettion times were of the order of 10^6 years, could have led to radiation-induced chemical organic synthesis (Irvine et al., 1980 a,b) although the effects of radiation of self-replicating systems arising under such conditions would also have caused the demise of any life forms which may have appeared (Bar-Nun et al., 1981). It may thus be concluded that the absence of a proper atmosphere, hydrosphere and lithosphere and the low temperatures (< 200°K) have precluded the emergence of life on comets, where it is not likely that the processes of abiotic organic synthesis have proceeded beyond the stage of chemical evolution of the organic matter in carbonaceous chondrites.

COMETARY COLLISIONS AND THE PREBIOTIC ENVIRONMENT

AT NO OTHER TIME DID MORE THUNDERBOLTS FALL IN A CLEAR SKY, NOR SO OFTEN DID DREAD COMETS BLAZE...

Virgil, *Georgics*.

The large number of impact craters which have been identified in the Moon, Mercury and Mars (Shoemaker, 1977) shows that collisional processes with interplanetary bodies played a major role in shaping the surfaces of the planets of the inner Solar System. This hypothesis is supported by the recent observations on the carbonaceous nature of Phobos (Pollack et al., 1978) and Deimos (Pang et al., 1980), the two Martian satellites, which are either the remnants of primeval processes or were captured later. In the case of the Earth, however, of all the 78 (probably) impact craters which have been identified (Grieve and Robertson, 1979), only three of them appear to date from Precambrian times (Table 4). Although the geological activity of our planet has obliterated most of the traces of its early history, initial megacratering processes (Goodwin 1976; Frey, 1978) are indicated from models of the formation of the terrestrial planets (Safronov, 1972; Wetherill, 1980), present influx of extraterrestrial material (Wetherill, 1974) and data from the late-heavy bombardment of the Moon which ended approximately 4.0 x 10^9 years ago (Tera et al., 1974; Wetherill, 1975), show that when the Earth had grown close to its final mass it was still suffering the effects of an intense bombardment by residual planetesimal swarm material.

Although the present terrestrial influx of cometary material is small (Urey, 1957, 1973; Whipple, 1976), the contribution of comet-like bodies from the outer Solar System to the early collisional history of the Earth must have been many orders of magnitude larger than the contemporary figure. In fact, Wetherill (1975) has demonstrated that although ~99% of interplanetary debris was ejected from the Solar System by Jupiter, perturbations from the giant planets sent a number of cold, volatile-rich, small bodies from the Uranus-Neptune region into the inner Solar System, where their residence times prior to removal by planetary impact or solar system escape would be ~10^8 years (Wetherill, 1977).

It has been estimated by Wetherill (1975) that the cometary material influx during the Moon's first 700 million years was ~2.0 x 10^{20} grams (Table 5). Due to the Earth's greater mass, it is therefore logical to conclude that during this period of time a greater mass of cometary nuclei collided with our planet. However, it should be noted that the large number of assumptions involved in such calculations make it difficult to give a precise estimate of the amount of cometary matter accreted by the Earth. In spite of these uncertainties, Joss (1974) has shown that during its 4.5 x 10^9 years in the main sequence, the Sun has captured ~10^{26} grams of cometary nuclei. Joss' estimate, which sets an upper limit for the number of comets captured by the Earth itself, is in fact comparable to an independent result from Whipple (1976), who has calculated that during the late-accretion period our planet could have captured less than 10^{25-26} grams of cometary material (Table 5) from a short-lived ($\sim 10^8$ years) cometary nebula of mass 10^{29} grams located within Jupiter's orbit.

Independent calculations based on dynamical considerations and lunar cratering rates (Oró et al., 1978, 1980; Pollack and Yung, 1980) and on solar system chemical abundances (Chang, 1979) suggest that the Earth could have accreted 10^{22-23} grams of cometary matter over different time-spans. These are shown in Table 5. It follows from the 10^{23} gram value derived independently by Oró et al., (1978, 1980), and Chang (1979), and from Delsemee's (1977) estimated elemental abundances, that since carbon is ten times more abundant in comets that in CI chondrites (where ~3.5% of the mass is carbon), that approximately 10^{22}g of carbon were added to the surface of the primitive Earth by cometary collisions. This later figure is in fact of the same order of magnitude than the 1.9 x 10^{22} (Hunt, 1972, 1977) and 1.2 x 10^{22} gram (Schidlowski, 1978) estimates of carbon buried in the Earth's sedimentary shell, and about four orders of magnitude larger than the $\sim 10^{18}$g of carbon calculated to be incorporated into living systems (Garrels and MacKenzie, 1972; Abelson, 1978). In doing this comparison, of course, we do not intend to imply that terrestrial life is of an ultimate cometary origin, but rather to show that comets may have contributed significantly to increase the terrestrial budget of H,C,N,O,S and other organogenic elements which acted as raw material (either in elementary form or as simple organic compounds) for further chemical abiotic organic synthesis. Thus, it appears that the capture of comets by the primitive Earth was significant in generating the appropriate aqueous and reducing environmental conditions necessary for the appearence and early evolution of life (Oró et al., 1980).

