

COMET HALLEY AS AN AGGREGATE OF INTERSTELLAR DUST AND FURTHER EVIDENCE FOR THE PHOTOCHEMICAL FORMATION OF ORGANICS IN THE INTERSTELLAR MEDIUM

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Abstract. Photolysis of mixtures of CO:NH₃:H₂O at 12 K results in the formation of an organic residue which is not volatile in high vacuum at room temperature. Analysis of this fraction by GC-MS resulted in the detection of C₂-C₃ hydroxy acids and hydroxy amides, glycerol, urea, glycine, hexamethylene tetramine, formamidine and ethanolamine. Use of isotopically labeled gases made it possible to establish that the observed products were not contaminants. The reaction pathways for the formation of these products were determined from the position of the isotopic labels in the mass spectral fragments. The significance of these findings to the composition of comets and the origins of life is discussed.

Introduction

It has been suggested (Anders and Owen, 1977; Chang, 1979; Delsemme, 1984; Oró, 1961; Greenberg and Mendoza-Gómez, 1991) that comets and other primitive solar system bodies must have been the major source of terrestrial volatiles. In the solar system, the comets together with the planets and other bodies formed from a contracting interstellar dust cloud where the dust aggregated into fluffy clusters of dust (Greenberg, 1985, 1989). Therefore, a very important problem is the study of this interstellar dust. The increase in the chemical complexity of interstellar dust is documented by astronomical observations of changes in the diagnostic infrared absorption bands (Allamandola *et al.*, 1980; Greenberg and Schutte, 1985; d'Hendecourt and Allamandola, 1986 and Greenberg, 1991). There are four basic mechanisms providing for the observed variations in the molecular composition of the grain mantles:

- (1) reaction of atoms and molecules in the gas phase
- (2) grain-surface reactions
- (3) photolysis of the grain mantles
- (4) accretion/desorption of atoms and molecules from/into the gas

Examples of each of the four mechanisms listed above include:

- (1) CO molecules are primarily produced in gas phase reactions but are accreted on the dust grains at low temperature (Lacey *et al.*, 1984; Larson *et al.*, 1987).

(2) Gas phase reactions alone result in a relatively low $\text{H}_2\text{O}:\text{CO}$ ratio but the $\text{H}_2\text{O}:\text{CO}$ ratio is generally greater than 5:1 on grains. The primary mechanism for producing the H_2O component of grain material is by the sequential reaction of H atoms with O atoms and then the reaction of the resulting OH radical with H atoms (Soifer *et al.*, 1979; Erickson *et al.*, 1981; d'Hendecourt *et al.*, 1985; Whittet *et al.*, 1988).

(3) Molecules and ions which are not observed in the gas phase such as OCN^- are not produced by gas phase reactions (although HOCN is formed in the gas phase, Ferris *et al.*, 1974). On the other hand, OCN^- is produced in radiated icy mixtures (Grim and Greenberg, 1982). The abundance of CO_2 predicted from theoretical models of gas phase reactions is much lower than that needed to account for the CO_2 abundance relative to CO in grain mantles. But CO_2 is produced abundantly by photo processing of H_2O , CO in grains and is observed to be comparable with the amount of CO in dust grains (Greenberg and d'Hendecourt, 1985; d'Hendecourt and Jourdain de Muizon, 1989).

(4) The gas phase abundance of HCO_2^+ and H_2CO in several regions of space have proven to be abnormally high when pure gas phase reaction schemes are considered (Minh *et al.*, 1988; van Dishoeck and Black, 1988). However, it has been shown that production rates of CO_2 and H_2CO by photoprocessing of grain mantles followed by explosive desorption provides a basis for explaining the observed HCO_2^+ and H_2CO abundances in the gas (Breukers, 1991; Greenberg, 1991) which is further confirmed by the most recent observations (Minh *et al.*, 1991).

Given the direct and indirect evidence for the presence of simple molecules and their photoprocessing leads to the prediction (Greenberg and Yench, 1972; Greenberg, 1979) that there should be a mantle material consisting of complex organic molecules. The fact that such molecules are a ubiquitous component on interstellar dust have now been supported by observation of the $3.4 \mu\text{m}$ absorption not only in dust towards the galactic center (Willner and Pipher, 1982; Butchart *et al.*, 1986) but also in more local diffuse cloud dust towards VI Cyg #12 (Adamson *et al.*, 1990) as predicted by Greenberg (1973). Direct evidence for the organic refractory component of Comet Halley dust (and, by inference, the Comet Halley nucleus) was provided by the mass spectra results of Kissel and Krueger (1987) later elaborated on by Jessberger *et al.* (1988) and also supported by the work of Mukhin *et al.* (1989). The presence of a number of structural types has been deduced by these authors in the dust mass spectra. The evidence for polyoxymethylene oligomers is claimed, but not firmly established (Huebner, 1987).

The results of the massive space and ground based observational program for Comet Halley appear to confirm the idea that comets are fluffy aggregates of interstellar dust and that a major component of the dust must be in the form of tenth micron silicate core-organic refractory mantle particles (refractory refers to those molecules which have a negligible vapor pressure at 160 K) (Greenberg and Hage, 1990). The justification for this has come most directly from the observation of Comet Halley dust although several of the observed properties of

Halley could already be simply accounted for by such a model. The silicate core-organic refractory mantle properties may be deduced from the time of flight Comet Halley mass spectrometry in which the low atomic weight elements arrive before the rocky elements (Jessberger, 1991). The low visual surface albedo may either result from the blackness of the material or from the open structures of submicron particles with substantially less absorption (Greenberg, 1986a). An absorptivity of the organic mantles of $m''(k) = 0.15$ is more than adequate and is not only derivable from the polarization properties of interstellar dust (Chlewicki and Greenberg, 1990) but is inferred from the visible absorptivity of laboratory created organic residues.

A significant factor in the mass spectra determination of the organic material of Comet Halley is that the dust has been heated to temperatures greater than 400 K so that, with the assumption that it starts out as interstellar dust organics, one has to accept the probability that a large fraction of these organic molecules have evaporated before the dust reached the mass spectrometer. In fact, the presence of the distributed species (those molecules formed by decomposition of higher molecular weight organics) CN, CO, etc. (Eberhardt *et al.*, 1987; A'Hearn *et al.*, 1986 and Marconi *et al.*, 1989) in the Comet Halley coma must be attributed to the gradual evaporation of the non-refractory organic components from the dust with subsequent photodissociation. Thus the quantity and quality of the organics in Comet Halley can not be claimed to have been fully sampled by mass spectra alone. This means, for example, that the 3.4 μm emission feature from Comet Halley dust organics can only have been due to the refractory components and that it should not be expected to compare precisely with the 3.4 μm absorption by interstellar dust.

