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FIRST POLYMER IN COMET HALLEY: POLYOXYMETHYLENE

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ABSTRACT

The RPA2-Positive Ion Cluster Composition Analyser (PICCA) on the Giotto spacecraft detected five mass peaks with regular spacing of about 15 amu up to about 120 amu. Starting at about 45 amu, the peaks decrease in intensity with increasing mass. Within their half-width they are in good agreement with dissociation products of formaldehyde polymer (POM). We suggest a production sequence in which cosmic radiation formed POM from water and carbon monoxide on grains that were aggregated into cometary dust. Other polymers, possibly containing CN, may also exist. Observations suggest that at least some of the H-, C-, and O-containing dust particles detected by the Particle Impact Analyser (PIA) on board of the Giotto spacecraft and its equivalent (PUMA) on the Vega 1 and 2 spacecraft contain POM. The properties of POM are consistent with many of the unexpected observations in the coma.

Keywords: Polymer, Polyoxymethylene, Coma, Composition, Ion Clusters

The Positive Ion Cluster Composition Analyser (PICCA) of Korth et al. (Ref. 1) on the Giotto spacecraft detected ion masses up to about 120 amu in the coma of comet Halley. These data were further analyzed by Korth et al. (Ref. 2) and Mitchell et al. (Ref. 3). Figure 1, taken from the last reference, shows intensity peaks at masses of about 43, 46, 61, 75, 91, and 105 amu. As pointed out by Mitchell et al. (Ref. 3), the leftmost part of the spectrum is completely saturated and the peak at 43 - 46 amu is partially saturated. Since the relative intensity at 46 is slightly higher than at 43, the real position of the peak is probably at 45 amu. The lighter ions have a smaller radial density gradient and a much larger range in the coma than the heavy ions, which are limited to about 25000 km. The higher masses reveal a very regular pattern: (a) Starting at 45 amu, peaks are in an alternating sequence with a separation of 16 and 14 amu up to 105 amu. (b) The half-intensity half-width is 2 or 1 amu, about constant from peak to peak. Because of the intrinsic uncertainty associated with this width, the separation between peaks could also be 15 amu. (c) The mass peaks show a smooth decrease of intensity with increasing mass. Peaks that exist beyond 105 amu are masked by a hot background component which also distorts the width of the high mass peaks. For this reason we use the 61 amu peak as the reference point. The next peak in the sequence after 105 amu should be

at either 120 or 121 amu. In the presentations of the spectrum by Mitchell et al. (Ref. 3) the signal to noise ratio is too small to identify this peak, but when data are summed into groups of four mass channels and an underlying background is subtracted, then the signal to noise is large enough to indicate an intensity peak between 117 and 130 amu (Ref. 4), with highest probability between 121 and 125 amu.

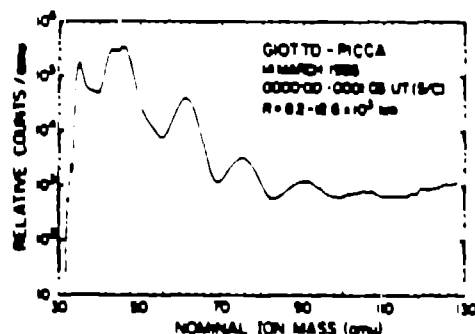


Fig. 1 Heavy ion mass spectrum from the PICCA instrument (Ref. 3). The peak at 43 - 46 amu is partially saturated and the left edge of the spectrum is completely saturated. A hot background component appears to dominate the cold ions beyond 105 amu.

The spectrum is too regular to be caused by a combination of unrelated molecular ions. A rather natural explanation for the regularity of the spectrum emerges if its sources are correlated decay products of a polymer. The decay products are either multiples of 15 amu or sums of alternatingly 14 and 16 amu.