Although the terrestrial depletion of noble gases relative to solar abundances (Moulton, 1905; Rusell and Menzel, 1933; Brown, 1952; Rasool, 1972) shows that the Earth acquired a secondary atmosphere from the release of internal volatiles (cf. Walker, 1977), the possibility of a primary atmosphere formed by impact with volatile-rich bodies has been discussed recently by a number of authors (Arrhenius et al., 1974; Benlow and Meadows, 1977; Henderson-Sellers et al., 1980). In fact due to similar mass and orbital parameters, the probability of minor-body collisions with the Earth would be approximately the same as the probability of collision with Venus. This conclusion, which has been demonstrated quantitatively by Everhart (1969) for 10^9 hypothetical random parabolic comets (Figure 2), implies that if cometary collisions with the Earth were the major source of volatiles, then the noble gas abundances and ratios of N to C should be approximately the same for both planets (Pollack and Black, 1979). This, however, is not the case: determinations of the non-radiogenic ^{36}Ar, ^{38}Ar and ^{20}Ne abundances in the Venusian atmosphere made by the Pioneer Venus probe show the existence of a large excess (~100 times) of primordial noble gases in Venus relative to Earth (Hoffman et al., 1979 a,b; Oyama et al., 1979 a,b). These measurements have led Pollack and Black (1979; see also Pollack and Yung 1980) to suggest that the solar nebula grains which accreted to form planetesimals and planets may have contained non-volatile organic compounds, which, due to later planetary evolution liberated volatiles that formed the atmospheres of Venus, Earth and Mars. However, the inhomogeneous accretion model for the origin of the Earth (Turekian and Clark, 1969; 1975; Grossman, 1972; Cameron and Pine, 1973; Grossman and Larimer, 1974), which is supported by a number of geological arguments, implies in turn that the terrestrial planets may have acquired a significant amount of volatiles from accreted chondritic material (Walker, 1977; Anders and Owen, 1977; Owen, 1978).

Although it is possible that if intense degassing took place during its accretional phase, then the Earth could have had a highly reducing atmosphere (Pollack and Yung, 1980), the presence of 3.8 x 10^9 years old metasedimentary rocks from Isua, West Greenland (Moorbath et al., 1973) formed at relatively moderate temperatures of less than 150°C, and probably below 80°C (Ahmad and Perry, 1980), show that even if methane was the dominant form of carbon in the primitive atmosphere, 800 million years after the Earth had formed it had already been replaced by carbon dioxide (Figure 3).

Thus, either the highly reducing atmosphere (H_2O, NH_3, CH_4, H_2S) postulated by Oparin (1936) and Urey (1952) had a relatively short lifetime, or as implied by the non-homogeneous accretion model, it never existed at all (Walker, 1976). Indeed, Walker (1976, 1977, 1978) has argued rather convincingly that the prebiotic atmosphere was dominated by CO_2 and H_2O, with N_2 as a minor constituent and only trace amounts of H_2 (≈1%) and CO.

However, when such weakly reducing atmospheres are reproduced in laboratory simulations, only negligible amounts of a few organic compounds are produced. In fact, as Chameides and Walker (1980) have shown, in a prebiotic atmosphere dominated by CO_2, shock processes from lightning and impacting bodies would yield small amounts of HCN, which is known to be a key intermediate in the synthesis of amino acids, purines, pyrimidines and condensing molecules (cf. Oró and Lazcano-Araujo, 1981). Thus, we may conclude that even though high partial pressures of free H_2 are known experimentally to inhibit the synthesis of partially dehydrogenated compounds like purines and pyrimidines (Ponnamperuma et al., 1963; see also Bar-Nun et al., 1981), the non-enzymatic synthesis of biochemical monomers and their polymers (Table 7) must have required a prebiotic environment that was neither too reducing (CH_4, NH_3, H_2S, H_2) nor with an early oxidized atmosphere where oxygen was more abundant than carbon.

Since shock waves appear to be an extremely efficient free-energy source for the abiotic synthesis of amino acids from a highly reduced precursor (Bar-Nun et al., 1970, 1971), it is conceivable that under the somewhat reducing prebiotic atmospheric conditions discussed above, comets captured by the primitive Earth may have played a significant role in chemical evolution because of the huge amounts of heat and shock waves liberated during cometary collisions. Indeed, the 1908 Tunguska explosion, which was probably due to a fragment of Comet Encke (Kresák 1977) or a small, ~10^{10} gram comet (Brown and Hughes, 1978), liberated 10^{23} ergs when the colliding body traveling at aproximately 50 km sec^{-1} (Levin 1954; Krinov 1966; Oró et al. 1980) exploded at ~8.5 km above the ground (Ben-Menahen, 1975). Under the anoxic conditions of the prebiotic environment such collisions would destroy most of the cometary organic compounds (Miller and Urey, 1964), but would liberate considerable amounts of excited molecules and radicals (OH, H, CH, CN, NH_2) directly into the atmosphere (Oró et al., 1978, 1980; Chang 1979) where they could undergo further chemical changes leading to more complex organic molecules. Since in the primitive Earth a very large fraction of carbon and other organogenic elements would be locked up in carbonates and other volatile-rich sedimentary rocks, this cometary input of excited precursors must have played an important role in the prebiotic formation of organic molecules and their intermediates.

