

Origin of cometary extended sources from degradation of refractory organics on grains: polyoxymethylene as formaldehyde parent molecule

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Abstract

The radial distribution of some molecules (CO, H₂CO, HNC, ...) observed in the coma of some comets cannot be explained only by a direct sublimation from the nucleus, or by the photolysis of a detected parent compound. Such molecules present a so-called extended source in comae. We show in this paper that extended sources can be explained by refractory organic material slowly releasing gas from grains ejected from the cometary nucleus, due to solar UV photons or heat. The degradation products are produced throughout the coma and therefore are presenting an extended distribution. To model this multiphase chemistry we derive new equations, which are applied to Comet 1P/Halley for the case of the production of formaldehyde from polyoxymethylene (POM), the polymer of formaldehyde (–CH₂–O–)_n. We show that the presence of a few percent of POM on cometary grains (a nominal value of ~ 4% in mass of grains is derived from our calculations) is in good agreement with the observed distribution, which so far were not interpreted by the presence of any gaseous parent molecule.

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1. Introduction

To date, about 25 molecules (excluding ions and radicals) have been detected in the atmosphere of comets (coma) (Crovisier and Bockelée-Morvan, 1999). Most of them are considered as parent compounds, i.e., they are ejected into the gaseous phase either directly from the cometary nucleus ices or within the first kilometers during the sublimation of ice coated grains. The abundance of such compounds relative to water is likely to be the same in the nucleus and in the coma. Parent compounds can be dissociated in the coma by solar photons and produce daughter fragments. The density of both gaseous parent and daughter species as a function of the distance from the nucleus are calculated as distributions consistent with Haser's hypotheses (those hypotheses are presented and discussed later in this paper) (Haser, 1957). However, some detected compounds present strong discrepancies with Haser's distribution and other mechanisms have been evoked.

- (1) Gas phase reactions between species in the coma, as seems to be the case for HNC produced by the reaction $\text{HCN} + \text{H} \rightarrow \text{HNC} + \text{H}$ in Comet C/1995 O1 (Hale-Bopp) (Irvine et al., 1998b; Rodgers and Charnley, 1998).
- (2) Production from an unknown parent compound for the origin of H₂CO and for the origin of HNC in Comets C/1996 B2 (Hyakutake) and C/1999 H1 (Lee) (Meier et al., 1993; Irvine et al., 1996; Rodgers and Charnley, 1998, 2001; Biver et al., 1999, 2000).

The difficulty of that latter approach is the identification of a relevant unknown parent whereas most of the abundant compounds in coma in the gaseous phase are probably now detected. From in-situ measurements (Kissel and Krueger, 1987), and from laboratory work on cometary and interstellar ice analogs (see for instance: Greenberg (1982), Allamandola et al. (1988) or Cottin et al. (1999a) for reviews), we know that cometary grains are rich in complex refractory organic material. So far, their potential degradation, and contribution to the gaseous phase, has never been quantitatively investigated. First and foremost, intrinsic degradation data (kinetics, products) for potential candidates are miss-

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ing. Candidate refractory parent compounds can potentially be established from results obtained on laboratory-irradiated interstellar and cometary ice analogs leading to the detection of large molecules likely to be present on comets. Second, new equations, different than those proposed by Haser, have to be developed. As a matter of fact, the production of gaseous daughter molecules from a solid parent compound involves mechanisms quite different than those usually included in models. In comets, a refractory molecule present on grains can be submitted to photodegradation, thermal degradation, or both, and release small gaseous molecules, whose spatial distributions cannot be described by a purely native source, nor solely to gas phase reactions in the coma.

In this paper, we propose to develop a new approach: the degradation of refractory organic material on cometary grains, and production of smaller gaseous molecules. To illustrate this process, the example of the production of H_2CO in Comet 1P/Halley from solid polyoxymethylene is chosen. Indeed, new quantitative data about the degradation of this polymer are now available (Cottin et al., 2000, 2001c). The first section of this paper is a review of the possible presence of polyoxymethylene in comets, and thus the validity of our study. Then we describe the classical Haser approach of cometary chemistry, and show that gaseous compounds cannot account for the observation of formaldehyde in Comet Halley. Then we present our new equations for three cases: photodegradation, thermal degradation, and a coupled modeling of both processes. Even if only the last and most complete approach is relevant in the case of POM, we chose to develop the three of them in the present paper, since any of the three cases might be the most adapted for specific molecules other than POM to interpret existing or future observations. Thus they are presented here and made available for any future work. In the last section we present a complete modeling of formaldehyde production from POM, with a relevant Halley-like dust distribution, and we discuss the extent to which our results are to be considered.

2. Why study polyoxymethylene?

2.1. Review of POM history in comets

The presence of polyoxymethylene in the interstellar medium was evoked for the first time in the middle 1970's by Bessel and Wickramasinghe (1975), and by Cooke and Wickramasinghe (1977). This hypothesis was put forward because of H_2CO detection in the gaseous phase (first detection reported by Snyder et al. (1969)), and because of good agreement between POM optical properties and observation (polarization spectra). Concerning comets, Vanysek and Wickramasinghe (1975) discuss the point that infrared signatures of silicates are similar to those of POM, and that detected silicates may in fact be formaldehyde polymers. Nevertheless, by calculating that POM formation in ISM environment is not favorable, Goldanskii (1977) showed that

the claim of the presence of POM in space has to be taken with caution, although it cannot be excluded. But our knowledge of interstellar chemistry has improved since that time, and his conclusions should be reconsidered. He was dealing with formation of 1000 monomer units at 4 K, whereas we presently know that the interstellar environment presents a wide range of temperatures, and experimental simulations show that POM formation occurs after thermal processes (Schutte et al., 1993b) and photolysis (Bernstein et al., 1995) of interstellar ice analogs. Moreover, shorter polymer molecules also have to be considered, and the study of 1000-unit molecules was an arbitrary choice. Woon (1999) has recently published *ab initio* calculations about $\text{H}_2\text{CO}/\text{NH}_3$ mixtures in water, which yield a production of small amine-terminated ($-\text{NH}_2$) POM-chains at temperatures as low as 40 K. The production of larger-chain polymers has not yet been theoretically explained, and might require higher temperatures.

Ten years after this first tentative detection, the presence of POM in comets was invoked again to interpret a mass spectrum obtained with the PICCA instrument on board the Giotto spacecraft, between 8200 and 12600 km from the nucleus of Comet Halley. Indeed, Huebner (1987) suggested that the alternation of patterns with $\Delta m/z = 14$ and 16 is consistent with a sequence of $-\text{CH}_2-$ ($m = 14$) and $-\text{O}-$ ($m = 16$), which comprises the polymer (Huebner, 1987; Huebner et al., 1987).

Huebner's hypothesis seems to be confirmed by Möller and Jackson (1990) and Moore and Tanabé (1990) who have performed POM mass spectra that fit observation. However, these conclusions have been reconsidered. Mitchell et al. (1992) have shown that the PICCA mass spectrum is not specifically characteristic of POM: the regular pattern observed is only the signature of a mixture of organic molecules composed of C, H, O, N atoms. Thus, even if the presence of POM cannot be ruled out, the observed spectrum is not sufficient to establish its presence definitively. Nevertheless, Mitchell's conclusion strengthens the idea that high molecular weight organic molecules are present in comets.

In addition to the PICCA observations, polyoxymethylene has been synthesized in experimental simulation of energetic processes on cometary or interstellar ice analogs. It is synthesized in ices containing H_2O , H_2CO , CH_3OH , CO , and NH_3 submitted to UV photolysis or thermal processing (Bernstein et al., 1995; Schutte et al., 1993a, 1993b). The latter mechanism seems to be the most efficient. Therefore, the presence of a significant amount of POM in comets could indicate a history of domination by thermal transformation rather than by UV or energetic particle bombardment (see Cottin et al. (1999a) for a review of experimental simulation on ice analogs). Thus, the presence of POM in comets is still an open and important question.

2.2. H_2CO extended source

Cometary formaldehyde was detected for the first time in 1986 in Comet Halley with the infrared instrument IKS

Table 1
Molecules with extended sources in comets (ions and radicals have been excluded)

Molecule with extended source	Comet	Reference
H ₂ CO	Halley	(Meier et al., 1993)
	Hyakutake	(Lis et al., 1997)
CO	Hale-Bopp	(Bockelée-Morvan et al., 1998; Wink et al., 1999)
	Halley	(Eberhardt et al., 1987)
	Hyakutake	(DiSanti et al., 2003)
OCS	Hale-Bopp	(DiSanti et al., 1999)
	Hale-Bopp	(Dello Russo et al., 1998)
SO	Hale-Bopp	(Bockelée-Morvan et al., 1998)
HNC	Hale-Bopp	(Irvine et al., 1998a; Rodgers and Charnley, 1998)

on board Vega 1. Its production rate from nucleus was then estimated to be 4% relative to water (Combes et al., 1988; Mumma and Reuter, 1989), whereas observations at radio wavelengths led to an estimate of about 1.5% (Mumma and Reuter, 1989; Snyder et al., 1989).

