

# Production and Chemical Analysis of Cometary Ice Tholins

GENE D. McDONALD, LINDA J. WHITED, CYNTHIA DERUITER, BISHUN N. KHARE,  
ARCHITA PATNAIK, AND CARL SAGAN

*Laboratory for Planetary Studies, Cornell University, Ithaca, New York 14853-6801*  
E-mail: mcdonald@astrosun.tn.cornell.edu

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Organic heteropolymers that we call here ice tholin II have been produced by plasma discharge irradiation of water/methanol/carbon dioxide/ethane cocondensed ices in a rough simulation of cometary chemistry. The radiation yield of these organic heteropolymers is approximately  $10^{-26}$  g/eV. Intermediate products including polyalcohols, ethers, esters, carboxylic acids, and hydrocarbons are also produced. No detectable polyoxymethylene is generated in this experiment. Preliminary chemical analyses of ice tholin using spectroscopic and chromatographic techniques lead to the conclusion that ice tholin contains a significant degree of polyalcohol functionality, as well as aliphatic hydrocarbon groups and carbonyl-containing groups such as ketones and esters. Ice tholin II shows some spectroscopic similarities to 1:6 ethane/water ice tholin (ice tholin I), but overall the two are chemically distinct. Ice tholins may be difficult to detect in comets due to their low volatility, but nevertheless may have been delivered to the early Earth by cometary impacts and interplanetary dust particles. These polyalcohol-containing molecules would then have been available to participate in prebiotic chemistry, such as the synthesis of acyclic nucleic acid analogues which have been suggested as the first biomacromolecules. © 1996 Academic Press, Inc.

## INTRODUCTION

After the 1986 spacecraft encounters with Comet Halley, comets are understood to correspond to Whipple's "dirty ice" model, being made mainly of water ice and perhaps 25% by mass of organic compounds; methane may constitute a few percent, with significant amounts of CO<sub>2</sub> ice varying from comet to comet (Delsemme 1991, Chyba *et al.* 1990). The latest interpretation of time-of-flight mass spectrometry of dust particles in the coma of Comet Halley, measured with the Vega and Giotto spacecraft, cautiously identifies particular molecules (Kissel and Krueger 1995; cf. Kissel and Krueger 1987, Jessberger *et al.* 1989). There seem to be large quantities of mainly unsaturated hydrocarbons, lesser quantities of such simple oxygen-containing organics as formic acid and methanol, and still lower abun-

dances of nitriles and other nitrogen-containing organics. The most thermodynamically favored cometary ices are clathrate hydrates (Delsemme and Swings 1952, Delsemme 1976); unprocessed hydrocarbons are expected primarily as the methane clathrate hydrate, with a maximum occupancy ratio of H<sub>2</sub>O to CH<sub>4</sub> of 5.75:1. Lower-occupancy clathrates are quite plausible.

Since meters of ice are lost with each perihelion passage by comets entering the inner Solar System, postaccretion solar wind and ultraviolet irradiation can play at most only minor roles in synthesizing involatile cometary organic matter (Chyba and Sagan 1989). Since their penetration depths are only on the order of meters, cosmic rays—even integrated over the history of the Solar System—cannot play a major role either. Instead (Chyba and Sagan 1989), the organics either must have been generated by irradiation of the bulk of undifferentiated comets by aluminum-26 and other now-extinct radionuclides, or they must have been present in the interstellar material which was gathered together to form the comets (Greenberg 1982). Despite higher UV doses in low-density regions of interstellar space (Greenberg 1982), cosmic ray doses may be fully sufficient to convert carbon-containing ice grains entirely to complex organics in less than the lifetime of the typical interstellar cloud (Strazzulla *et al.* 1983). Thus, experiments on the charged particle irradiation of mixed water and carbon-containing ices or their clathrates, using either high-energy ion sources (e.g., Strazzulla *et al.* 1983) or lower-energy inductively coupled plasma discharges, may have a bearing on the origin of cometary organic molecules.

In experiments on inductively coupled plasma irradiation of low-occupancy H<sub>2</sub>O/CH<sub>4</sub> clathrate and of intimate mixtures of H<sub>2</sub>O with CH<sub>4</sub> or C<sub>2</sub>H<sub>6</sub> (with and without NH<sub>3</sub>), initially white ices progressively darken and redden, reaching very low albedos after cumulative radiation dosages much less than what is expected in cometary nuclei (Comet Halley at least) and the interstellar grains that are precursors to comets (Thompson *et al.* 1987, Khare *et al.* 1989a). It is natural to suggest that the low albedo and at

least occasional red spectrometric slope in the visible spectra of comets are due to such irradiation processes. In the same experiments, after irradiation the ices were evaporated (under high vacuum at about 425 K—very close to what happens in some cometary comae, e.g., that of Comet Halley) and the solid organic residue examined. The involatile residues remaining after the irradiation of CH<sub>4</sub> clathrate and of C<sub>2</sub>H<sub>6</sub>/H<sub>2</sub>O mixtures show extremely similar UV/visible and infrared spectra (Thompson *et al.* 1987, Khare *et al.* 1989a,b), including the prominent triplet at 3.4 μm due to C–H vibration. Infrared spectra of the comae of Comet Halley (e.g., Combes *et al.* 1988, Baas *et al.* 1986, Knacke *et al.* 1986) and a number of other comets (e.g., Allen and Wickramasinghe, 1987) show a similar feature. A simple two-component thermal emission model of the fine particles in cometary comae, assuming that the organic residue in the ice irradiation experiments is responsible, is in agreement with the cometary observations and yields optical depths consistent with those implied by spacecraft data (Chyba and Sagan 1987, Chyba *et al.* 1989). More recent estimates (e.g., Di Santi *et al.* 1995; also see Bockelee-Morvan *et al.* 1995) attribute these features to a mix of solid and gas-phase (chiefly, gaseous CH<sub>3</sub>OH) organics.

Cometary contributions to the organic inventory of the Earth at the time of the origin of life may have been significant—especially if the early atmosphere was in an approximately neutral oxidation state (Oro 1961, Chang 1979, Greenberg 1981, Chyba and Sagan 1992). Cometary organics could have been delivered by airbursts, as interplanetary dust particles (IDPs) of cometary origin, or in the relatively unheated pole of intact impacting comets (Chyba *et al.* 1990). It is conceivable, although by no means certain, that delivered organic molecules might be significantly different from organics synthesized by endogenous processes on the early Earth (Chyba and Sagan 1992). Thus, even if cometary organic matter played a quantitatively minor role in the origin of life, it is still conceivable that its qualitative significance was disproportionately large.