Experimental

A. PRODUCTION OF ORGANIC RESIDUES

In order to study the physical and chemical processes taking place in the interstellar medium, the most relevant conditions in interstellar space are reproduced in the laboratory (Greenberg, 1986b). The ultra-high vacuum which occurs in interstellar space, is simulated by a chamber which is evacuated by means of a diffusion pump (Edwards MK2 Diffstak 63/150M) in series with a rotary pump (Edwards E2M8 double stage). The pressure can go down to about 10^{-7} mbar at room temperature (and 10^{-8} mbar at 10 K). In between the diffusion pump and the vacuum chamber, a filter is located to avoid pump oil coming into the system. Before each experiment, the entire set-up is warmed-up to about 320 K while pumping, in order to degas any possible deposition on the walls from previous experiments.

The silicate core of the dust particle is replaced by a rotatable aluminum block located in this vacuum chamber. For each sample, this block is washed with spectroscopic grade methanol, followed by spectroscopic grade chloroform, doubly distilled water, and then, again spectroscopic grade methanol. A cold shield consisting

of a hollow tube is placed on the block in order to prevent or minimize oil and air contamination which could condense on the shield rather than on the substance.

The low temperature is achieved by means of a closed cycle helium cryogen (Air Products Displex DE-202), which can cool down the block to at least 12 K. To improve the heat conduction, an indium plate is placed between the block and the cryostat. The temperature is recorded by means of a temperature indicator/controller (Air Products APD-G) and a silicon diode resistance temperature detector (Scientific Instruments, Si-400).

To mimic the condensable species freezing onto the silicate core, a mixture of gases are controllably admitted into the vacuum chamber through a narrow inlet directed to one of the sides of the aluminum block. The bulk of the studies in this report were performed either on a mixture of CO:H₂O:NH₃ (5:5:1), CH₄:NH₃ (1:1) or CH₄:H₂O (1:1). In most instances isotopically labeled gases were used with ¹³C in the carbon compounds, ¹⁸O in H₂O and ¹⁵N in NH₃. The gases were mixed in a greaseless glass line. The glass line was evacuated to pressures of the order of 10⁻⁵ mbar by the same combination of diffusion and rotary pumps, as for the system. A glass-bulb (vol. 3 L) was connected to the glass line by means of a metal O-ring compression connector, and was also evacuated. The gases are let in the gas bulb one by one, evacuating the line after each one. The pressures of the gases was controlled by a Leybold-Heraeus manometer (logarithmic range from 0 to 1200 mbar). The following high purity gases were used: unlabeled ammonia (Matheson, anhydrous, purity 99.6%), labeled ammonia (¹⁵NH₃, 99% ¹⁵N), unlabeled carbon monoxide (Matheson, purity 99.5%), labeled carbon monoxide (¹³CO, 99% ¹³C, Intersales Holland), unlabeled methane (4.5 Hoekloos, 99.995% purity), labeled methane (¹³CH₄, MSD Isotopes, 99% ¹³C), labeled nitrogen (¹⁵n₂, Sanbio b.v.), labeled water (H₂¹⁸O, Intersales Holland, 99.8%) are used directly, and the non-labeled water, which was doubly distilled and demineralized, was degassed by three free-thaw cycles.

Either simultaneously with the deposition, or subsequent to it, the gases were UV irradiated simulating the interstellar radiation field. This irradiation was achieved by means of a microwave stimulated hydrogen-flow vacuum ultraviolet lamp which has emission peaks at 1216Å (Lyα) and about 1600Å. The flux of photons from this lamp ($h\nu > 6\text{eV}$) is approximately 10¹⁵ cm⁻² s⁻¹ (Weber and Greenberg, 1985). Although such fluxes are approx. 10⁷ higher than in interstellar space, it can be shown that no spurious results occur in the laboratory analogue experiments (Hagen *et al.*, 1979; Greenberg, 1989). The lamp was first evacuated to pressures of the order of 10⁻³ mbar, by means of a rotary pump, and then hydrogen is let in until the pressure rose to about 0.1 mbar. The lamp was powered by a microwave discharge supply (Ophos instruments, 1450 MHz) operated at 120 W power level. The ices were irradiated by this lamp through a MgF₂ window for about 24 hr.

The thermal evolution of the grains in space can be simulated in the laboratory by heating the aluminum block, which was done by means of a resistive heater element (40 Ω) heater in conjunction with a temperature indicator/controller. Further

details of the experimental set-up can be found in Hagen *et al.*, (1979). The warm-up of the irradiated ices (the interstellar grain mantles in the molecular cloud medium) lead to the evaporation of the volatiles and an organic residue (Greenberg, 1982a; Schutte, 1988).

B. GC/MS OF THE TMS DERIVATIVES OF THE REACTION PRODUCTS

The organic residue was washed from the aluminum block with 1–2 mL of anhydrous methanol (distilled from magnesium) and the methanol was removed on a rotary evaporator using aspirator vacuum at 45–50°. The sample was further dried for 2 hr at room temperature using a vacuum pump. To the dried residue was added 50 μ L of silylation grade pyridine and 50 μ L of bis(trimethylsilyl)trifluoroacetamide (BSTFA) (Pierce, Rockford, III). The mixture was heated at 40° for 15 hr in an ampule sealed with a septum.

A procedure blank was performed which consists of washing the metal block with 2 mL of methanol after extracting the sample. The procedure blanks and the reference samples were derivatized by the same procedure as the photoproducts.

The BSTFA reaction mix was applied directly to the Carlo Erba Fractovap 4160 gas chromatographic system by on-column injection. The column used was a 30 M \times 0.25 mm fused silica column coated internally with a bonded 0.25 μ M layer of 5% phenyl 95% methyl silicone (RTX-5, Restek Corporation, Port Matilda, PA 16870). The temperature program was 10 min at 65 °C, 8 °C per min to 280 °C. The end of the column was connected to the source of the mass spectrometer with

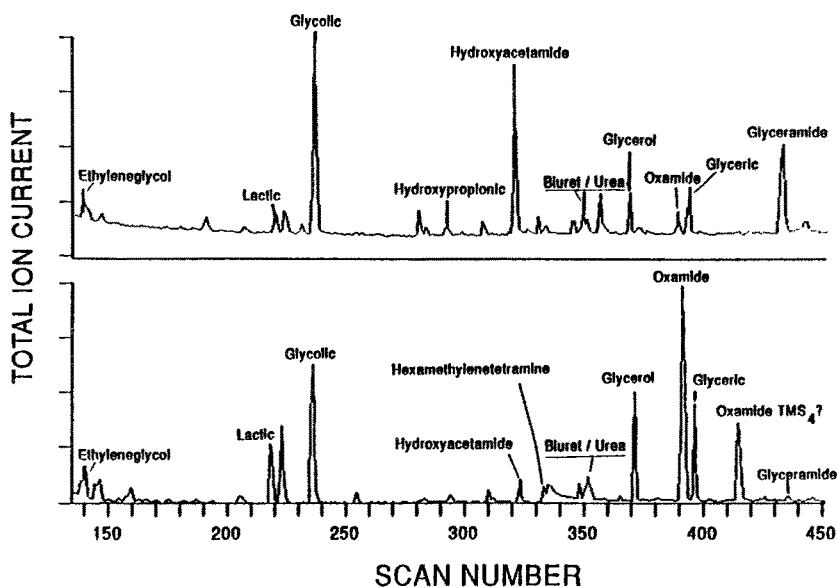


Fig. 1. Two gas chromatographic patterns observed from the refractory fraction obtained after photolysis of 5:5:1 H₂O:CO:NH₃.