Meier et al. (1993) studied measurements performed from 1740 to 4400 km from nucleus with the NMS mass spectrometer on board Giotto. They show that the formaldehyde density profile, as a function of cometocentric distance, cannot be explained by direct release of formaldehyde from the nucleus, expanding with spherical symmetry and photolyzed by solar UV. On the contrary, it looks like its production rate increases with the distance. Since these measurements were made within about one hour, native production (from the nucleus) would have had to increase by a factor three during that time period to account for observation, whereas the production rates of molecules like H₂S and CH₃OH were constant within an uncertainty of $\pm 20\%$. Moreover, it cannot be explained by inhomogeneous emission, since all the gaseous molecules are well mixed within the first kilometers of the coma.

This implies the presence of an *extended source* (or additional source) of formaldehyde in Comet Halley. It does not seem to be a direct H₂CO emission from cometary grains, because ices coating them sublimate within the first few kilometers from the nucleus. Moreover, if it were a consistent explanation, such a phenomenon should be observed for the other detected gaseous molecules, whereas it is only seen for few (Table 1). Therefore it is likely that the refractory organic component of comets might be involved in this process, through its degradation.

It must be noted that an extended source of formaldehyde has also been detected in Comets Hyakutake (Biver et al., 1999; Lis et al., 1997) and Hale-Bopp (Bockelée-Morvan et al., 1998; Wink et al., 1999). So that phenomenon is common to all comets that have been observed with sensitivity sufficient to detect it, yet there is no quantitative explanation to interpret it.

A fraction of the carbon monoxide extended source is associated to H₂CO, because the photochemistry of this mole-

cule produces CO. But the difference in abundance between these two molecules (about ten times less H₂CO than CO) demonstrates that the extended source of CO in Comet Hale-Bopp (50% of the total observed CO within 1.5 AU from the Sun (DiSanti et al., 1999)) cannot originate exclusively from formaldehyde chemistry.

Considering the points we discussed in the previous section of this paper, polyoxymethylene is often pushed forward to provide the H₂CO extended source (see, e.g., Boice et al., 1990; Meier et al., 1993; Biver, 1997; Greenberg and Li, 1998; Eberhardt, 1999). We now show that this idea is consistent with what was known about the physico-chemistry of the polymer, but until very recently important quantitative data were missing to allow a discerning analysis of that hypothesis.

2.3. POM photodegradation and radiolysis: previous works and latest results

Polyoxymethylene is commonly used as a source of pure formaldehyde by simple heating. Indeed, commercial H₂CO contains some methanol to avoid its polymerization. Thus pure thermal degradation of POM is one mechanism to consider for formaldehyde production in comets. Another mechanism is the degradation of the polymer by photons: photodegradation.

There are few data relevant to the cometary environment, related to POM photodegradation. Most studies have dealt with oxidative photodegradation of POM, i.e., in the presence of molecular oxygen. Chemical mechanisms, products and reaction yields should be very different from those that could be obtained without O₂ (Rabek, 1995). Irradiation of POM under vacuum and for wavelengths below 200 nm were first reported by Roessler et al. (1992). This work concludes with the detection of CO and H₂CO in the gas phase (identified by direct MS), while an infrared analysis of the solid irradiated residue reveals the presence of ester functions. Unfortunately, this study remains qualitative, and has not been pursued further to our knowledge. More is known about POM radiolysis, i.e., irradiation with particles with energy high enough to ionize the molecule (gamma rays, electrons, and photons below 100 nm). Under vacuum, the polymer irradiated by 1 MeV electrons produces several gaseous compounds such as H₂, CH₄, CO, H₂CO, CH₃CHO, CH₃OCHO, CH₃OCH₂OCH₃, CH₃OCH₂OCHO, and H₂O. The production yield of formaldehyde from the polymer is $G_{\text{H}_2\text{CO}} = 4 \pm 1$ (Fischer and Langbein, 1967; Dole, 1973; Shalaby, 1979) (note: *G*-value is defined as the number of molecules produced per 100 eV of energy absorbed from ionizing radiation).

Recently, we have performed a quantitative experimental study of polyoxymethylene degradation:

- Photodegradation: we have identified the main gaseous photodegradation products of polyoxymethylene:

H₂CO, CO, HCOOH, CO₂, CH₃OH, CH₃OCHO, CH₃OCH₃OCH₃, and C₃H₆O₃ (trioxane). We have determined the production quantum yields for formaldehyde ($\phi_{122\text{ nm}} = 0.75 \pm 0.21$, $\phi_{147\text{ nm}} = 0.96 \pm 0.19$) and formic acid ($\phi_{122\text{ nm}} = 0.13 \pm 0.05$, $\phi_{147\text{ nm}} = 0.26 \pm 0.10$), and roughly estimated the yields for the other compounds (Cottin et al., 1999b, 2000).

- Concerning thermal degradation, we have verified that H₂CO is the only product, and determined the variation of its production rate as a function of temperature (based on $A = 8.7 \times 10^5 \text{ mol g}^{-1} \text{ s}^{-1} \pm 60\%$ and $Ea = 74.2 \text{ kJ mol}^{-1} \pm 10\%$, for the Arrhenius constant and the activation barrier, respectively; see Cottin et al. (2001c)).

We expect these results (ϕ 's for photodegradation and A , Ea for thermal degradation) to be useful for interpreting cometary observations, as well as for further theoretical studies such the one we present below.

Polyoxymethylene seems to be a good candidate as a parent molecule for extended H₂CO based on the following:

- it is produced during experimental simulations performed with cometary and interstellar ice analogs;
- its detection in Comet Halley is controversial but cannot be ruled out;
- its degradation due to heating as well as photon and charged particle bombardment leads to the production of formaldehyde.

This polymer (POM) is therefore appropriate for studying the contribution of the solid organic phase of cometary grains to the gas phase composition of the coma.

3. Haser's model

A brief description of the model and its preliminary results have already been presented in Cottin et al. (2001a). We propose here to describe the algebraic approach we develop concerning the production of gaseous molecules from the solid phase. Equations involved to describe such heterogeneous chemistry derive but are different from the ones usually used for cometary gas phase chemistry. Our work differs from previous studies on this subject (Boice et al., 1990; Meier et al., 1993), where the POM photochemistry was modeled in the gaseous phase with estimated rate coefficients, with no parameterization for H₂CO thermal production.

First, the classical approach that describes density profiles for parent and daughter *gaseous* molecules in comets is recalled in detail. On this basis, we present extensions of those equations to the production of gaseous molecules from compounds in the *solid* phase. Three cases are developed below:

- photodegradation;

- thermal degradation;
- combined photo and thermal degradation.

Each model will be illustrated with solid POM producing gaseous H₂CO. Although only the last case will be used in this paper with a 'Halley-like' dust distribution (this appears to be the most relevant for the POM polymer case), we think it is worthwhile to describe each mechanism in this paper. All three cases can be more or less adapted according to the solid molecule considered. Therefore this detailed treatment might be useful for future studies of extended sources and/or precursors.

The complexity of comae dynamics leads to making simplifying hypotheses to describe the density profile of a particle (gaseous molecule or solid grain) in the inner coma. The most commonly used model is the one described by Haser (1957), and assumes the following:

- (1) spherically-symmetric outflow from the nucleus: the emission is uniform from all the nucleus surface, or the emitted particles are well mixed within the first kilometers;
- (2) steady state: the nucleus production is constant over the time-scale of the modeled process;
- (3) radial expansion at a constant velocity, which means no collisions, no excess velocities during photodissociation;
- (4) molecules and radicals are only destroyed by photochemistry with constant rate coefficients and without chemical reaction between two compounds.

Hypothesis (3) (constant outflow speed v) frees us from the dynamic equation. Only the budget of mass has to be considered, which is written under its Eulerian form:

$$\frac{\partial n}{\partial t} + \text{div}(nv) = \sum_i S_i, \quad (1)$$

where $n \text{ (cm}^{-3}\text{)}$ is the number density of the considered particle, and the S_i represent its sources and sinks.

In a simple case, with particles ejected from the nucleus and not being destroyed, one can write:

$$\frac{\partial n}{\partial t} + \text{div}(nv) = 0 \quad (2)$$

with $\partial n / \partial t = 0$, because of steady state (hypothesis (2)).

For particles undergoing spherically symmetric flow, with v being constant (hypothesis (3)), we obtain the density at a distance r from the nucleus in the absence of particle destruction:

$$n(r) = \frac{Q}{4\pi r^2 v}. \quad (3)$$

Where Q is the production rate of particles from the nucleus (s^{-1}). This allows to determine the density of grains as a function of the distance from the nucleus.