In an extension of earlier experiments with more reduced ice mixtures (Khare *et al.* 1989a,b, 1993, Thompson *et al.* 1987), we here describe experiments in which H<sub>2</sub>O/CH<sub>3</sub>OH/CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> cocondensed ices are irradiated. We report yields of a second class of higher-molecular-weight organics (ice tholin II), as well as identifications of several intermediate mass products, present chromatographic and spectroscopic analyses of ice tholin II, infer a generalized structure, and discuss the relevance of these experiments to cometary and prebiotic chemistry.

## ICE THOLIN II PRODUCTION

### *Ice Irradiation*

As in previous work (Khare *et al.* 1989a,b, 1993, Thompson *et al.* 1987), in this experiment ice tholin was generated

by inductively coupled plasma irradiation of cocondensed ices. The initial ice composition was 80% H<sub>2</sub>O, 16% CH<sub>3</sub>OH, 3.2% CO<sub>2</sub>, and 0.8% C<sub>2</sub>H<sub>6</sub>, chosen as a first-order approximation to known and inferred cometary composition (Allen *et al.* 1987, Balsiger *et al.* 1986, Woods *et al.* 1986, Bockelee-Morvan *et al.* 1994, Di Santi *et al.* 1995). A schematic of the system design is shown in Fig. 1. The reaction vessel was 11.5 cm in diameter and 15 cm tall. A Tesla coil was used to generate plasma in a 30-Torr He atmosphere overlying the ice. During deposition of the reagent ices, the walls of the vessel were periodically scraped by stirring blades in order to concentrate the ice in the vessel bottom and to maximize the surface area of ice to be irradiated. The result was a relatively smooth ice deposit on the vessel walls, with an irregular surface layer on the vessel bottom. A 24-hr control run using only H<sub>2</sub>O ice and the He discharge produced no tholin or volatile products detectable by either HPLC or GC/MS.

We report the results from two experimental runs of 10 and 14 days (Runs 1 and 2, respectively). The tholin produced from each run was recovered from the walls of the reaction vessel by extraction with HPLC-grade methanol (Fisher), and then concentrated in a preweighed vial by removal of methanol under vacuum. Weight of the dried methanol-soluble material (>95% of the total ice tholin produced) from Run 1 was 32.4 mg, yielding a production rate of  $3.8 \times 10^{-4}$  g tholin/g total reactant C/hr, or  $1.7 \times 10^{-4}$  g tholin/g CH<sub>3</sub>OH/hr. From Run 2, 46.2 mg tholin was produced, yielding a production rate of  $5.7 \times 10^{-4}$  g tholin/g total reactant C/hr, or  $1.8 \times 10^{-4}$  g tholin/g CH<sub>3</sub>OH/hr. Total radiation yields, assuming an average Tesla coil power of approximately  $10^{22}$  eV/hr (McDonald *et al.* 1992), were  $1 \times 10^{-26}$  g/eV for Run 1 and  $2 \times 10^{-26}$  g/eV for Run 2. These production rates and yields are constant between the two runs, within experimental error.

These ice irradiation experiments were carried out at 77 K for technical reasons. This makes the results entirely relevant to the situation in which cometary material is exposed to the temperatures at heliocentric distances of 10–30 AU, and perhaps somewhat less relevant to radiation-driven chemistry in icy interstellar grains at temperatures of 20 K or less. The kinetics of chemistry driven by plasma processes, however, are usually nonequilibrium, and so reaction rates in these systems are not highly dependent on temperature (Bugenko *et al.* 1993). The variation of ice structure with temperature might have some effect on this type of chemistry, but H<sub>2</sub>O/CH<sub>3</sub>OH ices deposited at 10 K and slowly warmed show little structural change until temperatures of 120–130 K are reached (Blake *et al.* 1991). The radiation-induced decomposition of water decreases approximately linearly with temperature below 195 K (Draganic *et al.* 1984), with a decrease of only 50% from 77 to 20 K indicated. It would appear, therefore, that simulations of the radiation chemistry of mixed ices at

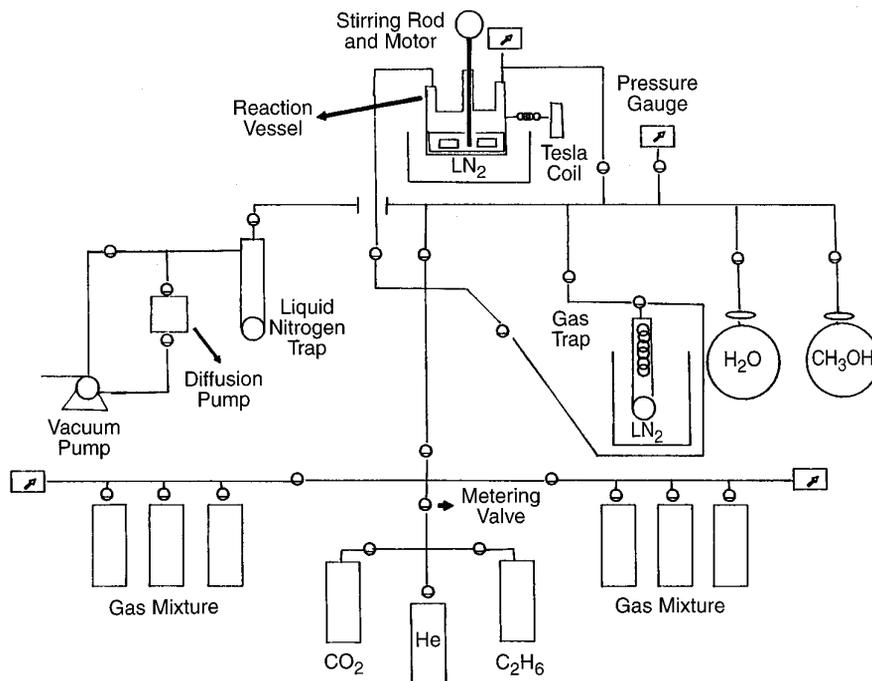


FIG. 1. Schematic diagram of the experimental system used to produce ice tholin.