TABLE I
Products from the photolysis of CO:H₂O:NH₃ mixtures at 10 K^a

Compound	Formula	Amount ^b (%)
1. Ethylene glycol ^c	HOCH ₂ CH ₂ OH	4.6 ± 4.4
2. Lactic acid ^d	CH ₃ CH(OH)CO ₂ H	21 ± 17
3. Glycolic acid	HOCH ₂ CO ₂ H	24 ± 12
4. 3-Hydroxypropionic acid	HOCH ₂ CH ₂ CO ₂ H	0.76 ± 0.52
5. Formamidine	HCNH(NH ₂)	0.10 ± 0.18
6. 2-Hydroxyacetamide	HOCH ₂ CONH ₂	17 ± 10
7. Hexamethylene tetramine	(CH ₂) ₆ N ₄	1.2 ± 1.4
8. Urea	NH ₂ CONH ₂	2.2 ± 6.2
9. Biuret	NH ₂ CONHCONH ₂	0.50 ± 0.96
10. Oxamic acid	NH ₂ COCO ₂ H	0.09 ± 0.20
11. Ethanolamine	HOCH ₂ CH ₂ NH ₂	0.38 ± 0.57
12. Glycerol	HOCH ₂ CH(OH)CH ₂ OH	4.4 ± 2.5
13. Glycine	NH ₂ CH ₂ CO ₂ H	0.27 ± 0.51
14. Oxamide	NH ₂ COCONH ₂	0.13 ± 8.6
15. Glyceric acid	HOCH ₂ CH(OH)CO ₂ H	5.9 ± 5.6
16. Glyceramide	HOCH ₂ CH(OH)CONH ₂	15 ± 10

^a The approximate ratio of CO:H₂O:NH₃ was 5:5:1 in the condensed phase.

^b The average of 10 analyses. The yields given in percent based on the response of the mass spectrometer assuming the same sensitivity for each compound. The error is given at the 95% confidence level.

^c It was not possible to determine if the ethylene glycol observed using ¹³C contains ¹³C.

^d Isotopic labeling studies have shown lactic acid to be a contaminant and not a photoproduct.

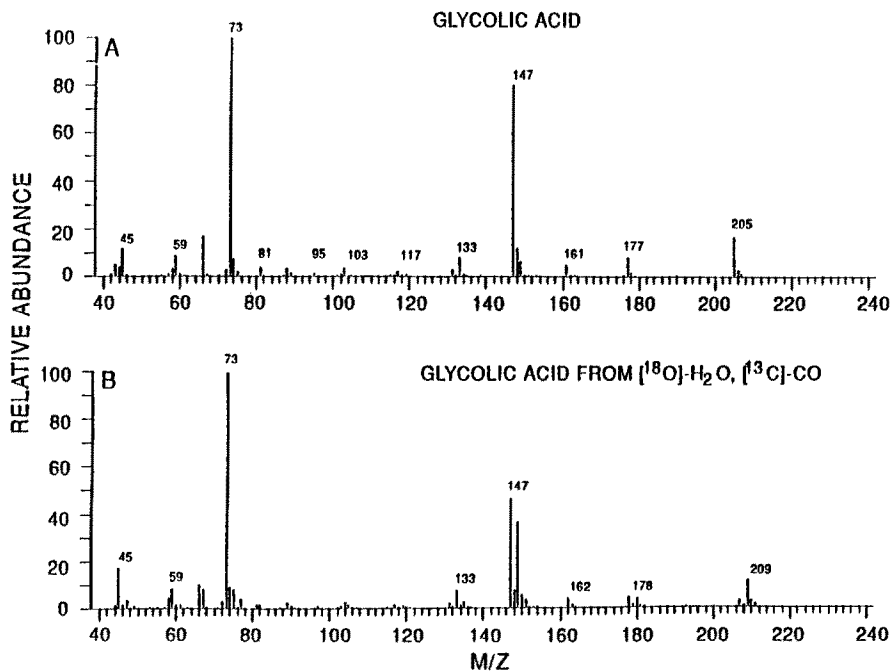


Fig. 2. Mass spectra of the TMS derivative of glycolic acid. (A) Without isotopic label in the starting CO and H₂O. (B) Using ¹³C-CO and ¹⁸O-H₂O as starting materials.

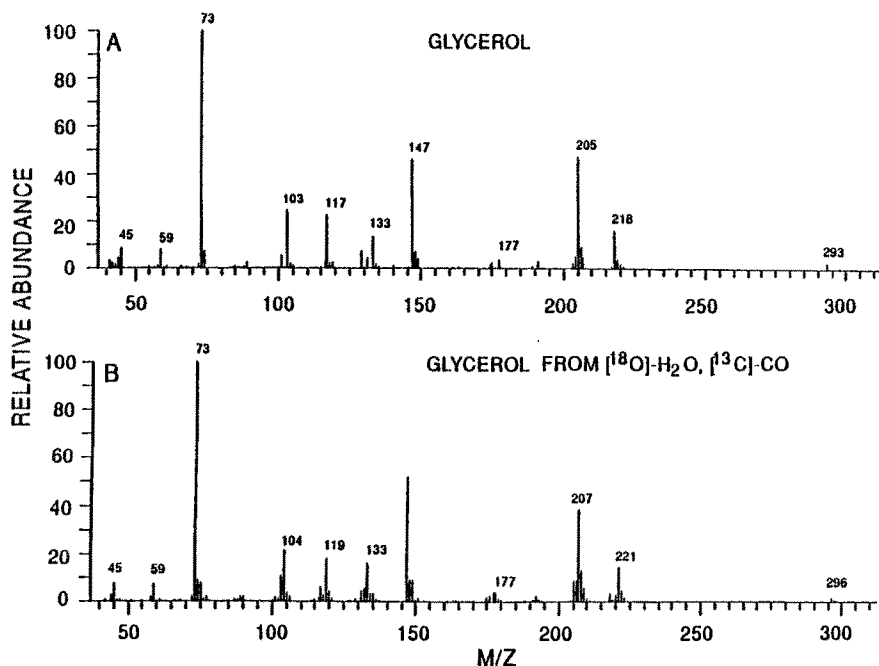


Fig. 3. Mass spectra of glycerol. (A) Without isotopic label in the starting CO and H₂O. (B) Using $^{13}\text{C}\text{-CO}$ and $^{18}\text{O}\text{-H}_2\text{O}$ as starting materials.

a heated interface. The Kratos MS-25 mass spectrometer was operated with accelerating voltage of 2 kilovolts, ionizing voltage of 70 eV, trap current of 250 μA , scan rate 2.87 sec/scan and source temperature of 270 $^\circ\text{C}$. The instrument was routinely calibrated from m/z 27 to m/z 606.