Although Levine et al. (1980) have shown that the influx of cometary volatiles, especially H_2O, would have led to a rapid chemical destruction of atmospheric CH_4, NH_3 and H_2S and other reduced molecules, it is also clear that the collisions of comets with the primitive Earth would produce highly reducing transient atmospheric environments rich in reactive chemical species. Upon quenching to low temperatures, due to the subsequent expansion and cooling of the gas ball (Raizer, 1960), the chemical species produced by the impact would recombine leading to the synthesis of a great variety of organic compounds (Oró et al., 1980) They could also undergo catalytic reactions on the surfaces of metallic and silicate particles which are known to exist as components of the cometary nucleus. This hypothesis is in fact supported by the Fischer-Tropsch-type reactions, which involve a mixture of simple precursors (NH_3, CO, H_2, etc) out of equilibrium reacting with or without a catalyst (Oró et al., 1977). The abiotic synthesis under such conditions of amino acids (Yoshino et al., 1971), purines and pyrimidines (Yang and Oró, 1971) and of C_{10} to C_{16} normal fatty acids (Nooner et al. 1976) supports the possibility that accreted cometary nuclei provided raw material and a free energy source that increased synthetic reaction rates in the primordial terrestrial environment.

EXTRATERRESTRIAL SOURCES OF CARBON

In addition to the internal sources of the atmosphere (Walker, 1977; Pollack and Yung, 1980), and the extraterrestrial influx of chondritic (Anders and Owen, 1977) and cometary material (Oró et al., 1980), the Earth has acquired over its history volatiles from two additional sources, namely solar wind particles and interstellar matter.[10] The amount of carbon thus accreted from these different sources in shown in Table 6, where the contribution of chondritic material clearly represents a lower limit, derived from the present annual influx of meteoroids of 10^{10} grams given by Wetherill (1974), and assuming that 50% of the infalling material has a carbonaceous chondritic composition.

The solar wind is a fully ionized gas that originates in the Sun's outer layers and has a chemical composition comparable to solar abundances. Since the abundance of ^3He in the solar wind relative to protons is $\sim 10^5$ (Bame et al., 1968), Walker (1977) has estimated that a ^3He terrestrial influx of 7 cm^5 sec^{-1} corresponds to a proton influx of 7×10^5 cm^2 sec^{-1}. Since carbon is 4×10^{-4} less abundant than hydrogen in the Sun, it follows that over its first 2 billion years the Earth accreted $\sim 10^{14}$ grams of carbon (Table 6). However, since it is likely that the Sun passed soon after its formation through a T-Tauri stage with an intense solar wind (Cameron and Pine, 1973), much more solar wind material could have been accreted by the Earth soon after it had formed (Pollack and Yung, 1980). It is possible that in the absence of the geomagnetic field, such excited carbon atoms may have provided an energy source for chemical synthesis in the upper paleoatmosphere (Sagan, 1965).

Because of the orbital motion of the Sun around the galactic center, it seems possible that encounters between the Solar System and dense interstellar clouds may occur. Although it is possible that such encounters may lead to changes in the terrestrial climate (McCrea, 1975; Talbot et al., 1976; Newman, 1980), it has also been suggested (Butler et al., 1978) that the accretion of interstellar cloud material by the terrestrial planets may be responsible for the accumulation of some isotopes, particularly Ne. Such encounter between interstellar clouds and the Sun are not rare; in fact, Talbot and Newman (1977) have estimated that the Solar System could have encountered over its 4.6×10^9 years of existence ~130 to 140 clouds with more than 10^2 hydrogen atoms per cm^3 and ~15 clouds with more than 10^3 hydrogen atoms per cm^3. From such cloud encounters, Butler et al. (1978) have shown that 1.5×10^{15} grams of carbon would have been accreted by the Earth (Table 6). Therefore, it can be concluded that the input of interstellar volatiles did not play a role as important as comets in shaping the environment in which the origin and early evolution of life took place.

THE ORIGIN AND ANTIQUITY OF TERRESTRIAL LIFE

The recent discovery of a $\sim 3.5 \times 10^9$ year old complex multicomponent microfossil assemblage in the laminated cherts of the Warrawoona Group in Western Australia (Awramik et al., 1980), and the reports of stromatolites from the same geological sequence (Lowe, 1980; Walter et al., 1980), imply that the origin and early evolution of life must have ocurred very early in the history of the Earth. Indeed, the earlier estimate that life arose ~4.0 x 10^9 years ago (Oró, 1968) has been supported by the molecular genealogical analysis of the size of the poly(A) segment of mRNA of extant organisms, which appears to indicate that mRNA, and possible life, emerged 3.85±0.2 billion years ago (Carlin, 1980).

As the origin of life is pushed further back into the beginnings of the Archean, and perhaps into the turbulent times of the Hadean, it becomes obvious that the emergence of the first living systems occurred when the phase of intense meteoritic and cometary collisions with the Earth's surface was ending (Fig. 3). It is therefore natural to ask whether a causal relationship may have existed between these two events, i.e., whether collisions with comet-like bodies and related meteoritic material played any role in shaping the environmental conditions of the primitive Earth, thus effecting the origin (Oró et al., 1980) and early evolution of life (Awramik, 1980).

It has been suggested that the shock wave energy from such collisions was an energy source for the primitive Earth's organic synthesis (Hochstim 1963, 1971). In fact, very high yields have been obtained for the synthesis of amino acids in shock tubes containing a highly reducing model atmosphere (CH_4, N_3, H_2O) (Bar-Nun et al., 1970, 1971). If comparable yields could have been obtained in naturally occurring shock waves generated during meteoritic and cometary collisions with the primitive Earth, then this energy source may have played an important role in organic compound synthesis (Oró et al., 1980). As we have already discussed above, the collision of a cometary nucleus with the anoxic primitive atmosphere of the Earth would very likely result in the destruction of most of the organic molecules present in the impacting bodies. Therefore, we may conclude that cometary collisions with the primitive Earth were not only a source of volatiles and of free-energy but also created highly reducing transient atmospheric environments rich in reactive chemical species, which would lead to the abiotic synthesis of organic compounds of prebiological and biological significance.