Because H, O, C, and N are astrophysically the most abundant, chemically active elements, polymers consisting of these elements are the most likely to form. With the abundance and mass separation restrictions, only a few possible polymers exist (NH) and (H₂CO). Of these, (H₂CO) is preferred because O and C are more abundant than N, astrophysically. In comet Halley, nitrogen appears to be even less abundant than the astrophysical ratios of N/C or N/O suggest. To explain the

observed spectrum requires easy dissociation, which makes polymers with a ring structure highly improbable. $(H_2CO)_n$ is polymerized formaldehyde, also known as paraformaldehyde or polyoxymethylene (POM, for short). Its structure is shown in Fig. 2. It has the following properties that are consistent with observations of the coma: (a) The bonds between C and O are symmetric; therefore, it is as easy to break the bond on either side of the CH_2 or O, resulting in an alternating sequence of six mass peaks at about 45, 61, 75, 91, 105, and 121 amu. (b) Chains with n equal to about 4, 5, or 6 have a large affinity to attach themselves to graphite or silicates in whisker-like structures. This is consistent with the composition of the carbonaceous particles identified with the PIA and PUMA instruments and with the increasing ratio of small to large particles with increasing cometocentric distance. (c) The unsaturated bonds on each end of the short chain can easily accept hydrogen atoms, protons, or hydroxyl radicals, which are all very abundant and the CH_2 components can lose one or two hydrogens, giving the POM dissociation products a spread in the mass peaks of about ± 2 amu. If a hydrogen is attached to the free end as indicated by (H) in Fig. 2, then progressive dissociation of any of the single bonds between C and O will produce the spectrum presented in Fig. 1. The heavy components are primarily destroyed, producing more of the light species, until they are destroyed also. Successive dissociations account for the large radial gradient of the heavy species in the coma, while the lighter species will have a smaller gradient and larger range. Ionization of the various products by photons, charge exchange, electron impacts, and protonization reactions makes them detectable in the PICCA instrument.

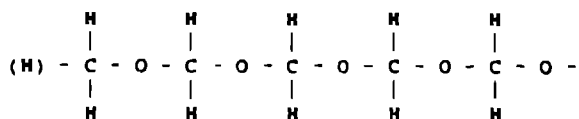


Fig. 2. A short formaldehyde polymer: $(H_2CO)_5$. The molecule can be dissociated with equal probability at any C-O bond. The free ends of the polymer have an affinity for graphite, silicates, and molecular species such as H, OH, and CN. If hydrogen is attached, as shown by (H), then dissociation of successive C-O bonds after the second CH_2 -group, counting from left, produces the observed mass peaks most closely.

The affinity that POM has for graphite and silicates suggests that it may be one of the constituents in the C-H-O-N dust particles found in comet Halley (Refs 5-6). There may also be other polymers, possibly containing N or CN, that are associated with dust grains. These may be more stable at higher temperatures than POM, which unspatters under vigorous heating. If whisker-like structures of POM unite the smallest grains into larger dust particles, then this would account for the observed increase in the ratio of small to large dust particles with increasing distance from the nucleus in comet Halley (Ref 7). It could also explain the low albedo of the nucleus (Ref 8). The inactive areas of the nucleus may be covered with these particles that can trap light in the spaces between the POM whiskers and the particles in a very fluffy layer. POM is also consistent with the highly porous and refractory surface layer material needed to insulate the ice below it from the solar radiation (Ref 9).

The idea that POM may be an astrophysical material is not new. Wickramasinghe (Refs. 10-11) suggested its existence as a component of the interstellar dust to explain the interstellar extinction in the 8 to 12 μ m wavelength region. He points out that condensation of formaldehyde on silicate grains at temperatures < 20 K is attended by polymerization in the form of whiskers. Formaldehyde has been detected as a common constituent in many interstellar clouds in its gas phase. Vanysek and Wickramasinghe (Ref. 12) and Mendis and Wickramasinghe (Ref. 13) notice that many observed features in comets can be explained through properties of POM. However, it is the mass spectrum from the PICCA instrument that takes the identification of POM out of the realm of speculation.