Figure 1 presents chromatograms illustrating two patterns seen with the present experimental conditions. In the upper chromatogram, 2-hydroxyacetamide and glyceramide are major products and hexamethylene tetramine and oxamide are either absent or minor components of the product mixture. In the lower chromatogram, the relative amounts of these four substances are reversed. An average yield of each product is shown in Table 1.

The unlabeled peaks in Figure 1 are almost all substances seen in blanks as well as samples. In addition, lactic acid and glycerol were frequently seen in blanks. In experiments where photo reactions involved isotopically labeled gases, glycerol always showed an admixture of labeled and unlabeled components. In no experiments was lactic acid found to be labeled. It has not been possible to determine the source of the unlabeled lactic acid and glycerol.

Figures 2-4 are mass spectra of labeled glycolic acid, glycerol and glyceric acid in an experiment where the reactants included $^{13}\text{C}\text{-CO}$ and $^{18}\text{O}\text{-H}_2\text{O}$ as compared to mass spectra of these substances in an experiment where no isotopic material was present.

Figures 5-7 illustrate the mass spectral fragmentation behavior of glycolic acid,

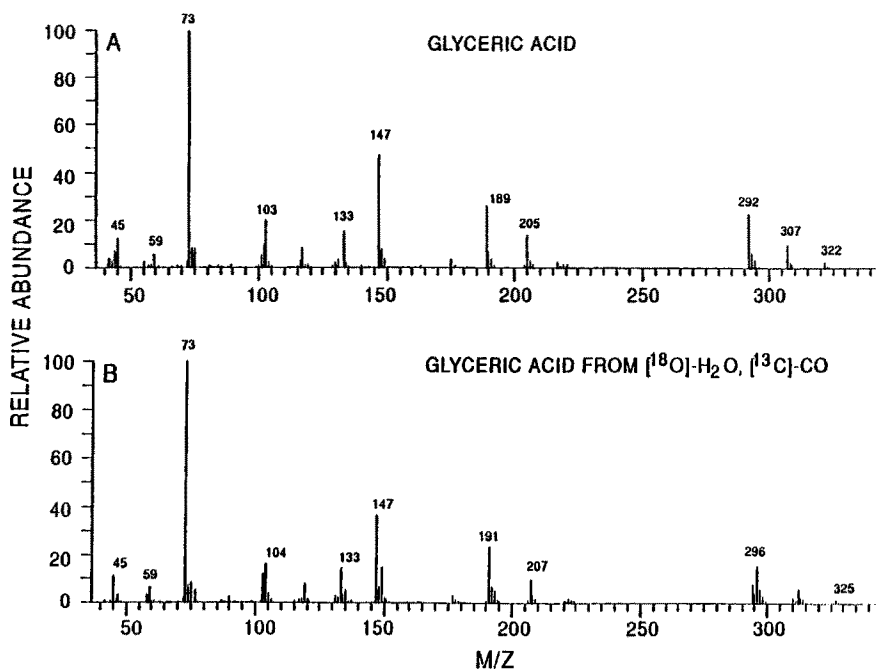


Fig. 4. Mass spectra of glyceric acid. (A) Without isotopic label in the starting CO and H₂O. (B) Using ¹³C-CO and ¹⁸O-H₂O as starting materials.

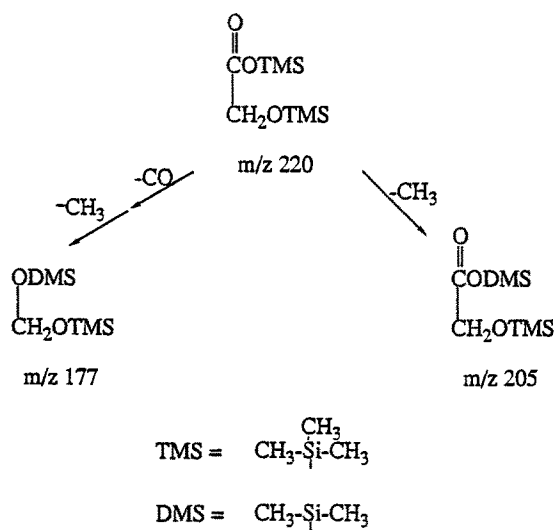


Fig. 5. Proposed mass spectral fragmentation pathway for the TMS derivative of glycolic acid.

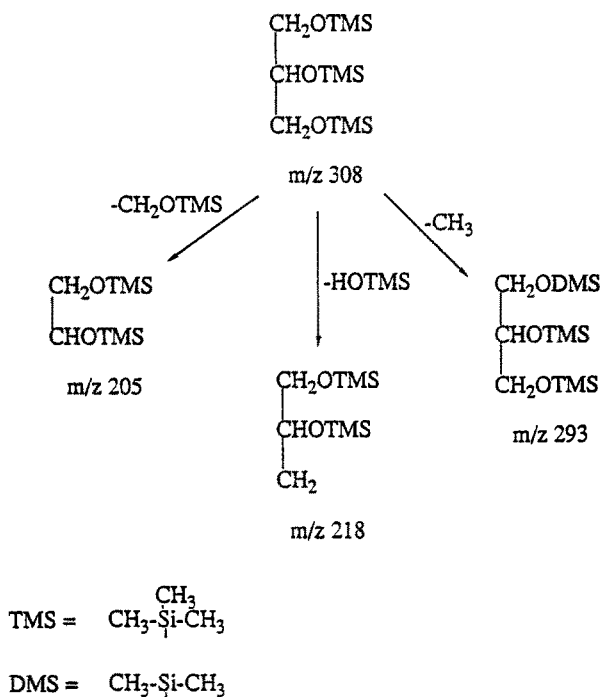


Fig. 6. Proposed mass spectral fragmentation pathway for the TMS derivative of glycerol.

glycerol and glyceric acid. The schemes presented are based in part on results with labeled compounds. These structures were used in calculating isotope distribution in mass spectral fragments (see below).

3. Results and Discussion

3.1. REACTION PRODUCTS

Eleven compounds were identified in our previous investigation of the products of the photolysis of CO, H₂O, NH₃ mixtures at 10–20 K (Agarwal *et al.* 1985). 3-Hydroxypropionic acid, formamidine, hexamethylene tetramine, ethanolamine and glycine (Table I) have also been identified in the present study. The presence of glycine was observed consistently while hexamethylene tetramine was detected in some of the product mixtures. The reported formation of hexamethylene tetramine from mixtures of formaldehyde and ammonia provides strong evidence for the photochemical formation of formaldehyde from carbon monoxide in our system (Walker, 1964).