Since Miller's classical simulation of the prebiotic atmosphere (Miller, 1953), the laboratory work done in the past three decades has strongly supported Oparin's (1924 et seq.) and Haldane's (1928) classical ideas about a non-biological primordial synthesis of organic molecules as a necessary prerequisite for the appearance of life. In fact, most researchers adhere to the view that simple molecules present in the anoxic atmosphere, the hydrosphere and the litosphere of the Earth reacted together as a result of the interaction between various forms of energy and catalytic effects (electric discharges, ultraviolet light, heat, Fischer-Tropsch-type catalyses, etc.) and formed a wide variety of monomeric substances including protein and non-protein amino acids, sugars, fatty acids and the purine and pyrimidine bases (Oró and Lazcano-Araujo, 1981). The further accumulation of these biochemical species in shallow bodies of water in the Earth's surface probably led to condensation and polymerization reactions which in turn yielded substances of higher molecular weight. The possible major reactions which led to the prebiotic synthesis of monomers and oligomers are shown in Table 7. Many of the products of these reactions have also been identified in carbonaceous chondrites (Oró, 1972; Nagy, 1975), therefore suggesting that they were present as components in the early Solar System and in the prebiotic terrestrial environment as a complex heterogeneous mixture of monomeric and macromolecular organic compounds.

Although it is possible that rudimentary replication, transcriptional and translational processes may have evolved from the adsorption of oligonucleotides and oligopeptides on clay surfaces, or from kinetic encounters of these type of molecules in solution, we favor the possibility that the cooperative association of prebiologically synthesized oligomers occurred within phase-separated thermodynamically open multimolecular microsystems (Oparin, 1971, 1972, 1978). The recent synthesis under model prebiotic conditions of amphiphilic lipids and phospholipids (Hargreaves et al., 1977; Hargreaves and Deamer, 1978; Oró et al., 1978a; Deamer and Oró, 1980) suggest that these amphiphilic molecules were available in the primitive Earth and led to the appearance of prebiotic liposomes (Figure 4), which provided with localized microenvironments whose selective absorption and concentration of ions, weak bases and other compounds (Deamer and Oró, 1980), led eventually to the evolution of systems of biocatalytic peptides (proto-enzymes), informational self-duplicating molecules (proto-tRNA) and peptide-synthesizing complexes (proto-ribosomes) from which the first living systems emerged (Oró and Lazcano-Araujo, 1981).

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INTERSTELLAR MOLECULES

__2 ATOMS__

H_2, OH, CH^+, CH, CO, CN, CS, NO, C_2, SO, NS, SiO, SiS

__3 ATOMS__

HCO^+, N_2H^+, H_2O, HCN, HNC, CCH, HCO, HNO, OCS, H_2S, SO_2

__4 ATOMS__

NH_3, H_2CO, HC_2H, C_3N, HNCO, H_2CS, HNCS

__5 ATOMS__

CH_4, C_4H, HC_3N, H_2CCO, NH_2CN, CH_2NH, HCOOH

__6 ATOMS__

CH_3CN, NH_2CHO, CH_3OH, CH_3SH

__7 ATOMS__

CH_3CCH, CH_3CHO, NH_2CH_3, CH_2CHCN, HC_5N

__8 ATOMS__

$HCOOCH_3$

__9 ATOMS__

CH_3CH_2OH, CH_3CH_2CN, CH_3OCH_3, HC_7N

__10 ATOMS__

NONE

__11 ATOMS__

HC_9N

Table 1

BIOCHEMICAL MONOMERS AND PROPERTIES WHICH CAN
BE DERIVED FROM INTERSTELLAR MOLECULES

INTERSTELLAR MOLECULES	FORMULAE	BIOCHEMICAL MONOMERS AND PROPERTIES
1. HYDROGEN	H_2	REDUCING AGENT, PROTONATION
2. WATER	H_2O	UNIVERSAL SOLVENT, HYDROXYLATION
3. AMMONIA	NH_3	BASE CATALYSIS AMINATION
4. CARBON MONOXIDE	$CO(H_2)$	HYDROCARBONS AND ACIDS
5. FORMALDEHYDE	CH_2O	MONOSACCHARIDES (RIBOSE) and GLYCEROL
ACETALDEHYDE	CH_3CHO	DEOXYPENTOSES (DEOXYRIBOSE)
ALDEHYDES (HCN)	RCHO	AMINO ACIDS
6. THIOFORMALDEHYDE	CH_2S	CYSTEINE AND METHIONINE
7. HYDROGEN CYANIDE	HCN	PURINES (ADENINE, GUANINE) AND AMINO ACIDS
8. CYANACETYLENE	HC_3N	PYRIMIDINES (CYTOSINE, URACIL THYMINE)
9. CYANAMIDE	H_2NCN	POLYPEPTIDES, POLYNUCLEOTIDES AND LIPIDS
10. PHOSPHINE (JUPITER)	PH_3	PHOSPHATES AND POLYPHOSPHATES