3.1. Parent compound

A first step in complexity can then be achieved: molecule M is emitted from the nucleus with a production rate Q_M , and is photodissociated by solar UV. The sink of this molecule can be written as a function of its number density n_M :

$$\frac{dn_M}{dt} = -Jn_M \quad (4)$$

with J being the photolysis rate (s^{-1}):

$$J = \int_{\lambda} \sigma I \Phi d\lambda. \quad (5)$$

In Eq. (5), σ is the photon–molecule cross section (cm^2), I is the solar irradiance ($photon\ s^{-1}\ cm^{-2}\ nm^{-1}$), and Φ represents the quantum yield.

With constant v , and assuming $r \ll l_M$ ($l_M = v/J$ being the scale length of M) we obtain by integration of Eq. (1):

$$n_M(r) = \frac{Q_M}{4\pi r^2 v} e^{-r/l_M}. \quad (6)$$

This expression is used to determine the density profile of H_2CO as a parent molecule, as shown in Fig. 4 (dotted line).

3.2. Daughter fragments

Molecules observed in the coma are not necessarily directly emitted from the nucleus. Photodissociation of a parent compound can produce new species, or an additional source for another parent molecule. Those photolysis products are called daughter species.

We now calculate the density profile $n_D(r)$ for such a molecule, photolyzed at a rate J_D , and emitted from a parent compound, whose production and photodestruction rates are respectively Q_M and J_M . Parent and daughter species are assumed to expand with a spherical symmetry and at the same velocity v (which is an approximation: photodissociation products receive an excess of kinetic energy compared to the parent molecule (Crifo, 1994), and in this case an equivalent scale length can be used (Combi and Delsemme, 1980)).

Thus we have:

$$\frac{\partial n_D}{\partial t} + \text{div}(n_D v) = J_M n_M - J_D n_D, \quad (7)$$

$$\Leftrightarrow \frac{dn_D r^2}{dr} + \frac{J_D}{v} n_D r^2 = \frac{J_M}{v} n_M r^2. \quad (8)$$

From Eq. (6) and since $l = v/J$, we obtain:

$$\frac{dn_D r^2}{dr} + \frac{n_D r^2}{l_D} = \frac{n_M r^2}{l_M} = f(r) \quad (9)$$

with

$$f(r) = \frac{Q_M}{4\pi v l_M} e^{-r/l_M}. \quad (10)$$

A general solution for Eq. (9) can be written as:

$$n_D r^2 = \frac{Q_M}{4\pi v} \frac{l_D}{l_M - l_D} e^{-r/l_M} + K e^{-r/l_D}, \quad (11)$$

K is an integration constant calculated from boundary conditions: $r \ll l_M$ and $r \ll l_D$, for which exponential terms tend towards 1 so that

$$n_D r^2 \rightarrow \frac{Q_M}{4\pi v} \frac{l_D}{(l_M - l_D)} + K.$$

Then we have two possibilities:

- The daughter molecule has no direct source from the nucleus. Then as a boundary condition: $n_D r^2 = 0$ and we get:

$$n_D(r) = \frac{Q_M}{4\pi r^2 v} \frac{l_D}{l_M - l_D} (e^{-r/l_M} - e^{-r/l_D}). \quad (12)$$

- The daughter molecule has also a direct source Q_D from the nucleus (which appears to be the case for H_2CO in some comets; see, e.g., DiSanti et al., 2002a, 2002b).

Then as a boundary condition, $n_D r^2 = Q_D/(4\pi v)$ and we get:

$$n_D(r) = \frac{1}{r^2} \left(\frac{Q_M}{4\pi v} \frac{l_D}{l_M - l_D} (e^{-r/l_M} - e^{-r/l_D}) + \frac{Q_D}{4\pi v} e^{-r/l_D} \right). \quad (13)$$

In order to discuss the relevance of a gaseous parent of formaldehyde, Fig. 1 and Table 2 present three fits of the previous equation to the Giotto measurements of formaldehyde in Comet Halley published by Meier et al. (1993). The absolute error of their measurements is reported to be less than 35%. To first order, this absolute error is a systematic error caused by uncertainties on reactions rates used to calculate the H_2CO density from in-situ MS measurements of the 31 $amu\ e^{-1}$ peak dominated by H_3CO^+ . These errors shift the density scale up or down. Nevertheless, the error on the slope of the curve is quite insensitive to these reaction rates, and the random error on each measurement can be estimated from the scatter of the date at the few percent level. Taking this discussion into consideration, Giotto measurements are plotted with 15% error bars in the figures of this paper. A detailed discussion about the adjustment of our

Table 2

Parameters for the calculation of the best fits to Giotto measurements of formaldehyde when considering a gaseous parent molecule (see also Fig. 1)

	J_{Biver}	J_{Meier}	$J_{\text{CH}_3\text{OH}}$
Q_{H_2CO} (s^{-1})	4.5×10^{27}	2.0×10^{27}	7.0×10^{27}
Q_M (s^{-1})	1.9×10^{28}	2.0×10^{28}	1.0×10^{29}
v (km/s)	7.8×10^{-1}	7.8×10^{-1}	7.8×10^{-1}
L_{H_2CO} (km)	3.9×10^3	3.9×10^3	3.9×10^3
L_M (km)	6.0×10^3	4.6×10^3	6.0×10^4

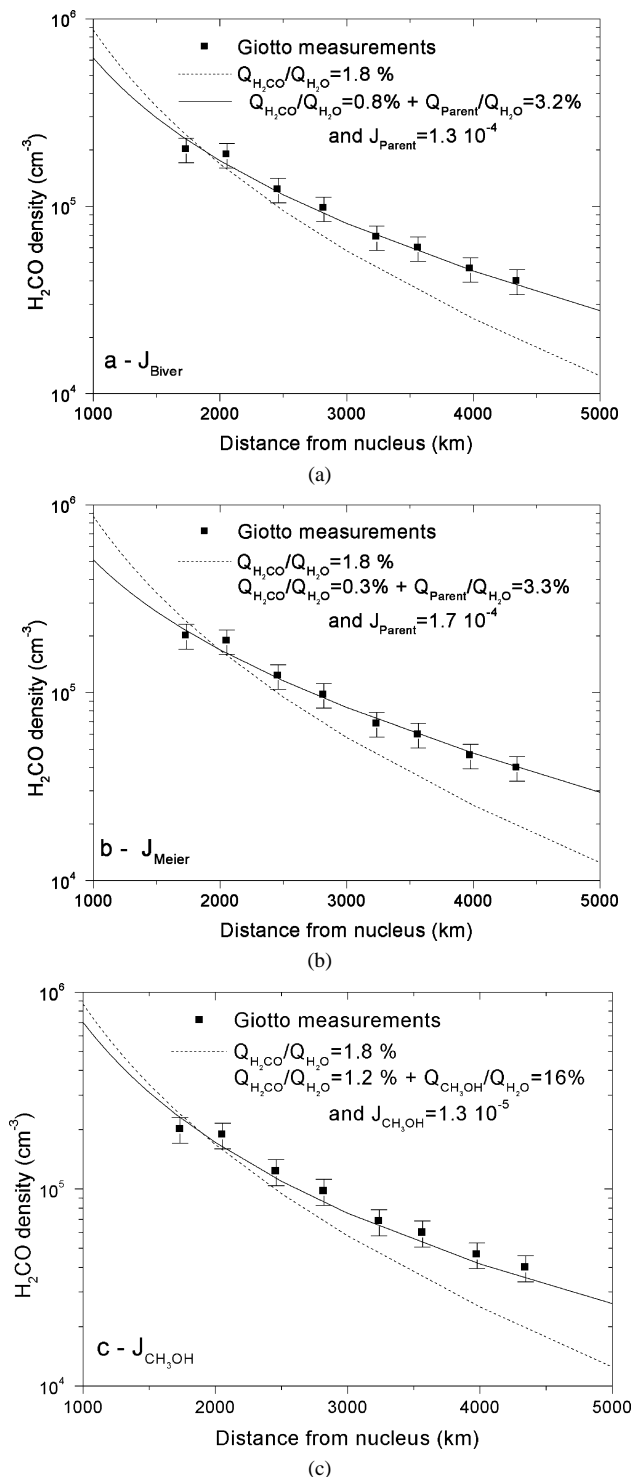


Fig. 1. Formaldehyde density profile in Comet Halley: measured by Giotto (squares), and calculated with (continuous line) or without (dotted line) extended source production. Several fits are presented (see text). The density profile without extended source is calculated with $Q_{\text{H}_2\text{CO}} = 1.1 \times 10^{28} \text{ s}^{-1}$ (i.e., $\sim 1.8\%$ relative to water production).

calculations to measurements will be given in the last section of the paper for a specific case. The coma expansion velocity has been set to 780 m s^{-1} , which is the mean value in the measurement zone (Meier et al., 1993). In the first

case (a), J_M is set to the value proposed by Biver (1997) and Biver et al. (1999) from estimates of the H₂CO parent scale-length in comets Hyakutake, Austin, Levy, and Swift-Tuttle: $J_M = 1.3 \times 10^{-4} \text{ s}^{-1}$. The best fit presented is achieved for a direct formaldehyde production of about 0.8% from the nucleus (relative to $Q_{\text{H}_2\text{O}} = 6 \times 10^{29} \text{ s}^{-1}$ from Fink and DiSanti (1990), for heliocentric distance = 0.9 AU, when the Giotto measurements were achieved) and 3.8% for the parent molecule. We use $J_{\text{H}_2\text{CO}} = 2 \times 10^{-4} \text{ s}^{-1}$ throughout this paper (Crovisier, 1994).