A search was made for the silylated derivatives of threonic and erythreonic acids in the reaction products with the aid of authentic samples (Fluka). These four-carbon, trihydroxyacids are homologs of glyceric acid. Surprisingly, neither was detected. Definitive mass spectra of the standard samples were obtained.

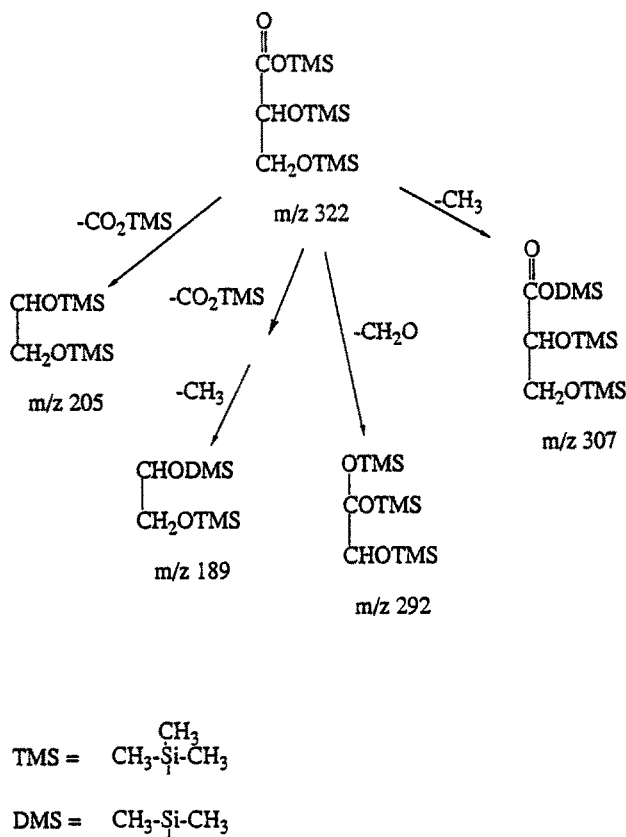


Fig. 7. Proposed mass spectral fragmentation pathway for the TMS derivative of glyceric acid.

The trimethylsilyl (TMS) derivatives of urea and biuret have the same retention times and similar mass spectral fragmentation patterns and their combined yield was reported in our initial study (Agarwal *et al.*, 1987). A procedure has now been devised to estimate the relative amounts of each compound. It was observed that the *m/e* 189 peak is greater in the TMS derivative of pure urea while the *m/e* 171 peak is greater in TMS-biuret. The relative amounts of each in a reaction mixture was estimated from the response factors of each compound at *m/e* 171 and 189 and the intensity of each of these mass peaks in the mass spectrum of the reaction mixture.

The yields of the products in Table 1 exhibited considerable variation. The cause of this variation is not clear. It was observed that the far UV output of the lamps decreased markedly with time. In particular, the $\text{Ly}\alpha$ output is most sensitive to lamp aging. This might explain some of the product variation if the synthesis of some of the compounds is dependent on the presence of highly energetic UV light.

It was attempted to expand the scope of the studies by using methane in place of carbon monoxide as the carbon source. But no non-volatile products were detected which could be attributed to the reaction of methyl radicals in mixtures of $\text{CH}_4:\text{NH}_3$,

$^{13}\text{CH}_4:\text{CH}_4:\text{H}_2\text{O}$, $^{13}\text{CH}_4:^{15}\text{N}_2:\text{H}_2\text{O}$ and $\text{CH}_4:^{15}\text{N}_2:\text{H}_2\text{O}$. It is likely that reaction products like hydrocarbons and alcohols were formed but they evaporated in the high vacuum when the aluminum block on which the reactions took place at 12 K was warmed to room temperature.

3.2. ISOTOPICALLY LABELED REACTANTS AND PRODUCTS

The bulk of the studies performed since our previous publication (Agarwal *et al.*, 1985) utilized stable isotopic labels in one or more of the reactant gases. Photoproducts can be easily distinguished from contaminants because the contaminants will not have more than the natural isotopic abundance of ^{13}C , ^{15}N or ^{18}O . The mass spectral fragments formed for a labeled compound will be one or more mass units higher than those observed from the unlabeled standards.

The use of isotopic labels clearly established that lactic acid is a contaminant by the absence of mass peaks at an m/e greater than is observed in the unlabeled standard. Lactic acid was incorrectly considered to be a photoproduct in previous studies where no isotopic labels were used (Agarwal *et al.*, 1985). A portion of the glycerol contains no label and a portion was completely labeled with ^{13}C when ^{13}CO was used as the carbon source. The unlabeled glycerol must be a result of adventitious contamination. The extent of labeled and unlabeled products in one of the photolysis mixtures is shown in Figure 8. Small amounts of other unlabeled contaminants have been detected.

It was not possible to determine if any of the ethylene glycol is labeled because it is eluted from the gas chromatograph at the same time as some of the unlabeled compounds used in the silylating reagent. The presence of a large background of

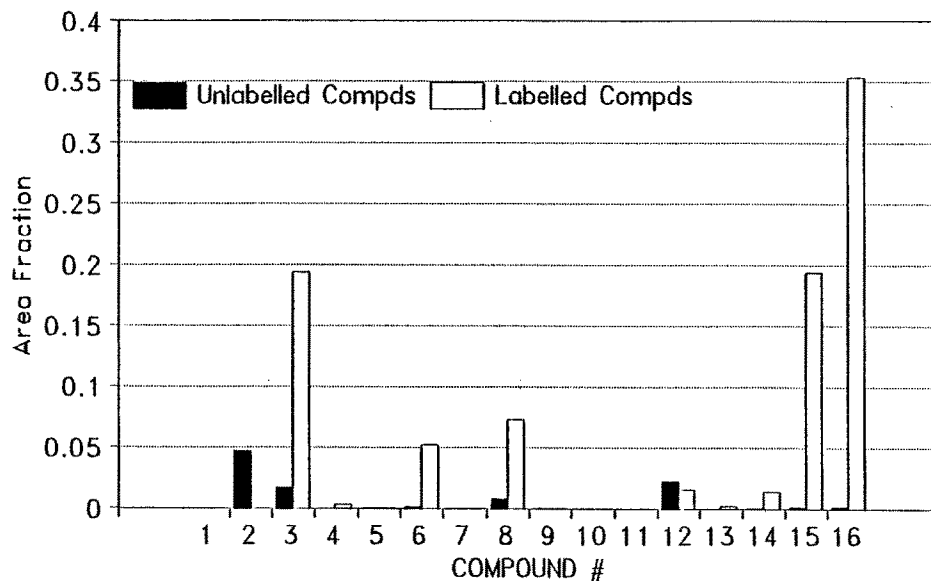


Fig. 8. The percent of labeled and unlabeled products in the refractory fraction after irradiation of a 5:5:1 $\text{H}_2^{18}\text{O}:\text{H}_2^{13}\text{CO}:\text{NH}_3$ mixture.