77 K are for the most part applicable to lower-temperature environments as well.

## CHEMICAL ANALYSIS OF ICE THOLIN II

### GC/MS Analysis

After irradiation was stopped, the volatile products were transferred into a smaller liquid nitrogen trap and warmed to room temperature. Both the gas-phase and liquid products were then analyzed by GC/MS. The nonvolatile ice tholin was then extracted from the reaction vessel with methanol, and this extract was also analyzed by GC/MS.

All GC/MS analyses were done on a Hewlett-Packard 5880A gas chromatograph coupled to a HP 5970 mass selective detector. A Chrompak CPWAX capillary column (25 m in length, 0.25 mm i.d.) was used, with He carrier gas at a flow rate of 0.4 ml/min. The initial temperature was 45°C, held for 8 min, and then increased at a rate of 5°C/min to 200°C. The mass range of the detector was 10–800 amu. The GC/MS chromatograms for ice tholin methanol extract at irradiation times of 10 days (Run 1) and 14 days (Run 2) are shown in Fig. 2. The methanol-soluble intermediate mass products, as well as the gas-phase products (chromatograms not shown), identified from mass spectral library searches of these data sets are listed in Table I. Gas chromatography of methanol extract derivatized with bis(trimethylsilyl)trifluoroacetamide (BSTFA) to produce trimethylsilyl derivatives was also carried out, but no additional products were detected.

The compounds listed in Table I include carboxylic acids, esters, saturated and unsaturated hydrocarbons, mono- and polyalcohols, hydroxy acids and hydroxy esters, and ethers. A few of the products did not match library mass spectra with a high degree of probability and are thus labeled as tentative identifications. Quantitative analysis of the intermediate mass products is not reported because many of them are volatile to some extent at low pressures, and thus may have been partially lost during transfer and concentration of the samples under vacuum.

### Infrared Spectroscopy

An aliquot of the ice tholin II methanol-soluble fraction was dried onto a KBr window, and infrared spectra were collected using a Mattson 6020 FTIR spectrometer. Figure 3 shows the infrared spectra of ice tholin after irradiation for 10 days (Run 1) and 14 days (Run 2). The bulk ice tholin spectrum shows a very strong O–H stretching band at 3306  $\text{cm}^{-1}$  (2.99  $\mu\text{m}$ ). C–H stretching bands at 2958, 2933, and 2876  $\text{cm}^{-1}$  (3.38, 3.41, and 3.48  $\mu\text{m}$ ), as well as C–H bending bands at 1458 and 1398  $\text{cm}^{-1}$  (6.86 and 7.15  $\mu\text{m}$ ), are also present. The strong band at 1664  $\text{cm}^{-1}$  (6.01  $\mu\text{m}$ ) is probably mostly due to C=O, with some C=C as well. The strong bands at 1105 and 1043  $\text{cm}^{-1}$  (9.05 and 9.58  $\mu\text{m}$ ) are attributed to C–O and C–C vibrational modes.

The infrared spectrum of ice tholin II appears to evolve slightly as irradiation time increases. The spectrum from Run 2 (Fig. 3B) contains two additional C=O stretching bands, one to either side of the original 1664  $\text{cm}^{-1}$  band

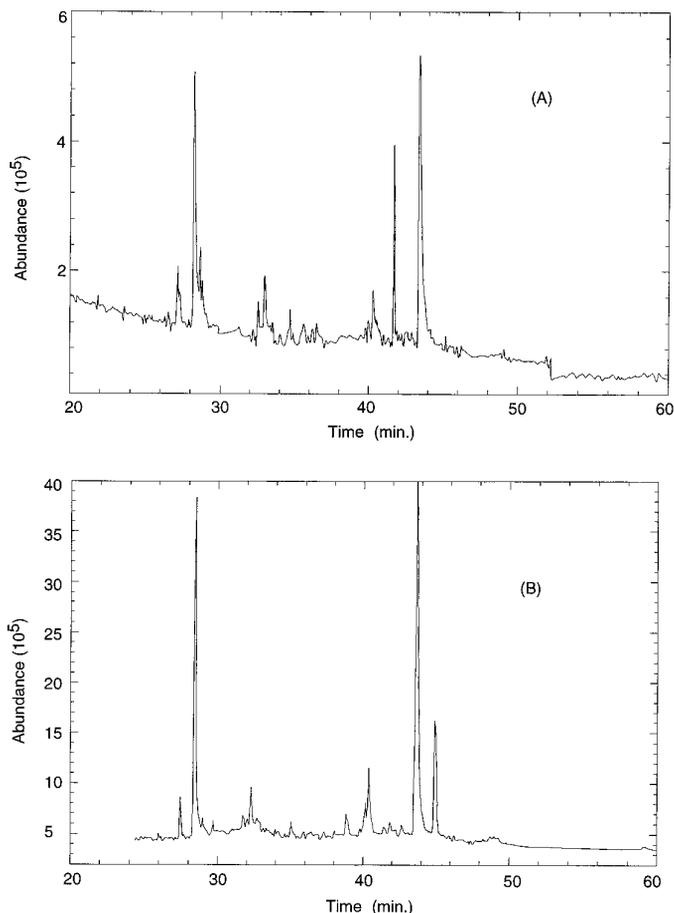


FIG. 2. GC/MS chromatogram of ice tholin II methanol fraction on a Chrompak CPWAX column: (A) Run 1 (10 days irradiation); (B) Run 2 (14 days irradiation).

in the spectrum from Run 1 (Fig. 3A). The  $3306\text{ cm}^{-1}$  ( $2.99\text{ }\mu\text{m}$ ) O–H band also appears to shift to shorter wavelength with increased irradiation time. The other infrared bands show no significant shifts in wavelength, although the ratios of the three C–H bands may change slightly.

#### Ultraviolet Spectroscopy

The ice tholin II methanol extract ( $1\text{ }\mu\text{l}$ ) was injected into the HPLC system described below with the column bypassed so as to function as a flow-through UV/Vis spectrophotometer. The detector was zeroed against the methanol mobile phase. The spectrum of this extract from 190 to 400 nm is shown in Fig. 4. The spectrum shows a single band with maximum absorbance at 200–205 nm. No absorbance at wavelengths longer than 400 nm was observed.