Based on thermodynamic data, Wickramasinghe (Ref. 11) argues that most POM should exist in the condensed phase. As he notes, interstellar clouds are rich in water and carbon monoxide. The formation of POM from these constituents requires further explanation.

Pirronello et al. (Ref. 14) report laboratory production of formaldehyde from an ice mixture of water and carbon dioxide through irradiation by 1.5 MeV helium ions at a temperature of about 9 K. Helium ions were used instead of astrophysically more abundant protons because of the chemically inert nature of helium to keep the experimental conditions well defined. They also note that the newly formed formaldehyde is not easily removed from the ice mixture by the direct action of the radiation. The experiment suggests that cosmic radiation can produce formaldehyde in mantles of frozen water and carbon dioxide on grains. This leaves the question of how much frozen carbon dioxide exists on interstellar grains.

Carbon dioxide is a molecule without a permanent dipole moment; it has no rotational spectrum that would make the gas phase component detectable with radio telescopes. Regardless of whether carbon dioxide is abundant in the gas phase, carbon monoxide, which is known to be very abundant in the gas phase, disproportionates on condensation to form graphite and carbon dioxide. Chemical equilibrium conditions under which this occurs are presented in the low temperature phase diagram in Fig. 3. The calculation was performed for a temperature of 200 K and a constant pressure of 0.001 atmospheres with a 0.25 gram-atom fraction of He as a source for the pressure. The results of the calculation are not sensitive over wide ranges in pressure and temperature. The chemical symbols on the sides correspond to the ratios that are the same as the stoichiometry of the respective molecules, which are the most important to form at intermediate and low temperatures. In the region delineated by the symbols $C - CH_2 - H_2O - CO_2 - C$, excess carbon forms graphite. Carbon dioxide forms in the triangular region bounded by $C - H_2O - O - C$. Water ice is present everywhere, except in the extreme corners C and O. Above the $C - H_2O$ line all gas-phase carbon is in methane while below that line it is in carbon dioxide.

At temperatures of about 1000 K, chemical equilibrium yields graphite in the left half of the triangle bounded by $H - CO - C - H$ (dashed line). On the right side of the triangle, carbon dioxide and water form (except at the extremes labeled H and O) and carbon dioxide dominates over carbon monoxide in the region $H_2O - CO_2 - O - H_2O$. The composition is not sensitive over wide ranges of temperature and pressure. On rapid cooling, a mixture of water and carbon dioxide ice forms.

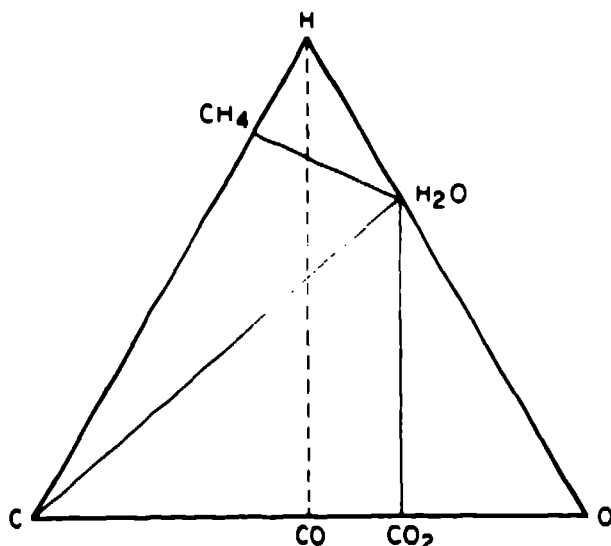
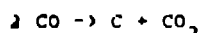
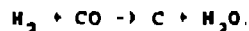


Fig. 3. H - C - O phase diagram. Ignoring the dashed line, at low temperatures (~ 200 K) carbon dioxide forms in the triangle C - H₂O - O - C. Water is present everywhere. At higher temperatures (~ 1000 K) carbon dioxide and water form inside the triangle H - O - CO - H.