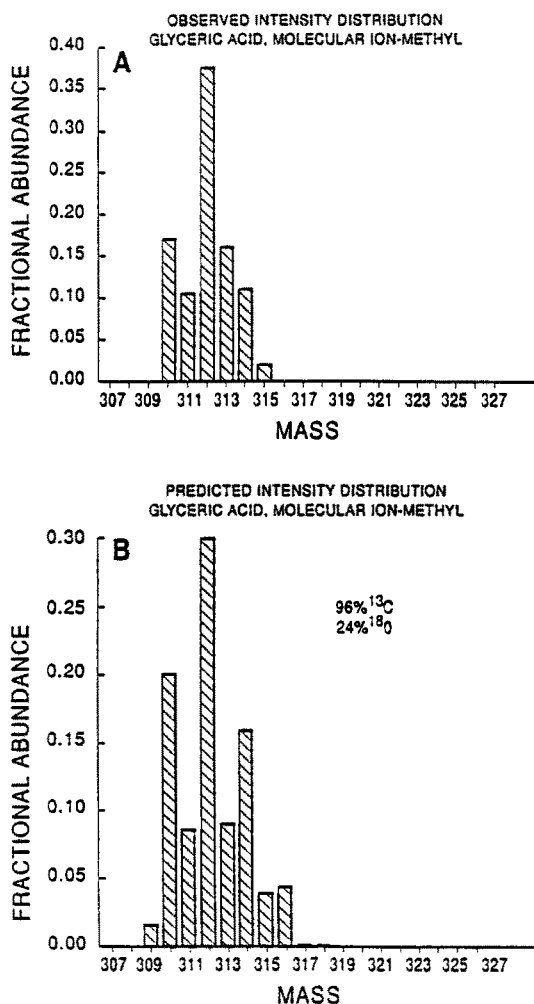


Fig. 9. The observed (A) and calculated (B) distribution of mass peaks in the M-15 region in the mass spectrum of TMS glyceric acid containing O-18 and C-13.

unlabeled organic material would mask the small amounts of ^{13}C present in the TMS derivative of ethylene glycol.

3.3. REACTION PATHWAYS

An algorithm was derived to determine the distribution of isotopic carbon and oxygen in products formed from isotopically labeled gases. A detailed description of the algorithm is given in the Appendix. In this procedure the observed intensities within a cluster of mass spectral ions assignable to a specific structure are compared to the theoretical intensities generated by the algorithm for a grid of all possible fractions of isotopic carbon and oxygen. The theoretical pattern which corresponds most closely with that of the experimentally observed mass spectral pattern is used

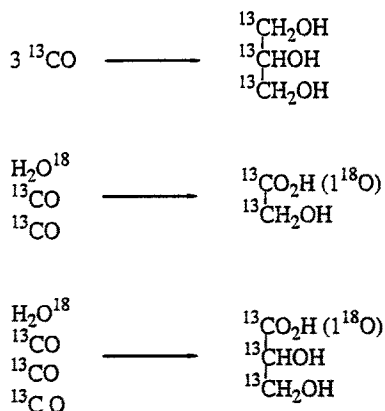
LOCATION OF ISOTOPIC LABELS

Fig. 10. Location of the isotopic labels in glycerol, glycolic acid and glyceric acid.

to determine the isotopic distribution pattern in that mass spectral fragment. An example of the comparison between a theoretical and experimental group of fragments for glyceric acid is given in Figure 9.

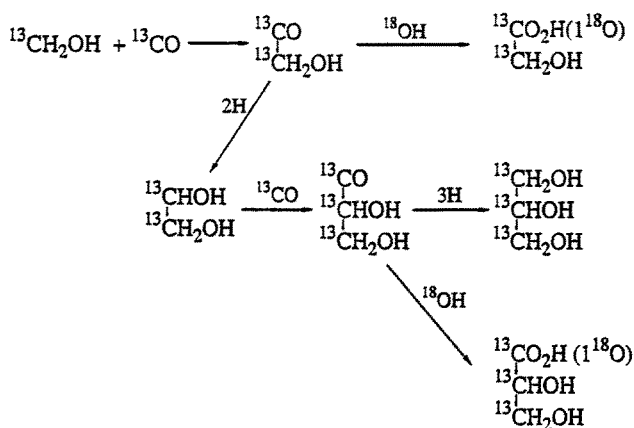
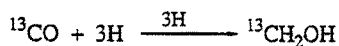
The ^{13}C and ^{18}O isotopic distribution was calculated for glycerol, glycolic acid and glyceric acid based on isotope fractionation processes shown in Figures 10–11. The isotopic ^{13}C and ^{18}O isotopic distribution for each fragment is listed in Table II. The data imply that the carbon atoms of glycerol, glycolic acid and glyceric acid contain ^{13}C when ^{13}C -carbon monoxide is used as carbon source. The only discrepancy in this implication is the fragment formed from the loss of CH_2OTMS from the parent molecule in which only 56% of the carbon has a ^{13}C label. This calculation is inconsistent with the results from four other fragments from the same molecule so is obviously incorrect.

The virtual absence of ^{18}O in glycerol shows that it is formed exclusively from ^{13}CO with none of the oxygen coming from H_2^{18}O . The presence of ^{18}O in the parent ion of glycolic and glyceric acids and its absence in peaks corresponding to the loss of CO_2 demonstrates the presence of ^{18}O exclusively in the carboxyl groups of these products. From the percentage of ^{18}O in each acid it is concluded that only one of the oxygens of the carboxylic acid originates from H_2^{18}O . The source of the carbon and oxygen in each of these three molecules is outlined in Figure 10.

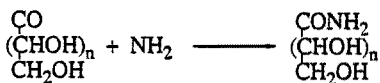
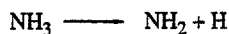
A postulated reaction scheme for the formation of the observed photoproducts was presented in our previous paper (Agarwal *et al.*, 1985). Now that the isotopic labeling pattern is known it is possible to write self-consistent reaction schemes for the photochemical formation of these three products (Figure 11). In part A of Figure 11 a reaction scheme derived from the carbon and oxygen isotopic labeling pattern is given. Hydrogen atoms formed by the photolysis of H_2^{18}O initiate the synthesis of the three molecules by adding to ^{13}CO to form CH_2OH . Additions

REACTION PATHWAYS

A. $\text{H}_2\text{O} + \text{CO}$



B. $\text{NH}_3 + \text{CO}$



$n = 0, 1$

Fig. 11. A. Proposed reaction pathway for the photochemical formation of glycolic acid, glycerol and glyceric acid. B. Proposed reaction pathway for the photochemical formation of amides.