#### Liquid Chromatography

Ice tholin II methanol extract was injected onto a Waters 600E high-pressure liquid chromatograph coupled to a Wa-

TABLE I  
H<sub>2</sub>O/CH<sub>3</sub>OH/CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> Ice Tholin Experiment:  
Intermediate Products Identified by GC/MS

Formic acid (t) <sup>a</sup>	HCOOH
Methyl formate	HCOOCH <sub>3</sub>
Acetylene	C <sub>2</sub> H <sub>2</sub>
Ethylene glycol	(CH <sub>2</sub> OH) <sub>2</sub>
Acetic acid	CH <sub>3</sub> COOH
Glycolic acid (t)	HOCH <sub>2</sub> COOH
Dimethyl ether	CH <sub>3</sub> OCH <sub>3</sub>
Methyl acetate	CH <sub>3</sub> COOCH <sub>3</sub>
Glycerol	(CH <sub>2</sub> OH) <sub>3</sub>
Hydroxypropanone	HOCH <sub>2</sub> COCH <sub>3</sub>
Methoxyacetaldehyde (t)	CH <sub>3</sub> OCH <sub>2</sub> COH
Dimethoxymethane (t)	CH <sub>3</sub> OCH <sub>2</sub> OCH <sub>3</sub>
1,3,5-trioxane (t)	(CH <sub>2</sub> O) <sub>3</sub>
Propane	C <sub>3</sub> H <sub>8</sub>
Methylpropane	C <sub>4</sub> H <sub>10</sub>
Butane	C <sub>4</sub> H <sub>10</sub>
Methylpropanoate	CH <sub>3</sub> CH <sub>2</sub> COOCH <sub>3</sub>
Hydroxybutanone	HOCH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub>
Butanediol	C <sub>4</sub> H <sub>8</sub> (OH) <sub>2</sub>
Methylbutane	C <sub>5</sub> H <sub>12</sub>
Pentane	C <sub>5</sub> H <sub>12</sub>
Cyclopentane/methylcyclobutane	C <sub>5</sub> H <sub>10</sub>
Pentanol/methylpropanol	C <sub>5</sub> H <sub>11</sub> OH
Methylbutenol (t)	C <sub>5</sub> H <sub>9</sub> OH
Hexane	C <sub>6</sub> H <sub>14</sub>
Methylpentane	C <sub>6</sub> H <sub>12</sub>
Methylhexane	C <sub>7</sub> H <sub>16</sub>

<sup>a</sup> (t), tentative identification.

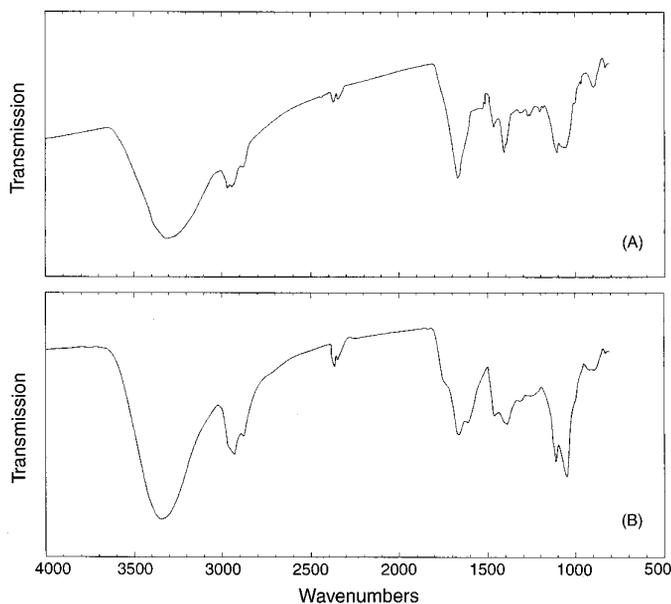


FIG. 3. Infrared spectra of ice tholin II produced from irradiation for 10 days (Run 1) and 14 days (Run 2).

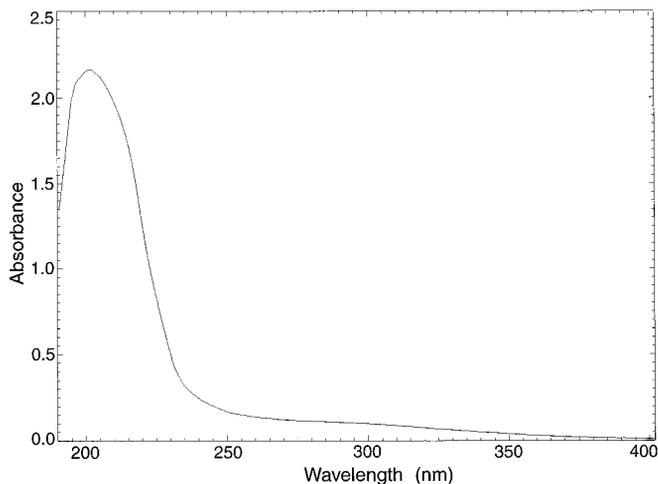


FIG. 4. Ultraviolet spectrum of ice tholin II from Run 1, in methanol.

ters 990 photodiode array detector. A Waters  $\mu$ -Bondapak  $\text{NH}_2$  column,  $3.9 \times 30$  cm, was used, with a mobile phase of 25% methanol and 75% acetonitrile, and a flow rate of 0.5 ml/min. The HPLC chromatograms from Runs 1 and 2 are shown in Figs. 5A and 5B, respectively. Integration of these chromatograms, and comparison with that of an equal amount of ice tholin methanol extract injected onto the system with the column removed, indicates that the material eluting from the column represents about 50% of the total material injected. The remainder of the injected material presumably does not elute from the column under the conditions used. Figure 5C shows the HPLC chromatogram of ice tholin I, the product of  $\text{H}_2\text{O}/\text{C}_2\text{H}_6$  ice irradiation (Khare *et al.* 1989a,b, 1993, Thompson *et al.* 1987). Although the chromatographic conditions are not identical to those used for ice tholin II, it is apparent that both ice tholins contain one major eluting fraction and two to three minor fractions.

Ultraviolet spectra of the ice tholin II  $\text{NH}_2$  column fractions from 190 to 400 nm were obtained online during separation, as shown in Fig. 6. All HPLC peaks show absorption maxima at 200–210 nm, probably due to  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$  functional groups. The major peak in each chromatogram also has an absorption band at 280–290 nm, while the other peaks have two additional broadbands at approximately 240 and 290 nm, suggesting either conjugated double bonds or aromatic structures.