Similar results are obtained in chemical non-equilibrium, although the low temperature region has not been studied exhaustively. Iron is known to be an active catalyst for the disproportionation reaction of CO:



The carbon formed by this reaction migrates across the surface to a nucleating center where cementite and free carbon are deposited. The reaction is autocatalytic. The rate of carbon formation by the disproportionation of carbon monoxide is much faster than the pyrolysis of methane under similar conditions. The rate of carbon deposition on an iron catalyst is accelerated in the presence of molecular hydrogen at temperatures below about 1100 K, but is a complicated function of temperature and the amount of molecular hydrogen. The hydrogen seems to have a dual role: at low concentrations it catalyzes the CO disproportionation reaction, at high concentrations it leads to deposition of graphite by the reaction:



Very little is known about carbon monoxide disproportionation at low temperatures. The above chemical equilibrium and high temperature non-equilibrium reactions are only intended as a guide to show that disproportionation of CO is an important process in the formation of icy mixtures of water and carbon dioxide.

Levis and Prinn (Ref. 15) come to very similar conclusions using chemical kinetics to model the presolar nebula. They show that the conversion from carbon monoxide to methane was too slow relative to radial mixing or evolution rates in the primitive solar nebula, so that most of the carbon monoxide converted to carbon dioxide.

As mentioned earlier, formaldehyde is formed by irradiation of a mixture of water and carbon dioxide ice and it remains in the ice. This property is important for the next step, the polymerization. Goldanskii et al (Ref. 16)

reported the formation of POM from formaldehyde at 77 to 140 K through irradiation with bremsstrahlung from 5 MeV electrons, and at 4 to 77 K through irradiation with ⁶⁰Co gamma rays (1.33 and 1.17 MeV). Gol'dyanskii (Ref. 17) concluded that at the low temperatures in space the only possible mechanism for polymerization is molecular tunneling. Again, cosmic radiation is the initiator that makes polymerization possible.

In the laboratory, formaldehyde in water solution polymerizes to a solid long-chain polymer H-O-(CH₂-O)_n-H, known as polyoxymethylene glycol. This end-capped polymer is more stable than the ordinary variety. Nevertheless, when strongly heated it reverts back to formaldehyde. The heat of polymerization of gaseous formaldehyde forming crystalline POM at a pressure of 1 atmosphere is about 16.7 kcal/mol.

POM could have formed under the action of cosmic radiation on the surface layer of comets in the Oort cloud. During the 30 known visits of Halley's comet into the inner solar system, this surface layer would have been eroded away through the evaporation of the ices that entrain the dust containing the POM. Orbital calculations of Halley's comet backwards in time suggest that this comet has visited the inner solar system thousands of times. Since POM is still present in the comet, it appears that the dust containing the POM is also deep in the interior of its nucleus. We suggest that POM was formed in interstellar space, the presolar nebula, or the solar nebula and was then incorporated into the cometesimals at the time of their formation. This would be consistent with the hypothesis that comets are the Rosetta stone of the solar nebula (Ref. 18). However, this concept must be viewed with caution. POM is not as volatile as the icy component of a comet nucleus and its affinity for dust grains makes it even more stable. Frozen water is the least volatile and most abundant component of the ices in comet nuclei and is also relatively stable. Most of the other volatile ice components are present only at the level of a few percent. Their primordial abundance in cometesimals may have been quite different.