Table 2

SOLID-PHASE ABIOTIC SYNTHESIS

PRECURSORS	TEMP. OF THE ICY MIXTURE (°K)	FREE-ENERGY SOURCE	PRODUCTS	REFERENCE
CH_4-N_2-C_2H_6	20	ELECTRONS	ACETYLENE, ETHYLENE, 1,3 BUTADIENE, H_2, PROPYLENE, PROPANE, BUTENES.	GLASEL 1961
CH_4-N_2	20	ELECTRONS	ACETYLENE, ETHYLENE.	IBID
CH_4-NH_3-H_2O	77	12MeV PROTONS	ACETONE, UREA, ACETAMIDE.	BERGER 1961
CH_4-NH_3-H_2O	77	5MeV ELECTRONS	GLYCINE, GLYCINAMIDE, ALANINE, ASPARTIC ACID, PURINES, PYRIMIDINES.	ORO 1963b
HCHO-NH_3-H_2O	77	5MeV $^{14}C^+$ IONS	GLYCINE, ALANINE, OXALIC ACID, GLYCOLIC ACID, FORMAMIDINE, CN, T-BUTANOL, N-PROPYL ALCOBOL.	LEMMON 1979

Table 3

SOLID-PHASE ABIOTIC SYNTHESIS

PRECURSORS	TEMP. OF THE ICY MIXTURE (°K)	FREE-ENERGY SOURCE	PRODUCTS	REFERENCE
CH_4-N_2-C_2H_6	20	ELECTRONS	ACETYLENE, ETHYLENE, 1,3 BUTADIENE, N_2, PROPYLENE, PROPANE, BUTENES.	GLASEL 1961
CH_4-N_2	20	ELECTRONS	ACETYLENE, ETHYLENE.	IBID
CH_4-NH_3-H_2O	77	12MeV PROTONS	ACETONE, UREA, ACETAMIDE.	BERGER 1961
CH_4-NH_3-H_2O	77	5MeV ELECTRONS	GLYCINE, GLYCINAMIDE, ALANINE, ASPARTIC ACID, PURINES, PYRIMIDINES.	ORO 1963b
HCHO-NH_3-H_2O	77	5MeV $^{14}C^+$ IONS	GLYCINE, ALANINE, OXALIC ACID, GLYCOLIC ACID, FORMAMIDINE, CN, T-BUTANOL, N-PROPYL ALCOHOL.	LEMMON 1979

Table 3

PROBABLE PRECAMBRIAN IMPACT CRATERS*

Name	Latitude	longitude	diameter (km)	Age (x10[9] years)
Vredefort, S. Africa	27°00'S	027°30'E	140	1.97±0.10
Sudbury, Canada	46°36'N	081°11'W	140	1.84±0.15
Janisjärvi, U.S.S.R.	61°58'N	030°55'E	14	0.70

*Adapted from Grieve and Robertson (1979).

Table 4

COMETARY MATTER CAPTURED BY SOLAR SYSTEM BODIES*

	COMETARY MATTER TRAPPED (GRAMS)	TIME	REFERENCE
Sun	10^{26}	Main-Sequence stage	Joss 1974
Venus	$>4X10^{20}$	$2X10^{9}$ years	Lewis 1974
Moon	$2X10^{20}$	Late-accretion period	Wetherill 1975
Earth	$2X10^{16-18}$	First $2X10^{9}$ years	Oró 1961
	$<10^{25-26}$	Late-accretion period	Whipple 1976
	$\sim 3.5X10^{21}$	Late-accretion period	Sill and Wilkening 1978.
	$\sim 7X10^{23}$	$4.5X10^{9}$ years	Chang 1979
	$\sim 2X10^{22}$	$4.5X10^{9}$ years	Pollack and Yung 1980.
	10^{23}	First $2X10^{9}$ years	Oró *et al.* 1978*b*, 1980

*modified after Oró *et al.* 1980.

Table 5

EXTRATERRESTRIAL SOURCES OF CARBON*

REFERENCE	SOURCE	TOTAL MASS ACCRETED (GRAMS)	AMOUNT OF CARBON ACCRETED (GRAMS)
WETHERILL 1974	METEOROIDS	$>2 \times 10^{19}$	$>5 \times 10^{17}$
ORO *et al.*, 1980	COMETS	1×10^{23}	10^{22}
BUTLER *et al.*, 1978	INTERSTELLAR MOLECULAR CLOUDS	1.5×10^{19}	1.5×10^{15}
THIS PAPER	SOLAR WIND	$>3.8 \times 10^{17}$	$>1.5 \times 10^{14}$

*Estimated for the Earth's first 2×10^9 Years.

Table 6

MAJOR PREBIOTIC REACTION PATHWAYS

	Reactants	Conditions	Products
1.	$CO + H_2$	FTT CATALYSIS	HYDROCARBONS, FATTY ACIDS
2.	CH_2O	BASE CATALYSIS	RIBOSE
3.	CH_3CHO CH_2O	BASE CATALYSIS	DEOXYRIBOSE
4.	RCHO HCN NH_3	STRECKER CONDENSATION	AMINO ACIDS HYDROXY ACIDS
5.	AS ABOVE + CH_2S	STRECKER CONDENSATION	CYSTEINE, METHIONINE
6.	HCN	BASE CATALYSIS	ADENINE, GUANINE
7.	HC_3N + UREA	CONDENSATION	URACIL, CYTOSINE
8.	AS ABOVE + CH_2O	HYDRAZINE	THYMINE
9.	AMINO ACIDS	CYANAMIDE	OLIGOPEPTIDES
10.	MONONUCLEOTIDES	CYANAMIDE	OLIGONUCLEOTIDES
11.	ISOPRENE	UV. ION. RAD.	POLYISOPRENOIDS
12.	FATTY ACIDS GLYCEROLS PHOSPHATE BASES	CYANAMIDE	NEUTRAL LIPIDS PHOSPHOLIPIDS