Other solutions fitting Giotto measurements can be achieved by adjusting the free parameters of the model: $Q_{\text{H}_2\text{CO}}$, Q_M , and J_M . Graph (b) is obtained for $J_M = 1.7 \times 10^{-4}$, which is the nominal value proposed by Meier et al. (1993) “We find that the lifetime of the parent is restricted to the range of 0.8 to 1.5 times the lifetime of H₂CO with the best fit obtained for a factor of 1.2,” i.e., $J_M = J_{\text{H}_2\text{CO}}/1.2$. This results in a production rate for the parent compound of $Q_M = 3.3\%$, and agrees with measurements with 0.3% of native formaldehyde.

None of these solutions corresponds to the photodissociation rate of an observed parent molecule likely to produce formaldehyde. Methanol, actually detected in Comet Halley, might be a relevant candidate. But if H₂CO is considered as the main CH₃OH photoproduct (Huebner et al., 1992), and adopting $J_{\text{CH}_3\text{OH}} = 1.3 \times 10^{-5} \text{ s}^{-1}$ (Crovisier, 1994), methanol should be produced at a level of 16% from nucleus relative to water (with $\sim 1\%$ of H₂CO) to obtain a good fit to measurements (c). But methanol is only produced in amounts ranging from ~ 1 to 6% in comets (Biver et al., 2002). Moreover, as discussed in Bockelée-Morvan et al. (1994), formaldehyde is not the main dissociation product of methanol, but rather the CH₃O^o methoxy radical. Therefore 16% is a lower limit for the amount of CH₃OH required.

Thus, the extended source of cometary H₂CO is not consistent with a CH₃OH parent.

4. POM grain model and its extension

Thanks to the new experimental data about POM degradation, we now establish a new set of equations that model the contribution of solid POM particles to the gaseous phase, through its photo and thermal degradation. Boice et al. (1990) tried to estimate the formaldehyde production from POM, but with the hypothesis that short polymer chains are emitted from grains and photodissociated in the gas phase. Because of the lack of experimental data, photodissociation rates were estimated from formaldehyde and related molecular bond strengths, without any direct laboratory measurement. Meier et al. (1993) showed that those data did not fit the Giotto measurements. On the other hand, as underlined by those authors, and as we have verified experimentally, thermal degradation of solid POM produces only formaldehyde. The presence of short polymer chains in the gas phase would then remain marginal.

Formaldehyde production from solid grains is a function of several unknown parameters: the matrix in which it is imbedded, the geometry of the grains, the chemical structure of the polymer, and its temperature. Here, we can only pretend to simulate the behavior of grains made of a polymer similar to the one studied in laboratory as a model of a high molecular weight compound self-degrading because of solar UV and heat.

As a first approach, we apply Haser's model to pure spherical POM particles uniformly emitted from the nucleus. Such hypotheses are certainly far from the reality and complexity of the cometary environment, but we shall keep in mind that our goal is to show whether there is a mechanism that can explain observation, for realistic abundances of the parent compound. First we will present the case of photodegradation and thermal degradation separately, before presenting a coupled model with both processes. Then we will use a "Halley-like" heterogeneous grain distribution to gain a better insight into our model results.

4.1. Photodegradation

4.1.1. Grain lifetime

Let us consider a spherical grain made of POM, with a radius R , exposed to solar UV. This grain will produce different gas-phase compounds in the gaseous phase (H_2CO , CO , HCOOH , CO_2 , CH_3OH , CH_3OCHO , $\text{CH}_3\text{OCH}_2\text{OCH}_3$, and $\text{C}_3\text{H}_6\text{O}_3$). If we assume that the grain rotates randomly, loss of mass will occur uniformly over its surface.

The grain being spherical, the equivalent cross-section exposed to solar UV is $\sigma = \pi R^2$.

The production rate of a molecule $[M]$ by photodegradation can then be written:

$$\frac{d[M]}{dt} = \sigma \int_{\lambda} f_{\lambda} \Phi_{\lambda} d\lambda, \quad (14)$$

where f_{λ} is the solar irradiance photon $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ and Φ_{λ} is the production quantum yield of M from the grain surface at wavelength λ . We also consider the grain to be sufficiently thick that each photon is absorbed. If not, we obtain an upper limit for the production rate of the parent.

If μ is the mass density of POM ($\mu = 1.46 \times 10^3 \text{ kg m}^{-3}$ —specification *ProLabo*-France), r is the cometocentric distance of the grain outflowing with velocity v_p calculated from Crifo (1995).¹ Then, the mass lost from the grain can be written:

$$\frac{dm}{dr} = 4\pi\mu R^2 \frac{dR}{dr}. \quad (15)$$

We take v_p to be constant (acceleration should occur within the first 100 or so km of the nucleus), and R_0 to be the initial radius of the grain.

As mentioned earlier in the paper, H_2CO , CO , HCOOH , and CO_2 are the dominant products of POM photodegradation. Then:

$$\begin{aligned} \frac{dm}{dt} = -\sigma C = -\sigma & \left(\left((m_{\text{H}_2\text{CO}} + m_{\text{CO}}) \int_{\lambda} f_{\lambda} \Phi_{\lambda}^{\text{H}_2\text{CO}} d\lambda \right) \right. \\ & + \left(m_{\text{HCOOH}} \int_{\lambda} f_{\lambda} \Phi_{\lambda}^{\text{HCOOH}} d\lambda \right) \\ & \left. + \left(m_{\text{CO}_2} \int_{\lambda} f_{\lambda} \Phi_{\lambda}^{\text{CO}_2} d\lambda \right) \right) \quad (16) \end{aligned}$$

with m_x representing masses of the molecules.

The Φ^X are from Cottin et al. (2000), and through lack of accurate data concerning CO we have assumed that its production quantum yield profile is identical to H_2CO . We have neglected production of CH_3OH , $\text{CH}_3\text{OCH}_2\text{OCH}_3$, and $\text{C}_3\text{H}_6\text{O}_3$.

The quantity C has been estimated using Cottin et al. (2000) and the solar spectrum published by Mount and Rottman (1981). Those measurements were made near solar maximum, in order to model photodegradation at its maximum efficiency:

$$C = 6.76 \times 10^{-9} \text{ kg m}^{-2} \text{ s}^{-1},$$

v_p , which is reached in the first few kilometers from the nucleus (Crifo, 1995) is supposed to be constant at our scale, thus $v_p dt = dr$. We can also assume that all the solar UV flux reaches up to 5–50 km from the nucleus depending on the comet (Crifo, private communication). We can then consider that a grain starts being photodegraded as soon it is emitted, thus:

$$\frac{dm}{dr} = -\frac{\sigma C}{v_p}. \quad (17)$$

Comparing Eqs. (15) and (17), we get:

$$4\pi\mu R^2 \frac{dR}{dr} = -\frac{\sigma C}{v_p}. \quad (18)$$

Integration with $\sigma = \pi R^2$ and $R = R_0$ at $r = 0$, we obtain after integration:

$$R = R_0 - \frac{C}{4\mu v_p} r \quad \text{for } r \leq \frac{4\mu v_p}{C} R_0. \quad (19)$$

If we set:

$$l^p = \frac{4\mu v_p R_0}{C} = \frac{3M_0 v_p}{\pi R_0^2 C} \quad (20)$$

as the POM scale length and M_0 the initial mass of an individual POM grain then:

$$R = R_0 \left(1 - \frac{r}{l^p} \right) \quad \text{for } r < l^p. \quad (21)$$

According to Lisse et al. (1998), a typical size range of most cometary grains is between 0.1 and 10 μm . We can then calculate l_{POM} (for which $R = 0$) of POM grains in the coma (Table 3).

¹ Equations to calculate the grain velocity are displayed latter in this paper (Eqs. (49)–(51)) with further comments, in order to not overload this section, which is devoted to the calculation of the density profile.

Table 3
Photodegradation scale length as a function of the grain size

R_0 (μm)	10	1	0.1
v_p (m s^{-1})	250	480	680
Grain lifetime (days)	100	10	1
l_p (km)	2.2×10^6	4.1×10^5	5.9×10^4

v_p is calculated using Eqs. (49) to (51).

The photodegradation rate of grain is low enough for its influence to be observed at the scale of observation in Halley's coma.