To further test our assumptions, we modeled a mixture of 90% water ice and 10% POM with $n = 5$ in our comet coma computer program (Ref. 19). In this simulation we allowed every C-O bond in the $n = 5$ POM and in all of its dissociation products to be broken with the same probability. In these preliminary calculations, only photodissociation, photoionization, and electron dissociative recombination processes were assumed to operate on the POM and its products. Average rate coefficients for photodissociation (0.0001 /s for each C-O bond), photoionization (0.00001 /s), and electron dissociative recombination (0.0000025 cm³/s for each C-O bond) were adopted, leading to a reduced range of POM products in the coma. The only exception to this was the formaldehyde monomer, water, and their dissociation, ionization, and chemical products for which we have a more complete reaction network available. In Table 1 the preliminary results at appropriate cometocentric distances R are summarized and compared to the PICCA peak count rates, normalized to the 61 amu peak. The calculation was repeated for a mixture of 90% water ice and 10% POM with $n = 4$. When normalized to the 61 amu peak, the results are virtually the same, indicating that the calculation is not very sensitive to the length of the original chain, as long as $n > 4$. The model results are within a factor of two of the observed PICCA ratios. We find this agreement encouraging considering the simplified reaction network and the neglect of the solar wind interaction. The model calculation also indicates

that POM is an additional source for ions of C, CH₂, CH₃, C₂H₂, CO, HCO, H₂CO, and CH₃OH as significant amounts of each of these ions were formed. A more complete POM reaction network is planned with the inclusion of charge exchange, protonization, end-capping with OH and its ion, and other appropriate processes that would influence POM products and broaden the mass spectra peaks.

Table 1
POM Intensities

Mass Group amu	PICCA ^a	Model Results ^b	
		n = 5	n = 4
45	>8.	7.73	7.53
61	1.00	1.00	1.00
75	0.08	0.13	0.13
91	0.015	0.017	0.017
105	0.004	0.0021	0.0019

^a Average for R = 8200 to 12600 km

^b Interpolated logarithmically to 10400 km

We suggest that dust particles containing POM are likely candidates for many of the H - C - O particles detected by the Giotto PIA instrument and Vega 1 and 2 PUMA instruments. In particular, Clark et al. (Ref. 20) find that these particles are concentrated closer to the nucleus and occur with much lower frequency outside of the inner coma. This is consistent with the rapid release of POM from particles through heating during their outward expansion, resulting in a short range (~10000 km) for these H - C - O particles. Schematically, a dust particle consistent with these properties, is shown in Fig. 4. It may be composed of silicate grains, carbonaceous material, and polymers such as POM. The affinity of POM whiskers for grain surfaces will bind submicrometer-sized components in the particle. Since POM is a volatile polymer, the dust particles, as they move outward in the inner coma, will heat from exposure to solar radiation and fragment.

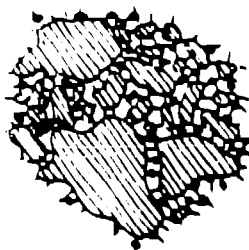


Fig. 4. Schematic presentation of a micrometer-sized dust particle composed of silicate grains, carbonaceous material including less volatile polymers and POM. Some of the connecting lines are polymers such as POM that disintegrate on heating and release the smaller units of the particle

In summary, we have shown that POM with n about 4 or 5 explains the mass spectrum obtained with the PICCA instrument during the Giotto encounter with comet Halley. Processes relevant to produce the observed spectrum include photodissociation, photoionization, dissociative electron recombination, charge exchange reactions, and end-capping

with ions of OH and H (protonization). Longer chains may be present, but their abundance in the PICCA instrument is too low to be observable. POM may also be the extended source for the CO production as observed with the neutral mass spectrometer on the Giotto spacecraft (Ref. 21). Other, somewhat more refractory polymers, possibly containing the source for the CN associated with dust observations, may also be present (Ref. 22). If POM formed on dust particles in interstellar space it is not likely that it vaporized in the heat of the solar nebula and recondensed as POM. Thus grains containing POM are important tracers for the early history of the solar system. A sequence of processes has been presented showing the likelihood that POM will form under interstellar conditions and a first, preliminary comet coma model that includes POM reproduces the observed mass spectrum. Although this is not the first time that polymers have been suggested as material of astrophysical significance, this is the strongest evidence suggested for them so far. More data analysis from the PICCA instrument, detailed modeling, and laboratory experiments are needed to extract additional information.

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