The ice tholin II HPLC peaks were collected during multiple runs, pooled, concentrated under vacuum, and dried onto KBr windows. The minor peaks were combined due to insufficient chromatographic resolution. IR spectra of the major peaks and the combined minor peaks were then collected using a Mattson 6020 FTIR spectrometer, as shown in Fig. 7. The spectrum of the major peak shows several C–H stretching bands at  $3024$ ,  $2968$ , and  $2930$   $\text{cm}^{-1}$

( $3.31$ ,  $3.37$ , and  $3.41$   $\mu\text{m}$ ). The broader band at  $3144$   $\text{cm}^{-1}$  ( $3.18$   $\mu\text{m}$ ) is probably an additional aromatic C–H band overlying an O–H band, which can be seen as a shoulder at around  $3400$   $\text{cm}^{-1}$  ( $2.94$   $\mu\text{m}$ ). The C–H bending mode at  $1404$   $\text{cm}^{-1}$  ( $7.12$   $\mu\text{m}$ ) is also strong, while the  $\text{C}=\text{O}/\text{C}=\text{C}$  band at  $1656$   $\text{cm}^{-1}$  ( $6.04$   $\mu\text{m}$ ) and the C–O/C–C band at  $1064$   $\text{cm}^{-1}$  ( $9.40$   $\mu\text{m}$ ) are less intense.

The spectrum of the minor peaks, in contrast, shows a very strong O–H band at  $3335$   $\text{cm}^{-1}$  ( $3.00$   $\mu\text{m}$ ), and a strong aliphatic C–H band at  $2924$   $\text{cm}^{-1}$  ( $3.42$   $\mu\text{m}$ ). The  $\text{C}=\text{O}/\text{C}=\text{C}$  band ( $1664$   $\text{cm}^{-1}$ ,  $6.01$   $\mu\text{m}$ ) and the C–O/C–C band ( $1053$   $\text{cm}^{-1}$ ,  $9.50$   $\mu\text{m}$ ) are relatively stronger than those in

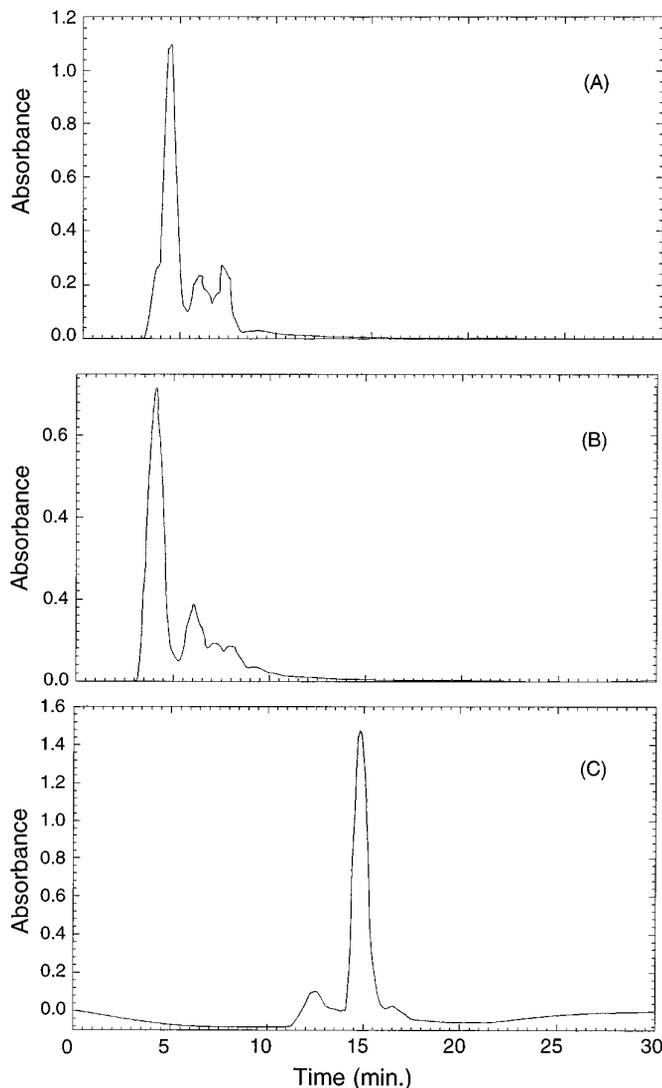
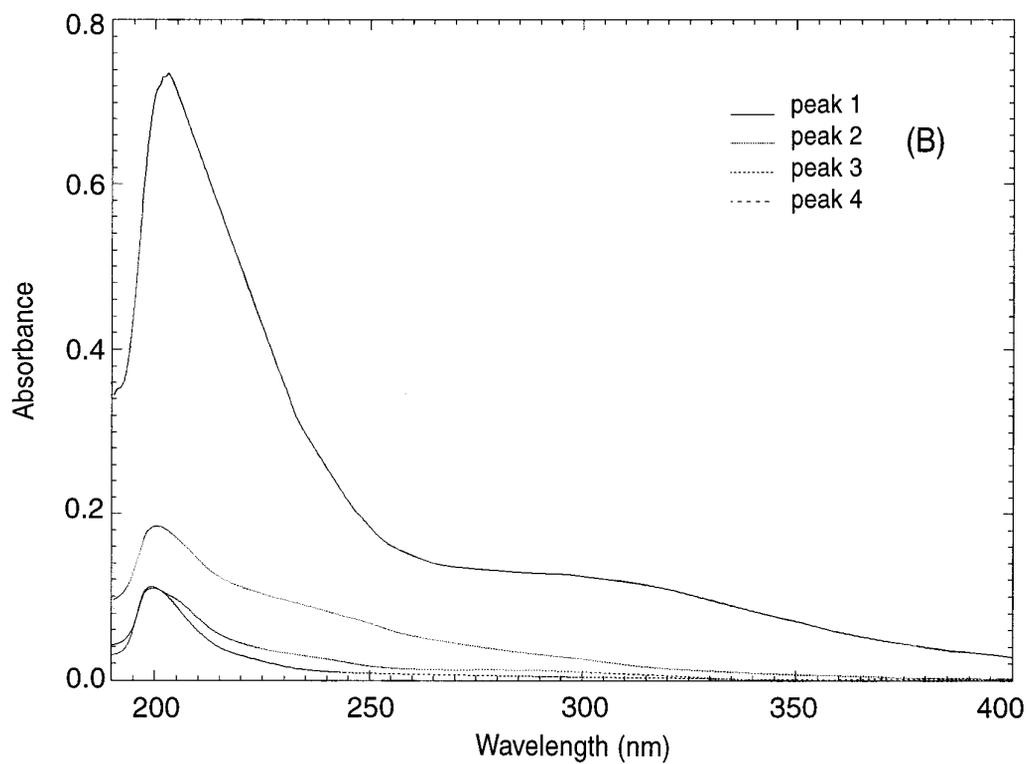
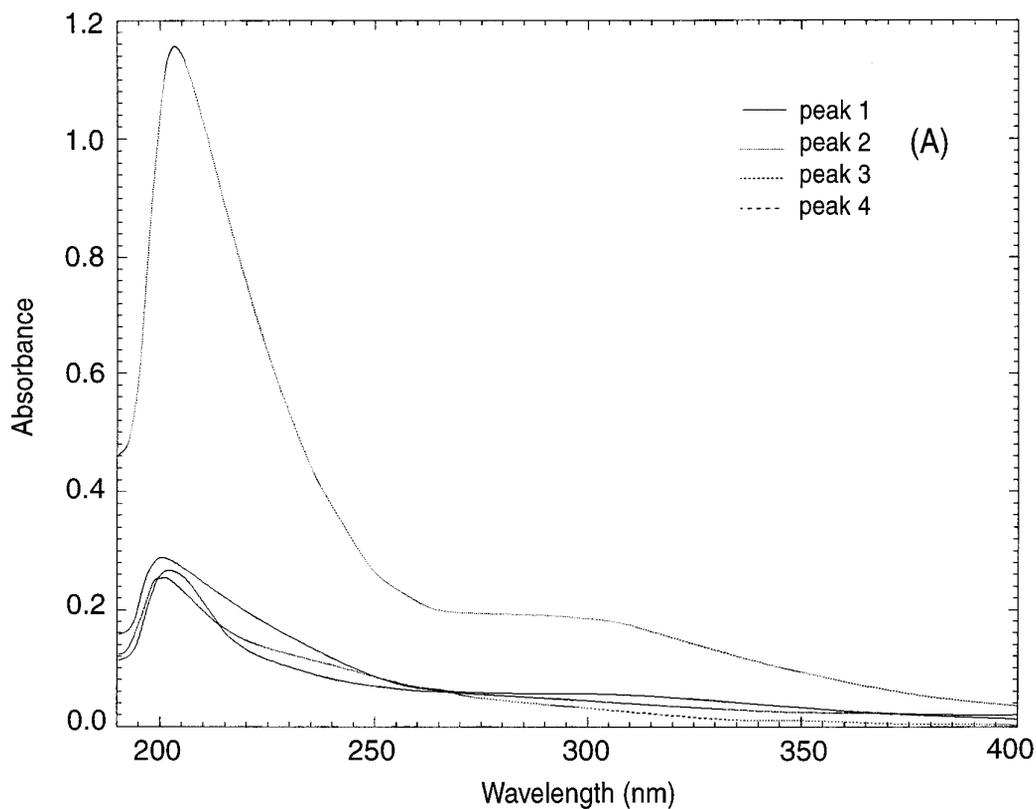