4.1.2. H_2CO density

Grain density n_p , as a function of the nucleus distance r , can be described by an equation similar to Eq. (7) if we assume uniform emission of particles Q_p and radial expansion with constant velocity v_p :

$$n_p = \frac{Q_p}{4\pi r^2 v_p}, \quad (22)$$

v_p is calculated according to the grain size. We consider here a single size grain population whose radius R decreases following Eq. (21). The formaldehyde production rate (calculated as a density number) from these POM grains at a distance r from the nucleus can be written:

$$\left(\frac{d\text{H}_2\text{CO}}{dt}\right)_p = n_p \sigma(r) \int_{\lambda} \underbrace{f_{\lambda} \Phi_{\lambda}^{\text{H}_2\text{CO}}}_{C'} d\lambda \quad (23)$$

$$\left(\frac{d\text{H}_2\text{CO}}{dt}\right)_p = \frac{Q_p}{4r^2 v_p} C' \left(R_0 - \frac{C}{4\mu v_p} r\right)^2. \quad (24)$$

The mass budget equation is then:

$$\frac{\partial n_{\text{H}_2\text{CO}}}{\partial t} + \text{div}(n_{\text{H}_2\text{CO}} v) = \left(\frac{d\text{H}_2\text{CO}}{dt}\right)_p - J_{\text{H}_2\text{CO}} n_{\text{H}_2\text{CO}}. \quad (25)$$

(Note: both v : gas velocity and v_p : grain velocity are used in the following equations.)

With Haser's model hypotheses we get an equivalent of Eq. (9):

$$\frac{dn_{\text{H}_2\text{CO}} r^2}{dr} + \frac{n_{\text{H}_2\text{CO}} r^2}{l_{\text{H}_2\text{CO}}} = \frac{r^2}{v} \left(\frac{d\text{H}_2\text{CO}}{dt}\right)_p = f(r) \quad (26)$$

with

$$f(r) = \frac{Q_p}{4\pi v_p l_{\text{H}_2\text{CO}}^p} \left(1 - \frac{r}{l_p}\right)^2 \quad (27)$$

and the two scale lengths of grain destruction l^p and of H_2CO production from grains $l_{\text{H}_2\text{CO}}^p$

$$l^p = \frac{4\mu v_p R_0}{C} = \frac{3m_0 v_p}{\pi R_0^2 C} \quad \text{and} \quad l_{\text{H}_2\text{CO}}^p = \frac{v}{\pi R_0^2 C'}.$$

The general solution for Eq. (26) is:

$$n_{\text{H}_2\text{CO}} r^2 = \frac{Q_p}{4\pi v_p} \frac{l_{\text{H}_2\text{CO}}}{l_{\text{H}_2\text{CO}}^p} \left[\left(1 + \frac{(l_{\text{H}_2\text{CO}} - r)}{l^p}\right)^2 + \left(\frac{l_{\text{H}_2\text{CO}}}{l^p}\right)^2 \right] + K e^{-r/l_{\text{H}_2\text{CO}}}, \quad (28)$$

where K is an integration constant set by boundary conditions. If we set for $r \rightarrow 0$, $n_{\text{H}_2\text{CO}} \times r^2 = Q_{\text{H}_2\text{CO}}/(4\pi v)$, we finally get:

$$n_{\text{H}_2\text{CO}} = \frac{Q_p}{4\pi r^2 v_p} \frac{l_{\text{H}_2\text{CO}}}{l_{\text{H}_2\text{CO}}^p} \left[\left[1 + 2 \frac{l_{\text{H}_2\text{CO}}}{l^p} \left(1 + \frac{l_{\text{H}_2\text{CO}}}{l^p}\right) \right] \times \left(1 - e^{-r/l_{\text{H}_2\text{CO}}}\right) - \frac{r}{l^p} \left(2 + 2 \frac{l_{\text{H}_2\text{CO}}}{l^p} - \frac{r}{l^p}\right) \right] + \frac{Q_{\text{H}_2\text{CO}}}{4\pi r^2 v} e^{-r/l_{\text{H}_2\text{CO}}}. \quad (29)$$

4.1.3. Results and discussion

Figure 2a and Table 4 presents one of the best fits to Giotto measurements that can be achieved from Eq. (29).

The result seems to be very good for 1 μm grains, but the amount of POM emitted from the nucleus ($3.48 \times 10^4 \text{ kg s}^{-1}$) is more than the average grain production estimated for Comet Halley ($\sim 10^4 \text{ kg s}^{-1}$ (Arpigny, 1994)). Thus, to explain the observations, it seems as though even if all grains were POM, the yield would still be too small by a factor of ~ 3.5 .

This demonstrates that POM photodegradation by itself cannot account for the observed formaldehyde. Let us now consider thermal degradation of the polymer.

Table 4

Parameters for the calculation of the best fits to Giotto measurements of formaldehyde when considering the degradation of polyoxymethylene (see also Fig. 2)

	Photodegradation	Thermal degradation	Coupled model
$Q_{\text{H}_2\text{CO}}$ (s^{-1})	6.50×10^{27}	3.30×10^{27}	3.30×10^{27}
Q_p (s^{-1})	5.70×10^{18}	1.10×10^{17}	1.10×10^{14}
v (km s^{-1})	7.80×10^{-1}	7.80×10^{-1}	7.80×10^{-1}
v_p (km s^{-1})	4.80×10^{-1}	4.80×10^{-1}	2.50×10^{-1}
$L_{\text{H}_2\text{CO}}$ (km)	3.90×10^3	3.90×10^3	3.90×10^3
μ (g km^{-3})	1.46×10^{15}	1.46×10^{15}	1.46×10^{15}
R_0 (km)	1.00×10^{-9}	1.00×10^{-9}	1.00×10^{-8}
T (K)	–	345	336
k ($\text{g}^{-1} \text{s}^{-1}$)	–	3.55×10^{-6}	1.90×10^{-6}
$l^p/l^T/l^T$ (km)	4.15×10^5	6.39×10^3	1.34×10^4
$l_{\text{H}_2\text{CO}}^p/l_{\text{H}_2\text{CO}}^T/l^p$ (km)	4.90×10^{-6}	4.90×10^{-6}	2.16×10^6
Emitted mass (kg s^{-1})	3.48×10^4	6.72×10^2	7.34×10^2

T and R_0 are free parameters. They are adjusted to obtain the best fit to measurements. This is the reason why T and R_0 may vary from one process to another.

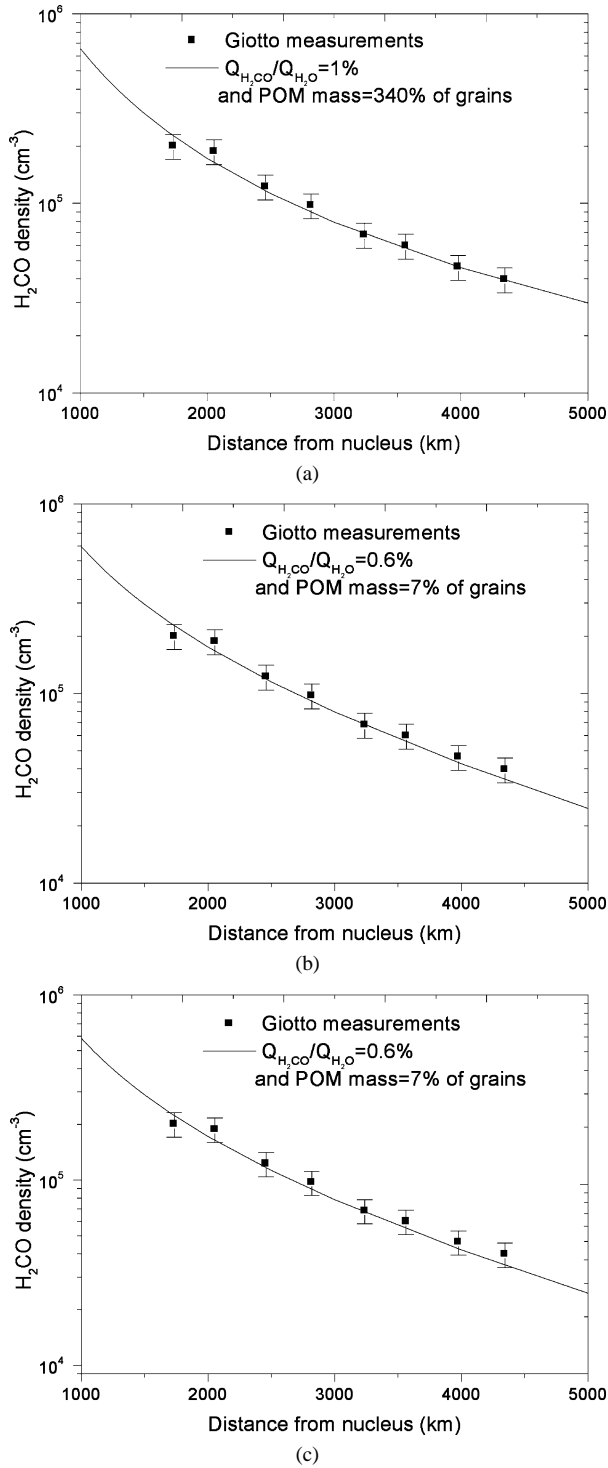


Fig. 2. Formaldehyde density profile in Comet Halley: measured by Giotto (squares), and calculated with an extended source from polyoxymethylene (continuous line) if the degradation of the polymer is (a) photodegradation, (b) thermal degradation or (c) both.