Table 7

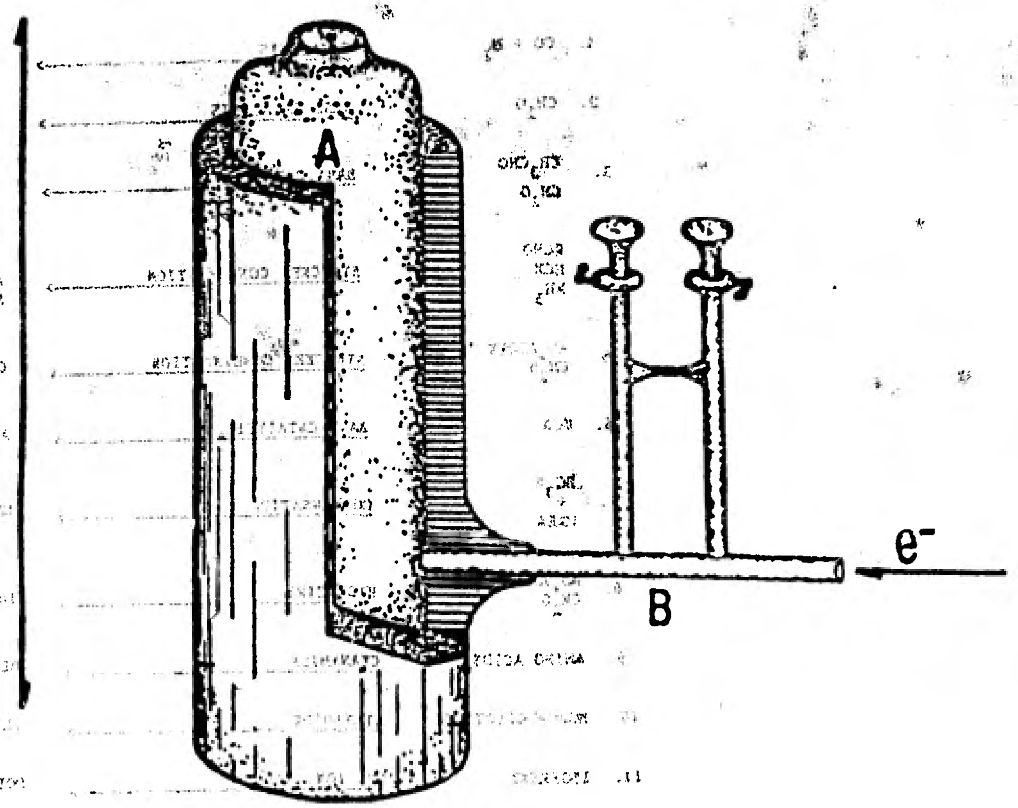

Figure 1. Solid-phase irradiation experiment. A mixture of ammonia, water and ^{14}C-labelled methane was introduced at ambient temperature at tube B. When liquid nitrogen was added to vessel A, the reactants condensed in a solid layer where A and B are in contact. Irradiation with high-energy (5 MeV) electrons then took place (modified from Oró, 1963).