FIG. 5. HPLC chromatogram of ice tholin II methanol extract from (A) Run 1 and (B) Run 2 on a  $\text{NH}_2$  column (mobile phase 25% methanol/75% acetonitrile). (C) HPLC chromatogram of ice tholin I on a CN column (mobile phase 10–90% 1-propanol in hexane). Detection wavelength was 206 nm.



**FIG. 6.** Ultraviolet spectra of ice tholin II HPLC fractions. (A) Run 1. Retention times are as follows: peak 1, 3.85 min; peak 2, 4.45 min; peak 3, 5.9 min; peak 4, 7.35 min. (B) Run 2. Retention times are as follows: peak 1, 4.1 min; peak 2, 5.95 min; peak 3, 7.15 min; peak 4, 8.05 min.

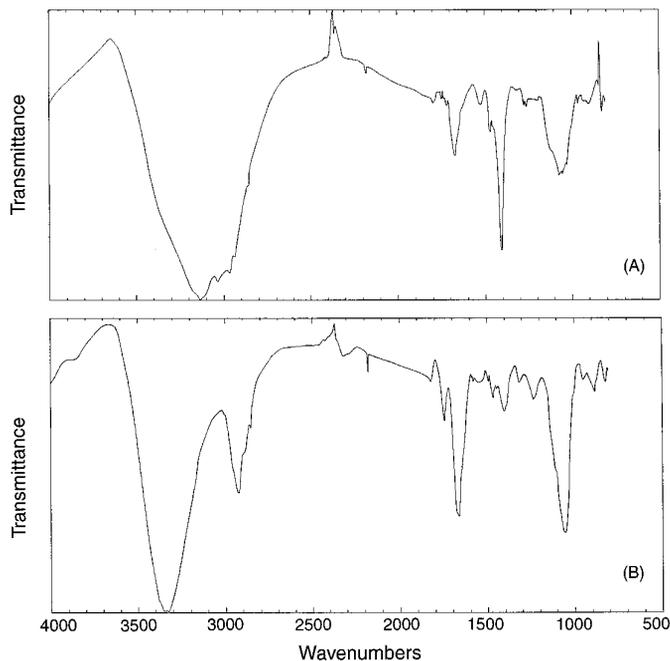


FIG. 7. Infrared spectra of ice tholin II HPLC fractions from Run 1: (A) peak 1; (B) peaks 2–4.

the major peak, while the C–H bending band at  $1400\text{ cm}^{-1}$  ( $7.14\text{ }\mu\text{m}$ ) is weaker.

#### Comparison of Ice Irradiation Products

Figure 8C shows the infrared spectrum of the ice tholin II discussed above, while Fig. 8A shows the spectrum of ice tholin I made with similar apparatus from a 1:6 ethane: water ice mixture. The overall shapes of the two spectra are similar, but there are noticeable differences. Both spectra contain O–H and C–H stretching bands, but in ice tholin II the O–H band is at least twice as intense as the C–H band, while the reverse is true for ice tholin I. This is consistent with the higher hydrocarbon/hydroxyl ratio of the ethane/water mixture relative to the water/methanol/carbon dioxide/ethane mixture used in the current work. The shapes and wavelengths of the C=O/C=C stretch, C–H bend, and C–O/C–C stretch bands are also not identical in the two spectra. Overall, it appears from the infrared spectra that the current ice tholin is not identical to earlier ethane/water ice tholins for which optical constants have been determined (Khare *et al.* 1993).