TABLE II

Incorporation of isotope precursor gases into photoproducts: fraction of product carbon and oxygen as isotopic series

Glycolic Acid	^{13}C	^{18}O	Glyceric Acid	^{13}C	^{18}O	Glycerol	^{13}C	^{18}O
-Me	0.98	0.32	M ⁺	0.98	0.200	-Me	0.94	0.06
-Me-CO	0.86	0.26	-Me	0.96	0.24	-HOTMS	0.90	0.08
-Me-CO ²	0.92	0.08	-CH ₂ O	0.96	0.28	-CH ₂ OTMS	0.084	0.08
			-CH ₂ OTMS	0.56	0.30			
			-COOTMS	0.92	0.08			

Calculations were carried out only to the nearest 0.02. The percent label is based on the carbon and oxygen present before adding the TMS group to these molecules.

of CO to CH₂OH and subsequent reduction steps yielded glycerol. Oxidation with the ¹⁸OH radical generates the carboxylic acids containing one ¹⁸O in the carboxyl group.

It is possible to extrapolate from the mechanism in Figure 11 part A to a mechanism for the formation of carboxamides when NH₃ is present in the starting gas mixture (Figure 11, part B). The addition of NH₂, formed by the photolysis of NH₃ to the intermediates required for the formation of carboxylic acids yields the corresponding amides. The simple reaction pathways outlined in Figure 11 account for five major photoproducts formed from CO:H₂O:NH₃ mixtures.

Other analyses of the refractory material (see Mendoza-Gómez *et al.*, 1992) by various spectroscopic methods (electron impact mass spectrometry, fast atom bombardment mass spectrometry and tandem mass spectrometry) revealed the presence of higher molecular weight compounds which were not detected by GC-MS.

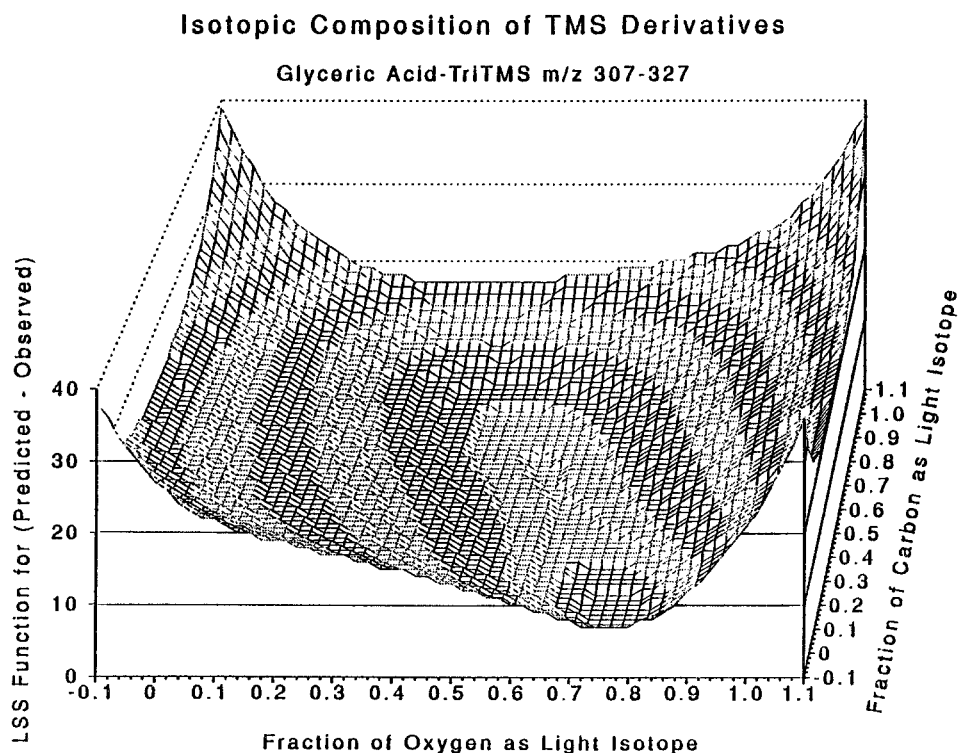


Fig. 12. Least sum of squares function of estimated minus observed intensities within the isotope cluster for the molecular ion minus methyl fragment of ¹³C- and ¹⁸O-labeled glyceric acid. The X- and Y-axes are the fraction of ¹⁸O- and ¹³C-respectively corresponding to the sum of the squares difference of each estimated value.)

Conclusions

The fact that the H_2O is a far more abundant species than CO shows that Halley is more representative of interstellar dust mantles composition (Greenberg, 1982b) than of the gaseous interstellar molecules (Mann and Williams, 1980). On the other hand the excess CO observed in comet Halley, relative to H_2O , as compared with the interstellar dust ratio, is observed as a distributed species and is therefore a decomposition product of species more refractory than H_2O (Eberhardt *et al.*, 1987).

The organic residues created in the laboratory have been subjected to two forms of analysis: GC/MS and electron impact mass spectroscopy (Mendoza-Gómez *et al.*, 1992). The component used in the GC/MS procedure generally consists of the more volatile species which are soluble in methanol and which pass through a GC column after derivatization. The total residue treated by electron impact-mass spectrometry (EI-MS) contains both molecules which pass through the GC column as well as those which do not. The more volatile species, those which evaporate at temperatures less than 400 K, are presumed to make up the difference between what exists in the interstellar grain organic refractory mantles and what is observed in comet Halley mass spectra. According to Kissel and Kruger (1987), only about 1/2 of the original comet organic refractory molecules remain as solid fractions of the comet dust, the rest appearing as part of the volatile coma molecules in the mass spectrometer. The non-refractory fraction which is either evaporated or pyrolyzed or both is needed to account for the excess simple molecular species CO, CN, C_2 , C_3 in the comet Halley coma.

It is generally assumed that polymers (CHON particles) are the distributed sources of the CO and CN observed in cometary comas (Ahearn *et al.*, 1986). However, we feel that the small molecules observed in the current and previous photochemical studies (Agarwal *et al.*, 1985; Ferris *et al.*, 1974) are more likely distributed sources of CO and CN. These compounds would have higher vapor pressures than polymers so would be more likely to vaporize before decomposing. Although it is not yet claimed to be a distributed molecule we note, for example, that CO_2 is formed by pyrolysis of oxalic and oxamic acids at 413–483 K (Clark, 1969) or photolysis of carboxylic acids (Wilkerson and Guillory, 1977; Ferris and Joshi, 1979; Epling *et al.*, 1980). CO is formed by pyrolysis of formamide at 470 K (Yasuda, 1967) and formaldehyde at temperatures greater than 423 K (Walker, 1964). CO is also formed by the photolyses of formaldehyde and other aldehydes and ketones (Walker, 1964; Lee and Lewis, 1980) and by photolysis of isocyanic acid (Wolley and Back, 1968). Isocyanic acid is formed by pyrolysis of urea at temperatures greater than 393 K (Smolin and Rapoport, 1959). HCN is formed by pyrolysis of formamide at 470 K (Yasuda, 1967). The CN observed could then be formed by photodissociation of the distributed HCN. We would attribute the distributed CN to pyrolysis of the volatile fraction of the organic refractories rather than photosputtering of CHON particles (Clairemidi *et al.*, 1990). On the other hand, the C_2 , C_3 jets may come from the fine dust. Vaisberg *et al.* (1986) observed a change in grain size distribution

with distance from nucleus. Fine grains become overabundant and the relative abundance of medium size grains seem to decrease with increasing distance. The overabundance of C^+ in the coma of comet Halley has been attributed to the CHON grains which may correspond to the organic residue prepared in this study (Neugebauer *et al.*, 1991).