4.2. Thermal degradation

We are now going to describe the thermal production of a gaseous compound from a solid precursor, in the case of H_2CO production from solid POM.

4.2.1. Grain lifetime

Let us consider a spherical grain made of POM, with radius R , mass m , and temperature T .

The H_2CO production rate (mol s^{-1}) can be written:

$$\frac{d\text{H}_2\text{CO}}{dt} = km \quad (30)$$

with k given by the Arrhenius law:

$$k = Ae^{-Ea/(RT)}, \quad (31)$$

where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

As already mentioned in this paper, the Arrhenius constant $A = 8.7 \times 10^5 \text{ mol g}^{-1} \text{ s}^{-1} \pm 60\%$ and the activation barrier $Ea = 74.2 \text{ kJ mol}^{-1} \pm 10\%$ (Cottin et al., 2001c).

Then we have:

$$\frac{dm}{dt} = -M_{\text{H}_2\text{CO}}km. \quad (32)$$

As v_p is assumed constant we can write with $M_{\text{H}_2\text{CO}}$ being the mass of H_2CO per mol:

$$\frac{dm}{dr} = -\frac{M_{\text{H}_2\text{CO}}}{v_p}km \quad (33)$$

comparing with Eq. (15) leads to:

$$\frac{dR}{dr} = -\frac{R}{3} \frac{M_{\text{H}_2\text{CO}}}{v_p}k \quad (34)$$

with $l^T = 3v_p/(M_{\text{H}_2\text{CO}}k)$ representing the thermal degradation scale length. The previous equation can be written as follows:

$$\frac{dR}{dr} = -\frac{R}{l^T}. \quad (35)$$

By integration and again with boundary condition $R = R_0$ for $r = 0$:

$$R = R_0 e^{-r/l^T}. \quad (36)$$

The grain lifetime depends only on T and v_p . The scale length l^T is the distance at which R_0 is decreased by the factor $1/e$. As shown in Table 5, thermal degradation of grains is very sensitive to temperature and is very efficient for $T > 300 \text{ K}$.

Table 5

Thermal degradation scale length as a function of the grain size and temperature

Temperature (K)	l^T (km)		
	R_0 (μm)		
	10	1	0.1
250	8.9×10^7	1.7×10^8	2.4×10^8
300	2.3×10^5	4.5×10^5	6.3×10^5
350	3.3×10^3	6.4×10^3	9.1×10^3
400	1.4×10^2	2.7×10^2	3.8×10^2

v_p is the same than in Table 3 for each grain size and is calculated using Eqs. (49) to (51).

4.2.2. H₂CO density

The mass budget equation in this case is the same as Eq. (26):

$$\frac{dn_{\text{H}_2\text{CO}r^2}}{dr} + \frac{n_{\text{H}_2\text{CO}r^2}}{l_{\text{H}_2\text{CO}}} = \frac{r^2}{v} \left(\frac{d\text{H}_2\text{CO}}{dt} \right)_p = f(r). \quad (37)$$

The formaldehyde production from POM grains can be written:

$$\left(\frac{d\text{H}_2\text{CO}}{dt} \right)_p = Nkm, \quad (38)$$

where N is the Avogadro number ($N = 6.02 \times 10^{23} \text{ mol}^{-1}$), and m the total mass of POM per unit volume unit in the coma at a distance r from the nucleus (i.e., in our case the POM grain mass density).

$$m = \frac{4}{3}\pi R^3 \mu n_p = \frac{4}{3}\pi R^3 \mu \frac{Q_p}{4\pi r^2 v_p} = \frac{R^3}{3} \frac{\mu Q_p}{r^2 v_p}. \quad (39)$$

Then we have:

$$f(r) = \frac{Q_p}{4\pi v_p} \frac{1}{l_{\text{H}_2\text{CO}}^T} e^{-3r/l^T}, \quad (40)$$

where the H₂CO production scale length by thermal process and the initial mass of the grain are given by

$$l_{\text{H}_2\text{CO}}^T = \frac{v}{Nm_g^0 k} \quad \text{and} \quad m_g^0 = \frac{4}{3}\pi R_0^3 \mu,$$

respectively. We can then solve the differential equation (Eq. (37)):

$$\begin{aligned} A &= \int_r f(r) e^{r/l_{\text{H}_2\text{CO}}} dr \\ &= \frac{Q_p}{4\pi v_p} \frac{1}{l_{\text{H}_2\text{CO}}^T} \int_r e^{\frac{r}{l_{\text{H}_2\text{CO}}} (1-3l_{\text{H}_2\text{CO}}/l^T)} dr. \end{aligned} \quad (41)$$

Then:

$$\begin{aligned} n_{\text{H}_2\text{CO}r^2} &= \frac{Q_p}{4\pi v_p} \frac{l^T}{l_{\text{H}_2\text{CO}}^T} \left(\frac{l_{\text{H}_2\text{CO}}}{l^T - 3l_{\text{H}_2\text{CO}}} \right) e^{-3r/l^T} \\ &\quad + K e^{-r/l_{\text{H}_2\text{CO}}} \end{aligned} \quad (42)$$

if $r \ll l_{\text{H}_2\text{CO}}$ and $r \ll l^T$:

$$n_{\text{H}_2\text{CO}r^2} = \frac{Q_{\text{H}_2\text{CO}}}{4\pi v} = \frac{Q_p}{4\pi v_p} \frac{l^T}{l_{\text{H}_2\text{CO}}^T} \left(\frac{l_{\text{H}_2\text{CO}}}{l^T - 3l_{\text{H}_2\text{CO}}} \right) + K \quad (43)$$

and we finally obtain:

$$\begin{aligned} n_{\text{H}_2\text{CO}} &= \frac{Q_p}{4\pi r^2 v_p} \frac{l^T}{l_{\text{H}_2\text{CO}}^T} \left(\frac{l_{\text{H}_2\text{CO}}}{l^T - 3l_{\text{H}_2\text{CO}}} \right) \\ &\quad \times (e^{-3r/l^T} - e^{-r/l_{\text{H}_2\text{CO}}}) + \frac{Q_{\text{H}_2\text{CO}}}{4\pi r^2 v} e^{-r/l_{\text{H}_2\text{CO}}}. \end{aligned} \quad (44)$$

4.2.3. Results and discussion

Figure 2b and Table 4 present one of the best fits to Giotto measurements that can be achieved from Eq. (44) for 1 μm grains.

For thermal degradation, POM production is about 7% of the total dust amount emitted from Comet Halley if one consider a 345 K/1 μm grain population. For larger grains (10 μm for example), with a smaller radial velocity in the coma, an equivalent fit can be achieved with $T \sim 335$ K. For smaller grains (0.1 μm), with a larger radial velocity in the coma, the same fit is achieved with a higher grain temperature ($T \sim 350$ K). The formaldehyde production directly from nucleus as parent molecule can be increased up to 2% relative to water of compensated by small decrease of T (-5 K) for a result similar to the one presented Fig. 2b. Such a formaldehyde production rate is consistent with measurement in Halley ranging from 1.5 to 4.5% (Combes et al., 1988; Mumma and Reuter, 1989; Snyder et al., 1989), but it cannot be better constrained here.

Thus, the thermal degradation of POM is much more efficient than photodegradation. Moreover the amount of POM required to account for the Giotto NMS measurements is realistic, compared to what might be expected in cometary comae. Indeed Greenberg (1998) has estimated from observations and laboratory investigations that a cometary nucleus is made (by mass) of 26% silicates, 23% refractory organic molecules, 9% polycyclic aromatic hydrocarbons, and a mixture of volatiles (dominated by water) as the remainder. The refractory organic molecules would then represent about 40% of the non-volatile component of comets. On the other hand, a laboratory photolyzed H₂O:CH₃OH:CO:NH₃ ice mixture (ratio 10:5:1:1) leads to the formation of a refractory organic residue containing 20% ethers and POM-like polymers (Bernstein et al., 1995), i.e., 8% of the cometary nucleus and refractory component of grains (20% of the 40% of organics in the non-volatile component of comets = 8% of ethers and POM-like polymers). As already noted, POM production is more efficient in ices containing H₂CO and NH₃ when they are submitted to a simple warming process (Schutte et al., 1993b); in this case they could reach a mass fraction higher than 8%. Good fits to observations can also be achieved for higher amounts of POM and lower T , but we assume that the more polymer is required, the less realistic the results of our calculations.