It should be noted, however, that in previous work (Khare *et al.* 1993), the O–H/C–H band intensity ratio of unheated ice tholin I more closely resembles that of ice tholin II; when ice tholin I is heated, this ratio becomes less than unity. The O–H/C–H ratio is also not constant in various other hydrocarbon/water ice tholins (Khare *et al.* 1989a,b, Strazzula *et al.* 1984). The O–H/C–H ratio

may be affected by occluded or adsorbed water in tholin thin films, although O–H bands due to water of crystallization are usually weak (Dean 1992). In any case, caution should be used in the interpretation of the O–H/C–H ratio in ice tholin spectra.

Among the intermediate mass products, ethylene glycol, glycerol, glycolic acid, and formic acid have been identified as products of  $\text{H}_2\text{O}/\text{CO}/\text{NH}_3$  ice photolysis experiments (Agarwal *et al.* 1985). Agarwal *et al.* (1985) also obtained infrared spectra of involatile residue from these experiments. These spectra are somewhat similar to our ice tholin spectra in the ratios of O–H, C=O/C=C, and C–H bands, but lack the strong C–O bands.

#### Structure and Formation of Ice Tholins

From the data reported above, we can draw a few general conclusions about the structure of ice tholins. Hydroxyl groups are present in significant numbers, as shown by the strong O–H bands in the infrared spectra (Figs. 3 and 8). The C–H bonds appear from the infrared spectra of bulk ice tholin (Fig. 3) to be mostly aliphatic. However, the infrared spectrum of HPLC peak 1 (Fig. 7A) shows C–H bands above  $3000\text{ cm}^{-1}$  ( $3.33\text{ }\mu\text{m}$ ) which could be associated with aromatic structures, and weak absorbance bands characteristic of aromatics (250–300 nm) can be seen in the UV spectra of the major HPLC peaks (Fig. 6). The C–H bands in HPLC peaks 2–4 (Fig. 7B) appear to be mostly aliphatic. We can infer from these data that the overall degree of saturation in ice tholin II is high, although some aromatic structures may also be present. In this respect both ice tholins I and II appear to resemble involatile residues produced by photolysis of water/methanol ice mixtures (Allamandola *et al.* 1988).

The presence of the smaller polyalcohols ethylene glycol, butanediol, and glycerol among the intermediate mass products (Table I), as well as the strong O–H bands in the infrared spectra, supports the conclusion that the generalized ice tholin structure is that of a substituted polyalcohol. Ethers, esters, carboxylic acids, ketones, hydrocarbons, and possibly an aldehyde are also listed in Table I, raising the possibility that the structure of ice tholin contains all these functional groups to a greater or lesser extent. The identification of the hydroxyketones hydroxypropanone and hydroxybutanone implies the occurrence of beta- or gamma-hydroxy ketone groups in ice tholin. The presence of the major C=O band in Fig. 3 at around  $1660\text{ cm}^{-1}$  ( $6.02\text{ }\mu\text{m}$ ) is consistent with carbonyl groups beta to hydroxyls (Dean 1992).

Some inferences can be made concerning the mechanism of formation of ice tholins in our experiments. The known radiation chemistry of water (Draganic and Draganic 1971, Draganic *et al.* 1984) suggests that hydroxyl (OH) radicals are formed in our experiment and play a major role in the

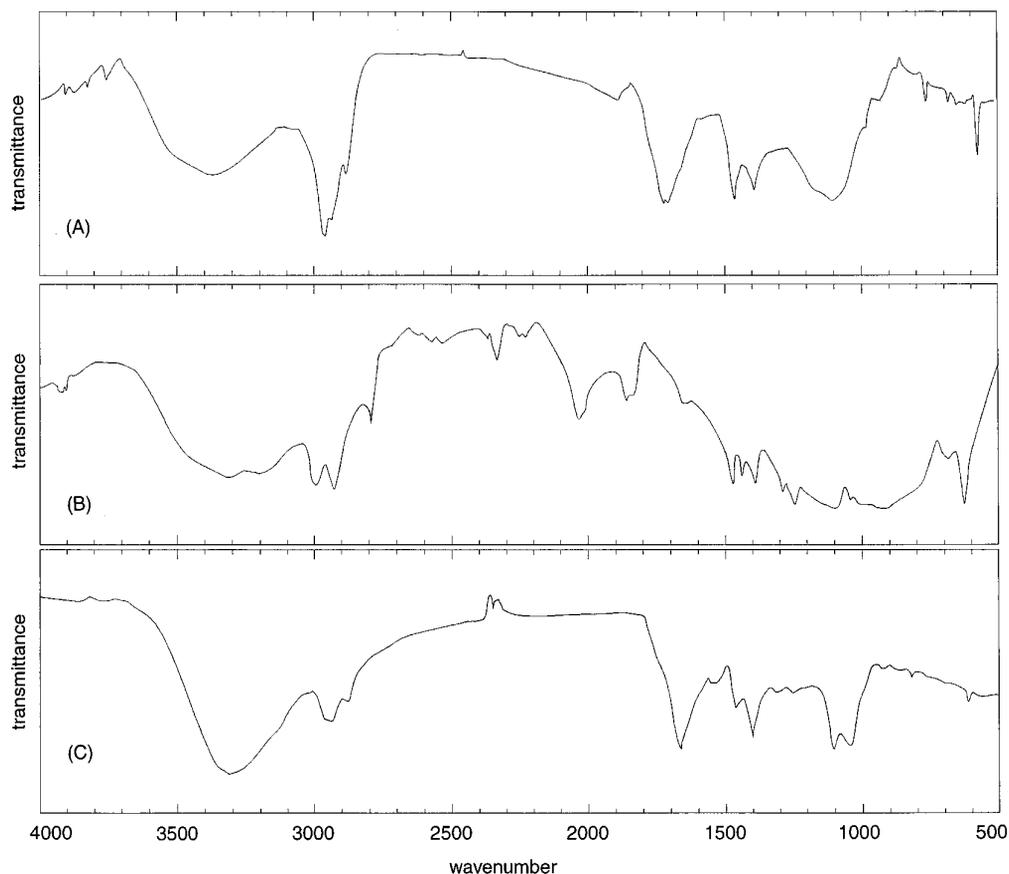


FIG. 8. Infrared spectra of (A) ice tholin I, (B) paraformaldehyde, and (C) ice tholin II (Run 1).

chemistry involved. This could include addition to carbon-containing molecules to form alcohols. Hydroxyl radicals are also strong oxidizing agents for organic compounds and could drive the oxidation of methanol and other alcohols to aldehydes, ketones, and esters.