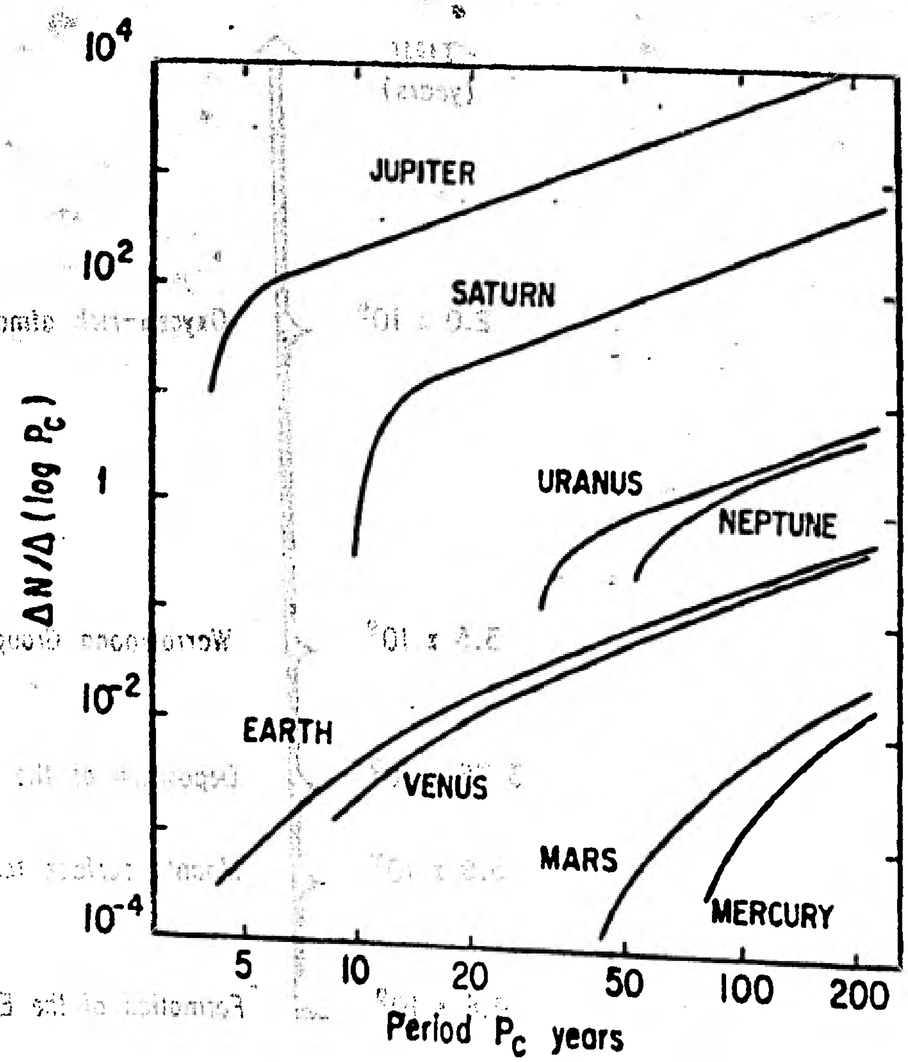

Figure 2. Distributions of periods for 10^9 hypothetical random parabolic comets captured by several planets. The ordinate is the number ΔN of captured comets for equal increments in the logarithm of the period P_c which is given in years (adapted from Everhart, 1969).

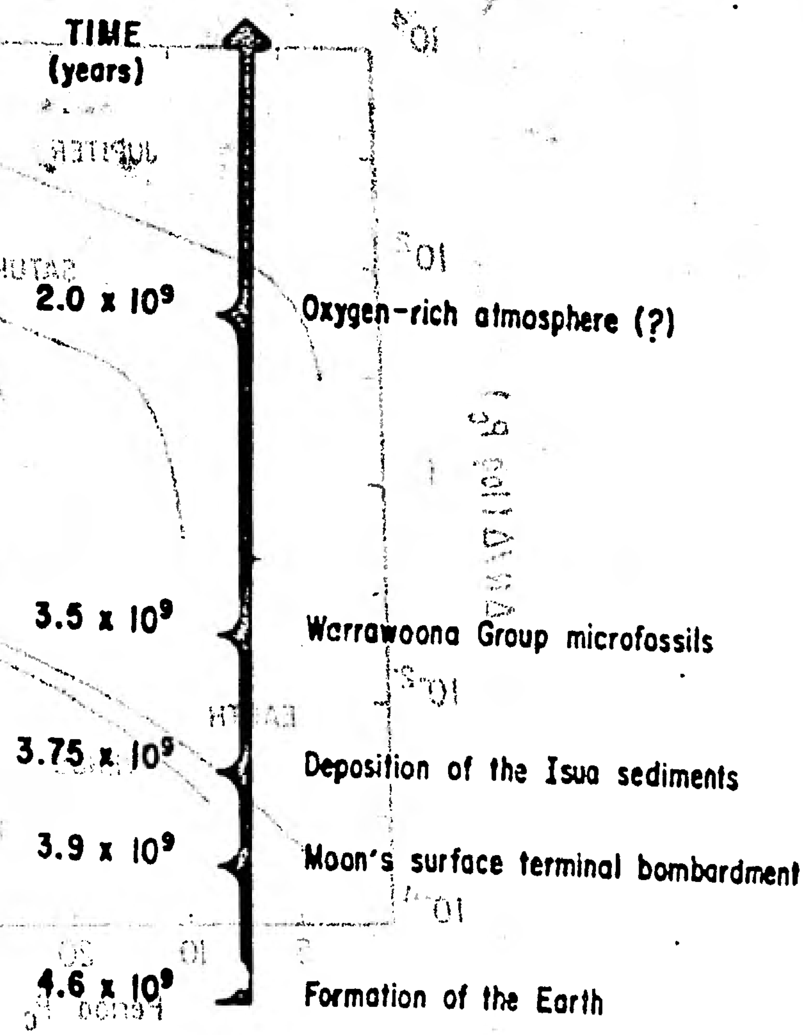

Figure 3. Some major landmarks in the early history of the Earth.