Finally, we can extend our conclusions concerning thermal degradation of POM to heterogeneous grains. Cometary grains themselves are usually considered porous aggregates, where organic refractory molecules like POM are expected to be synthesized on the outer layers. The porosity, which is not parameterized here, is an important factor that could change our results, because some H₂CO diffusing within the grain might be trapped. But if we assume that the grain temperature is the only influential parameter controlling a H₂CO production rate proportional to the mass of POM, the geometry, composition and size of grains would not influence our results. This reasoning can then be extended to heteroge-

neous grains made of refractory material including a certain amount of POM emitting formaldehyde throughout its volume, as described in this paper. Then we can assume that our results can be extended to cometary grains made of about 7% of POM.

4.3. Coupled model

Let us now consider the production of formaldehyde from combined photo- and thermal-degradation of polyoxymethylene. In the next section of this paper, we use our modeling with a ‘Halley-like’ grain distribution. For such a study, even if thermal degradation remains the dominant mechanism for most grains, this may not be the case for all of them. Some are slower, colder, and have different photodegradation cross sections exposed to solar UV, which could then be the major process. Our model therefore has to take into account both mechanisms.

Preliminary results of this model have been presented in Cottin et al. (2001b), but we present here in further detail the calculations to obtain the density equation, and we extend our model to the ‘Halley-like’ grain distribution.

4.3.1. Grain’s lifetime

Considering a spherical grain made of a fraction α of POM by mass, with radius R , mass m , density μ , and temperature T . The grain is supposed to be an homogeneous mixture of POM and other materials, rather than consisting of a silicon core coated with a POM layer.

With $m_\alpha = \alpha m$ the mass of POM in the grain, r the distance from nucleus, and μ' the POM density (1.46×10^3 kg m⁻³-*Prolabo*), assuming Haser’s model hypotheses, the mass loss by photo- and thermo-degradation can be written:

$$\frac{dm_\alpha}{dr} = -\frac{1}{v_p}(\sigma C + M_{\text{H}_2\text{CO}} k m_\alpha). \quad (45)$$

Where σ is defined Section 4.1.1, C in Eq. (16) and k Eq. (31). In this section we still consider virtual pure POM grains, i.e., $\mu = \mu'$ and $\alpha = 1$, but we develop the general equation that will be used in our Halley-like dust case in the next section, with

$$m_\alpha = \frac{4}{3}\pi R_\alpha^3 \mu' = \alpha m \Rightarrow R_\alpha = \left(\alpha \frac{\mu}{\mu'}\right)^{1/3} R$$

so

$$\sigma = \pi R_\alpha^2 = \left(\alpha \frac{\mu}{\mu'}\right)^{2/3} \pi R^2$$

since

$$\frac{dm_\alpha}{dr} = 4\pi \mu' R_\alpha^2 \frac{dR_\alpha}{dr}.$$

With $l^T = 3v_p/(kM_{\text{H}_2\text{CO}})$ and $l^p = 4\mu' R_\alpha^0 v_p/C$, representing the thermal and photo degradation scale lengths respectively, the previous equation can be written as follows:

$$\frac{dR_\alpha}{dr} + \frac{R_\alpha}{l^T} = -\frac{R_\alpha^0}{l^p}. \quad (46)$$

Table 6

Photo/thermo degradation scale length as a function of the grain size and temperature

Temperature (K)	Distance at which R_0 is divided by e (km)		
	R_0 (μm)		
	10	1	0.1
250	1.4×10^6	2.6×10^5	3.7×10^4
300	1.9×10^5	1.6×10^5	3.5×10^4
350	3.3×10^3	6.2×10^3	7.1×10^3
400	1.4×10^2	2.6×10^2	3.7×10^2

v_p is the same than in Tables 3 and 5 for each grain size and is calculated using Eqs. (49) to (51).

By integration with boundary condition $R_\alpha = R_\alpha^0$ for $r = 0$:

$$R_\alpha = R_\alpha^0 [-\beta + (1 + \beta)e^{-r/l^T}] \quad (47)$$

with $\beta = l^T/l^p$.

As previously, we can calculate the lifetime for the grains as a function of the size and temperature of grains (Table 6). Since over 300 K thermal degradation dominates, the results for realistic coma temperatures are very similar to those presented in the previous section, for thermal degradation only.

4.3.2. H_2CO density

The mass budget equation take the same form as Eqs. (26) and (37) and the H_2CO production from grains is the sum of photo- and thermo-production (Eqs. (23) and (30)). To solve the differential equation we proceed with the same integration method as used previously, obtaining:

$$\begin{aligned} n_{\text{H}_2\text{CO}}(r) = & \frac{1}{4\pi r^2 v} \left\{ \frac{3Q_p \beta^3 m_\alpha}{m_{\text{H}_2\text{CO}} l^T X} \right. \\ & \times \left[l_{\text{H}_2\text{CO}}(1 - X)(1 - e^{-r/l_{\text{H}_2\text{CO}}}) \right. \\ & + \frac{(3X - 2)(1 + 1/\beta)}{(1/l_{\text{H}_2\text{CO}} - 1/l^T)} (e^{-r/l^T} - e^{-r/l_{\text{H}_2\text{CO}}}) \\ & + \frac{(1 - 3X)(1 + 1/\beta)^2}{(1/l_{\text{H}_2\text{CO}} - 2/l^T)} (e^{-2r/l^T} - e^{-r/l_{\text{H}_2\text{CO}}}) \\ & \left. \left. + \frac{X(1 + 1/\beta)^3}{(1/l_{\text{H}_2\text{CO}} - 3/l^T)} (e^{-3r/l^T} - e^{-r/l_{\text{H}_2\text{CO}}}) \right] \right\} \\ & + Q_{\text{H}_2\text{CO}} e^{-r/l_{\text{H}_2\text{CO}}}, \quad (48) \end{aligned}$$

where $X = C/m_{\text{H}_2\text{CO}} C'$ is the inverse of the relative photo-production of H_2CO from POM grains.

This is the general equation for a daughter molecule emitted from refractory organic material on grains. Its structure differs from Eq. (13), which describes emission of a daughter species from *gas phase* photochemistry. There is no direct equivalent to the scale length as with Eq. (13), therefore a discussion about this parameter is useless for identifying a parent compound in the solid phase. Here, the free parameters are $Q_{\text{H}_2\text{CO}}$, Q_p , R_0 , and T , and these can vary from grain to grain according to its size and composition.

4.3.3. Results and discussion

Figure 2c and Table 4 present one of the best fits to Giotto measurements obtained from Eq. (48). It is achieved with 10 μm grains.

This result is similar to the one presented and discussed in Cottin et al. (2001b). A small difference with previously published results is due to the fact we adopted smaller error bars on Giotto measurements in this paper (15% instead of 35%). The amounts of required parent H_2CO and POM are similar to the one obtained in the previous section with $T = 336$ K. Since $Q_{\text{H}_2\text{O}} \sim 6 \times 10^{29} \text{ s}^{-1}$, and the grain production from Halley near perihelion was $\sim 10^4 \text{ kg s}^{-1}$ (Arpigny, 1994), we conclude that the direct H_2CO production from the nucleus (i.e., as a monomer) was $\sim 0.6\%$ relative to water, and that assuming a grain size of $R_0 = 10 \mu\text{m}$ POM grains amount $\sim 7\%$ of the total dust mass. From Eq. (48) we can verify that the grain lifetime is consistent with our results at 336 K. An initial POM grain radius of 10 μm (assuming $v_p = 0.25 \text{ km s}^{-1}$ (Crifo, 1995)) is reduced by $\sim 40\%$ at 5000 km, thus grains can contribute to the extended source throughout all the studied part of the coma. Our model leads to the same fit for the same relative mass of POM ($\sim 7\%$) for any grain size between 0.1 and 10 μm with T ranging from 320 to 336 K. Concerning the other free parameters in our model, $Q_{\text{H}_2\text{CO}}$ variation from 0 to 1.5% relatively to water can be compensated simply by small variation in T (± 5 K). Less native formaldehyde requires warmer grains, whereas more native formaldehyde requires colder grains.

As discussed in the thermal degradation section, these conclusions also apply to heterogeneous grains.

5. Halley-like dust model

We now extend our model to a ‘Halley-like’ dust distribution. Figure 3 presents the dust production calculated from Crifo and Rodionov (1997) (see Table II in this paper), assuming a density of 1 g cm^{-3} for grains. Those data are derived from in-situ measurements presented in McDonnell et al. (1991).

It must be noted that data for grains up to 1 mg (i.e., $\sim 6 \text{ cm}$ in size, points 1 to 29 in Fig. 3) are direct in-situ measurements, whereas higher values are extrapolation relevant within an order of magnitude uncertainty (Crifo, private communication).