Direct polymerization of methanol radicals ( $\text{CH}_2\text{OH}$ ) could also account for polyalcohol formation. This mechanism has been suggested for the formation of polyalcohols in photolysis experiments involving  $\text{H}_2\text{O}/\text{CO}/\text{NH}_3$  ices (Agarwal *et al.* 1985). The predominance of this mechanism in our experiments is supported by the production of ethylene glycol and glycerol, which can be thought of as the dimer and trimer of methanol, respectively.

Infrared spectra of residue from  $\text{H}_2\text{O}/\text{CO}_2$  ice proton irradiation (Moore and Khanna 1991) show little similarity to ice tholin. Moore and Khanna (1991) identified carbonic acid ( $\text{H}_2\text{CO}_3$ ) as a major component of their residue, but  $\text{H}_2\text{CO}_3$  was not detected among the products of our experiments. This is not surprising, since  $\text{H}_2\text{CO}_3$  dissociates into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  when warmed to room temperature from the solid phase (Moore and Khanna 1991). Formaldehyde, methanol, and ethanol were also detected by Moore and Khanna among their products, but are not among ours.

## IMPLICATIONS FOR COMETARY CHEMISTRY

### *Formaldehyde Chemistry in Comets*

Polyoxymethylene (POM), the polymerization product of formaldehyde [ $(-\text{CH}_2\text{O}-)_n$ ], has been suggested as a major component of the higher-molecular-weight organic component of cometary material, based on a repetitive pattern of 14- and 16-amu fragments in mass spectra taken by the Giotto spacecraft during passage through the coma of Comet Halley (Huebner 1987; Mitchell *et al.* 1987). This identification is problematic, however, due to the  $>1$ -amu resolution of the Giotto mass spectral data (Mitchell *et al.* 1992). Even so, the presence of POM in cometary material cannot be excluded by these observations.

Figure 8 shows a comparison of the infrared spectrum of ice tholin II (Fig. 8C) with that of paraformaldehyde (Fig. 8B), the commercially available form of POM (Moller and Jackson 1990, Moore and Tanabe 1990). The spectra are dissimilar, leading to the conclusion that POM is not a significant component of ice tholins. No formaldehyde was observed in GC/MS analyses of the gas-phase products remaining in the sample vessel after the experiment. The formaldehyde trimer 1,3,5-trioxane was tentatively identi-

fied among the intermediate mass products of the experiment (Table I), suggesting that small amounts of formaldehyde may have been synthesized. It might be expected that formaldehyde synthesis would occur in this system through the oxidation of methanol by hydroxyl radicals produced from radiolysis of water (Draganic and Draganic 1971, Draganic *et al.* 1984). Formaldehyde appears to be the principal product of the ultraviolet photolysis of methanol in water-rich ices (Allamandola *et al.* 1988). Our data, however, show little evidence that significant amounts of formaldehyde or POM are produced in cometary ices as a result of charged-particle-driven chemistry.

If formaldehyde is produced in cometary ices only by ultraviolet photolysis, and not by radiation chemistry, then comets that have passed through the inner Solar System should have higher formaldehyde (and presumably POM) abundances than those that have spent their entire lifetimes in the Oort cloud. It also follows that formaldehyde and POM levels in short-period comets should be higher than those in comets with longer periods. The detection of formaldehyde and possibly POM in Comet Halley is consistent with this hypothesis. However, this may be a small effect due to the fact that the depth of ice lost at each perihelion passage greatly exceeds the UV penetration depth. Detection of formaldehyde has also been reported in nonperiodic comets; such identification, though, can be problematic (e.g., Snyder *et al.* 1990; also see Reuter *et al.* 1992, and references therein). The primordial ultraviolet flux on the interstellar grains that presumably make up comets (Delsemme 1991) may be high enough to result in the production of some formaldehyde even in comets that have never approached the sun.

#### *Detection of Tholin-like Materials in Comets*

POM is an organic polymer with a similar molecular weight range to that of cometary tholins. It might be presumed, therefore, that any cometary tholin-like molecules that might exist within cometary comae would also be detectable by spacecraft instruments such as mass spectrometers. Polyalcohol-based ice tholins, however, would be much less volatile than POM of the same molecular weight. This is due to the strong hydrogen bonding interactions between molecules containing  $-OH$  functional groups, which are present in ice tholin but not in POM. To illustrate this point, the boiling point of glycerol (which can be thought of as a trimer of methanol) at 1 atm is 563 K, while that of 1,3,5-trioxane (formaldehyde trimer) is 388 K (Lide 1995). POM itself has been shown to sublimate under vacuum at temperatures as low as 300 K (Moller and Jackson 1990). Polyalcohols would also be much less volatile than either saturated or unsaturated hydrocarbons, such as those inferred in comet Halley from spacecraft data (Jessberger *et al.* 1989). Any failure to detect ice-

tholin-like molecules in cometary comae remotely cannot therefore be taken as firm evidence for the absence of such molecules from the cometary nucleus.

#### *Implications for the Origin of Life*

The “RNA world” hypothesis (Gilbert 1986) proposes that RNA was the first self-replicating molecule. This hypothesis has been strengthened by the discovery of catalytic RNA, but weakened by the observation that ribose, the sugar which forms the backbone of RNA, is difficult to make in a plausible prebiotic manner (for a review see Chyba and McDonald 1995). Derivatives of glycerol and similar polyalcohols have been proposed as substitutes for ribose in acyclic nucleotide analogues (Joyce *et al.* 1987, Joyce 1989, Schwartz 1993), although problems of duplex stability remain (Schneider and Benner 1990). These simpler, achiral molecules may have combined with purine and pyrimidine bases and polymerized to form the first nucleic-acid-like biomolecules, capable of both genetic and catalytic functions. Our experiments with ice tholins suggest that polyalcohols may be present in cometary organic matter. This raises the possibility that such molecules could have been delivered to the early Earth by cometary impactors and IDPs (Chyba *et al.* 1990, Chyba and Sagan 1992). Questions of impact survivability and chemical reactivity in the prebiotic environment remain, but large polyalcohols may have been available for prebiotic chemistry and synthesis of nucleic acid analogues on the early Earth.

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