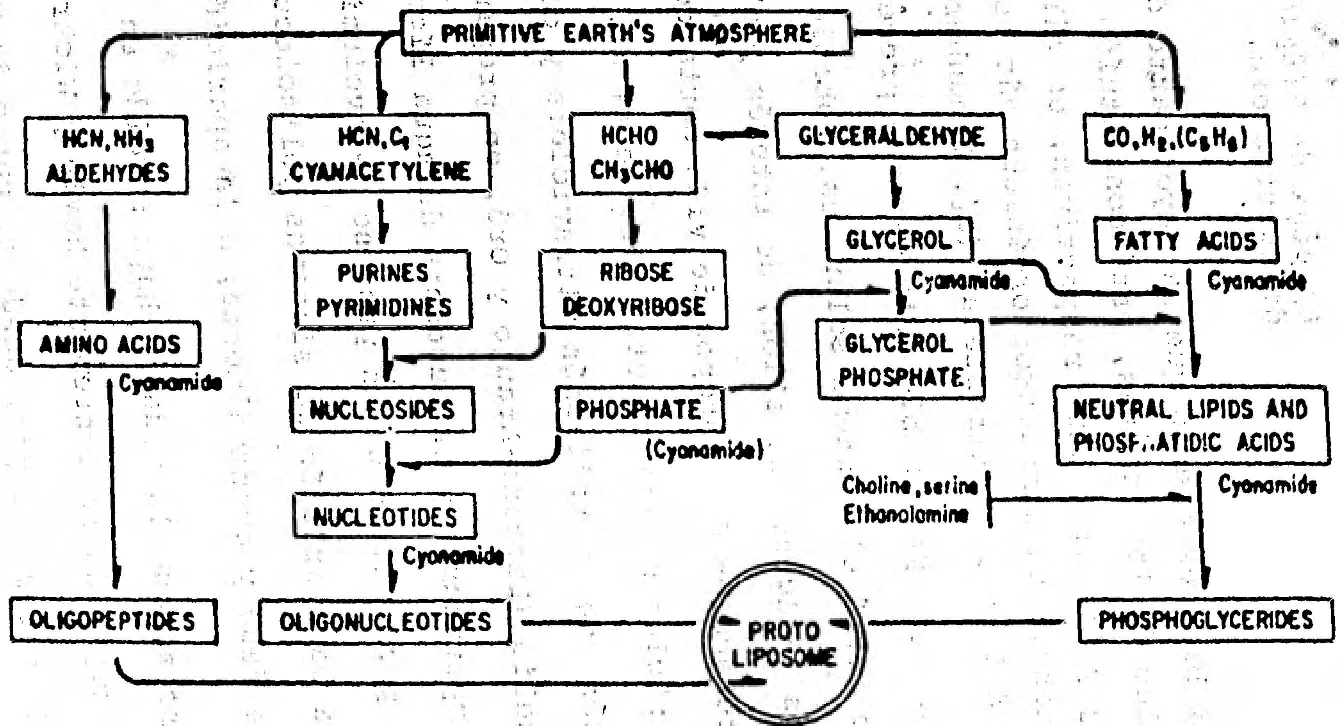

Figure 4. Abiotic organic synthesis of biomonomers and polymers and the appearence of precellular systems (after Oró and Lazcano-Araujo, 1981).

III. CONCLUSIONES

> Porque nada es eterno, porque todo perece...
> Dime Gilgamesh, ¿es que acaso los muros de
> las casas que construímos se habrán de
> mantener para siempre en pie?
>
> *Epopeya de Gilgamesh*, tercer milenio antes
> de nuestra era.

Si bien es cierto que la mayor parte del componente volátil de del núcleo de los cometas, está constituído por hielos de H_2O, CO_2, CH_4, NH_3 y los clatratos respectivos, es válido suponer, sin embargo la existencia de compuestos orgánicos más complejos heredados directamente del medio interestelar (*cf.* Greenberg 1978). Además de estas moléculas, que presumiblemente estaban presentes en la nebulosa de donde se formó el Sistema Solar, es probable que existan compuestos orgánicos -algunos de ellos, de interés prebiótico- formados gracias a la interacción de isótopos de vida corta con los componentes volátiles del núcleo de los cometas (Irvine *et al.* 1980) y otros originados por acción de la radiación ultravioleta y del viento solar durante el perihelio (Lazcano-Araujo y Oró, en preparación). Sin embargo, las bajas temperaturas y la ausencia de agua líquida en los cometas, excluye la posibilidad de un proceso de evolución prebiológica que llevase a la aparición de sistemas polimoleculares abiertos con separación de fase y eventualmente, a la aparición de seres vivos.

Pero aunque la vida no haya surgido en los núcleos de cometas, como han sugerido recientemente Hoyle y Wickramasinghe (1978), el estudio de estos cuerpos, desde el punto de vista de la teoría Oparin-

Haldane, no se limita a su utilización como referencia de los procesos de síntesis abiótica de materia orgánica. En efecto, la historia temprana del Sistema Solar estuvo caracterizada por un gran número de colisiones de meteoritos, asteroides y cometas que chocaron contra la superficie de los planetas interiores, y en particular, contra la Tierra. Es importante entonces, estudiar la importancia que este tipo de colisiones tuvieron en la modulación de las condiciones medioambientales en las que surgió la vida.

Con la excepción de los compuestos orgánicos presentes en el material condrítico asociado al núcleo de los cometas, es poco probable que la fracción de moléculas de interés prebiótico sintetizadas en la fase volátil de estos cuerpos sobreviviese a las condiciones generadas durante la colisión de un cometa contra la Tierra primitiva. Sin embargo, estos choques deben haber contribuído al enriquecer la atmósfera anoxigénica de la Tierra en volátiles, lo cual a su vez implica que la formación de la atmósfera secundaria de la Tierra no es debida tan solo a procesos de degasamiento temprano. Por otra parte, la liberación de una gran cantidad de energía bajo la forma de ondas de choque generadas durante la colisión, puede haber contribuído a la síntesis, ya en la Tierra primitiva, de una gran cantidad de compuestos orgánicos. En este sentido, cobran una relevancia particular los experimentos de Bar-Nun *et al.* (1970) en los que se han obtenido los rendimientos más altos en la síntesis de aminoácidos haciendo pasar una onda de choque por una atmósfera de CH_4, NH_3 y agua.

Finalmente, es necesario agregar que aún cuando el análisis *in situ* del núcleo de un cometa es evidentemente la mejor oportunidad para determinar la existencia de compuestos orgánicos de interés prebiótico (cf. Neugebauer *et al.* 1979), son igualmente significativos los experimentos en los que mezclas de compuestos que presumiblemente existen en los cometas, son sometidas a bajas temperaturas e irradiadas. Desafortunadamente, son pocos los experimentos que se han realizado en esta dirección. Un proyecto a realizar en el futuro contempla precisamente este tipo de experimentos, encaminados a estudiar el grado de evolución química de los núcleos de cometas y su posible conexión con la química prebiótica y del medio interestelar.

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