One is led to conclude that the interstellar dust molecular compounds, from the most volatile to the least volatile, are carried forward into comets in ratios characteristic of observations of interstellar dust, a possible exception being CO, which has variable abundances in comets (Mumma *et al.*, 1992; Yamamoto, 1991). Not only the complex organic molecules but the simpler molecules in the other interstellar dust mantles appear to have largely preserved their integrity in the process of comet aggregation and as comet volatiles are in relative proportions more like that produced in the interstellar environment than in the solar nebula (Mumma *et al.*, 1992).

To a lesser extent, this is evidently true for meteorites where, based on arguments like that of Yamamoto (1991) for comets, perhaps some, but less, of the volatiles were preserved in the parent asteroid body. The preservation of H_2O in *liquid form* in asteroids would be the means by which the anhydrous silicates of interstellar dust are converted to hydrated (layer lattice) silicates similar to the suggestion by Bunch and Chang, 1980 that meteoritic organic compounds may have resulted from aqueous reactions of organics brought into the parent body. Along with the (liquid) H_2O , if the interstellar dust CO_2 is preserved, one has a basis for producing carbonic acid and consequently this would explain the presence of carbonates in meteorites. The evidence that volatiles such as H_2O and CO_2 were preserved in meteorite parent bodies automatically leads to the conclusion that interstellar organics were also preserved. Although heating to ~ 400 K has been inferred (Chyba *et al.*, 1990), this temperature is low enough not to have greatly altered the initial organic molecular composition. For example, three of the compounds identified in our study as being formed on interstellar grains, oxalic acid, glycolic acid and glycine, have been detected in the Murchison meteorite (Cronin *et al.*, 1988; Peltzer *et al.*, 1984; Peltzer and Bada, 1978). A puzzle still remains as to why meteorites whose parent bodies preserved the H_2O contain about a ten times less organic:silicate ratio than comets. Even if their parent bodies resulted from accretion of rocky planetesimals along with icy planetesimals as suggested by Bunch and Chang (1980), it is not clear why the mix occurs on the small scales of meteorites.

Calculations show that an enormous rate of mass input by comets was made to the earth in its first 500 million years (Chyba *et al.*, 1990). If comets were compact objects most of the organics would have been pyrolyzed as a result of shocks induced during impact with the earth. On the other hand, very fluffy comets whose morphological structure consists of interstellar core-mantle grains are highly likely to have preserved a large fraction of the interstellar organics in unaltered form (Greenberg, 1986c).

The conclusion that comets consist of unaltered interstellar dust grains provides

a direct link between interstellar dust and the origins of life. Since one Halley size comet carries $\sim 1/10$ of the present earth's biomass in the form of these refractory organics, it is plausible to conjecture that one comet or only a few comets impacting the earth at the tail end of the major comet impact epoch could have provided all the organic material needed for the origins of life. The two important presumptions here are that the very fluffy character of a comet aggregated from interstellar dust sized particles will easily fragment upon impact on the earth's atmosphere and that the atmosphere was thick enough to cushion the flying fragments during their passage to the surface (Greenberg and Mendoza-Gómez, 1992).

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Appendix: Calculation of Ratios of Isotopes in Mass Spectral Fragments – A First Approximation

The distribution of isotopic carbon and oxygen in selected analytes was determined by use of a sum of squares function: the squared sum of observed intensities within a cluster of ions assignable to a specific structure subtracted from corresponding theoretical intensities for given carbon and oxygen isotopic abundance. Values of the function were calculated for a grid of all possible fractions of isotopic carbon and oxygen from minus 0.1 to plus 1.1 at fraction intervals of 0.02. Theoretical intensity at a given fragment mass was determined by summing the probabilities of all structures having that mass.

Probabilities were calculated as follows:

Suppose a molecule is composed of i atoms of a given element where each element occurs in one of J_i isotopic forms. Let $P_{i,j}$ denote the probability of observing isotope j of element i , $0 \leq P_{i,j} \leq 1$. $\sum_{j=1}^{J_i} P_{i,j} = 1$. A given spectrometrically observed

mass, in general, arises from a set of molecular species. Suppose there are n_ϱ members of the set with mass ϱ . Let $V_{i,j,k,\varrho}$ denote the number of atoms of element i in isotopic form j in the k th species of the set of molecular species with mass ϱ . Then ρ_ϱ , the probability of spectrometrically observing mass ϱ , is computable as:

$$\rho_\varrho = \sum_k \prod_{i=1}^I \prod_{j=1}^{J_i} P_{i,j} V_{i,j,k,\varrho}.$$

The constraint that, for every k and ϱ , $\sum_i \sum_j V_{i,j,k,\varrho}$ is the number of atoms in the molecule assures that $\sum \rho_\varrho = 1$.

For carbon, only ^{12}C and ^{13}C isotopes were considered while for oxygen, only ^{16}O and ^{18}O were used. Thus, for these elements, $p_{i,2} = 1 - p_{i,1}$. TMS (trimethylsilyl) and DMS (dimethylsilyl) groups were treated as elements with four isotopic forms with fixed fractional abundances of 0.892, 0.075, 0.032, 0.001 and 0.902, 0.066, 0.031, 0.001 at mass increments of 0, 1, 2, 3 for TMS and DMS respectively.

Calculations were performed using IMID (©1989, WCL&R), a program written in Turbo Basic (ver. 1.1, Borland International, Scotts Valley, CA), run on a 20 MHz IBM AT-compatible computer with Intel 80386 processor and a 20 MHz Intel 30387 math coprocessor. IMID was optimized by assuring that only those values affected by the changed test values were recalculated with each of the 3721 iterations. Algorithms for rapid approach to minima in the matching function were not applied. Calculation times ranged from a few minutes to over an hour depending on the number of atoms in the fragment of concern.

Figures 9a and b depict the intensities for the mass 307 cluster of glyceric acid labelled with ^{13}C and ^{18}O and the theoretical intensities which correspond to the least sum of squares-best fit. Observed cluster intensities do not perfectly follow the theoretical distribution, particularly at even masses. Nevertheless, there is but a single minimum for the least sum, of squares function (Figure 12). The differences evident in this comparison may be due to our first approximation model which treats all positions on the molecule as having equivalent relative abundances for the appropriate isotopes. A model based on incorporation of CO as a unit rather than on independent incorporation of carbon and oxygen might improve the fit. This will be an aspect of future efforts.

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