The grain velocity is calculated with the following equations from Crifo (1995):

$$v_p(X) = \frac{W}{(0.9 + 0.45X^{0.615/2} + 0.275X^{0.615})}, \quad (49)$$

$$W = \sqrt{\left(\frac{\gamma + 1}{\gamma - 1}\right) \left(\frac{\gamma k T_g}{m_g}\right)}, \quad (50)$$

$$X = \frac{2\pi R \mu W r_n}{m_g Q_g} \quad (51)$$

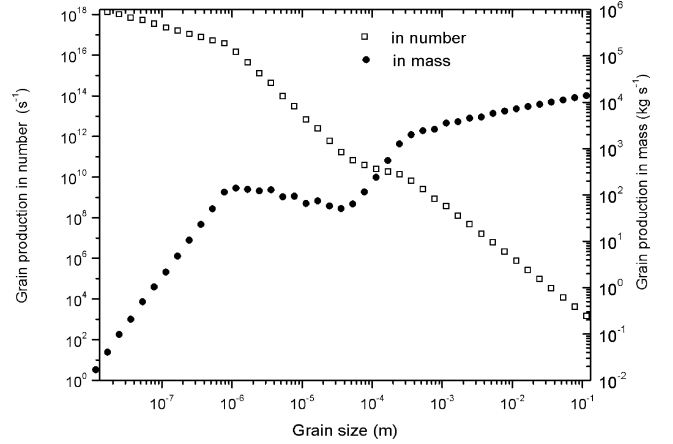


Fig. 3. Dust grain production from Comet Halley nucleus.

with (according to the same reference) $\gamma = 4/3$ (specific heats ratio), k the Boltzman constant, $T_g = 162$ K (gas kinetic temperature), $m_g = 3 \times 10^{-26} \text{ kg}$ (molecular mass of the gas, assumed to be equal to the mass of the water molecule), $Q_g = 6 \times 10^{29} \text{ s}^{-1}$ (native gas production), R is the grain radius, $\mu = 1000 \text{ kg m}^{-3}$ (grain density), $r_n = 3.8 \text{ km}$ (nucleus radius). Figure 10 in Crifo (1995) shows that this velocity is achieved between 10 and 100 km from the nucleus surface.

The temperature of grains can be calculated from an assumption about their shape (spherical) and composition (Crifo, 1988). Two extreme temperatures for each grain size are achieved according to whether the grain is made of olivine (low temperature) or amorphous carbon (high temperature). Olivine stands for the silicate nucleus of grains with a very low absorption in the visible; it is a temperature lower limit for grains. Amorphous carbon (aC) is representative of black matter, and stands as an upper limit for a strongly absorbing organic component of grains. As grain composition is poorly known, one cannot pretend to better constrain their temperature than between those two extremes.

Grain temperatures are presented on Table 7 and Fig. 4 (data from Crifo, private communication), those temperatures are reached in the first few tens of kilometers from nucleus and can be assumed constant (Crifo, 1991).

We have calculated the best fits to Giotto measurements, taking into account the grain distribution, their velocities and their temperatures in the following cases:

- temperature lower limit (olivine case);
- temperature upper limit (aC case);
- intermediate temperature (mixture of olivine and organics), considering grains made of 30% of aC and 70% of olivine.

For each case we have considered both the first 29 i labels (actual measurements in the coma up to 1 mg) and the all 43 labels (representing extrapolation up to 10 kg, see Table 7).

Table 7
Halley-like dust model—temperature

i	m_i (g)	T (K) olivine	T (K) aC
1	1.00×10^{-17}	324	681
2	3.16×10^{-17}	325	684
3	1.00×10^{-16}	328	689
4	3.16×10^{-16}	333	696
5	1.00×10^{-15}	343	701
6	3.16×10^{-15}	360	695
7	1.00×10^{-14}	377	669
8	3.16×10^{-14}	387	625
9	1.00×10^{-13}	390	568
10	3.16×10^{-13}	384	502
11	1.00×10^{-12}	369	434
12	3.16×10^{-12}	349	373
13	1.00×10^{-11}	328	329
14	3.16×10^{-11}	307	305
15	1.00×10^{-10}	287	297
16	3.16×10^{-10}	270	297
17	1.00×10^{-9}	264	302
18	3.16×10^{-9}	263	307
19	1.00×10^{-8}	267	312
20	3.16×10^{-8}	271	317
21	1.00×10^{-7}	276	321
22	3.16×10^{-7}	280	324
23	1.00×10^{-6}	283	327
24	3.16×10^{-6}	285	330
25	1.00×10^{-5}	287	332
26	3.16×10^{-5}	288	335
27	1.00×10^{-4}	289	337
28	3.16×10^{-4}	290	339
29	1.00×10^{-3}	291	340
30	3.16×10^{-3}	292	341
31	1.00×10^{-2}	293	342
32	3.16×10^{-2}	294	343
33	1.00×10^{-1}	294	344
34	3.16×10^{-1}	294	344
35	1.00×10^0	295	344
36	3.16×10^0	295	345
37	1.00×10^1	295	345
38	3.16×10^1	295	345
39	1.00×10^2	295	345
40	3.16×10^2	295	346
41	1.00×10^3	295	346
42	3.16×10^3	295	346
43	1.00×10^4	295	346

Temperature of grains for olivine and amorphous carbon (aC) composition. The index i labels the grain mass m_i .

For the last case (intermediate temperature), we have also considered an intermediate solution with grains up to 1 g.

The free parameters are:

- $Q_{\text{H}_2\text{CO}}$ parent (s^{-1}).
- Q_{POM} on grains (% in mass of grains). An arbitrary upper limit of 20% is set on Q_{POM} . Considering laboratory experiments on cometary and interstellar ice analogs (Cottin et al., 1999a) and the complexity of residues after photolysis or irradiation, we consider that it is quite unrealistic to assume that a single molecule may repre-

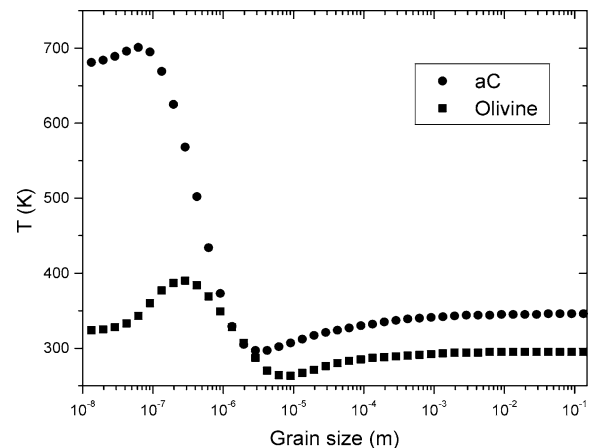


Fig. 4. Grain temperature as a function of size and composition.

sent more than 20% of the amount of complex organics by itself.

As discussed previously in this paper, we consider both thermal degradation and photodegradation. For any distance from the nucleus, if the whole initial amount of POM has already been degraded, the grain is no longer taken into account.

The best fit is calculated by minimizing

$$S = \sqrt{\frac{\sum (\text{Giotto measurement} - \text{calculation})^2}{\text{Giotto measurements} \cdot n}}$$

n being the number of Giotto measurements available ($n = 8$). E is an average value of the difference between Giotto and our calculation. We have chosen to display only results with $S < 25\%$, and as discussed earlier in this paper, we consider that only results with $S < 15\%$ are consistent with Giotto measurements.

5.1. Low temperature model

Results are shown in Table 8 and Figs. 5a and 5b. For the first case, with only the grains measured in the coma of Comet Halley, the upper limit of 20% of POM is reached. Best fits may be obtained with more POM, but are not presented here since they do not appear relevant to us. Best results, in terms of POM amount and adjustment to data, are achieved with the whole grain distribution considered (classes 1 to 43): $S = 7\%$. Thus, in the present temperature hypothesis the distribution of formaldehyde can be interpreted with a rather large amount of grains, no parent formaldehyde, and with about a percent of POM in mass on grains.

5.2. High temperature model

Results are shown in Table 8 and Fig. 5c. For the calculation including all the grains (classes 1 to 43) we do not obtain any consistent solution to display. With a smaller

Table 8
Best fits with different temperature hypotheses

Grains	Low temperature		High temperature		Intermediate temperature (%org = 30)		
	$i = 1-29$	$i = 1-43$	$i = 1-29$	$i = 1-43$	$i = 1-29$	$i = 1-35$	$i = 1-43$
$Q_{\text{H}_2\text{CO}} \text{ (s}^{-1}\text{)}$	1.1×10^{28}	0	0	–	7.14×10^{27}	0	0
% H_2CO	1.8	0	0	–	1.19	0	0
$Q_{\text{POM}} \text{ (%)}$	20.0	1.15	11	–	20	4	0.79
S	22%	7%	22%	> 35%	11%	6%	19%

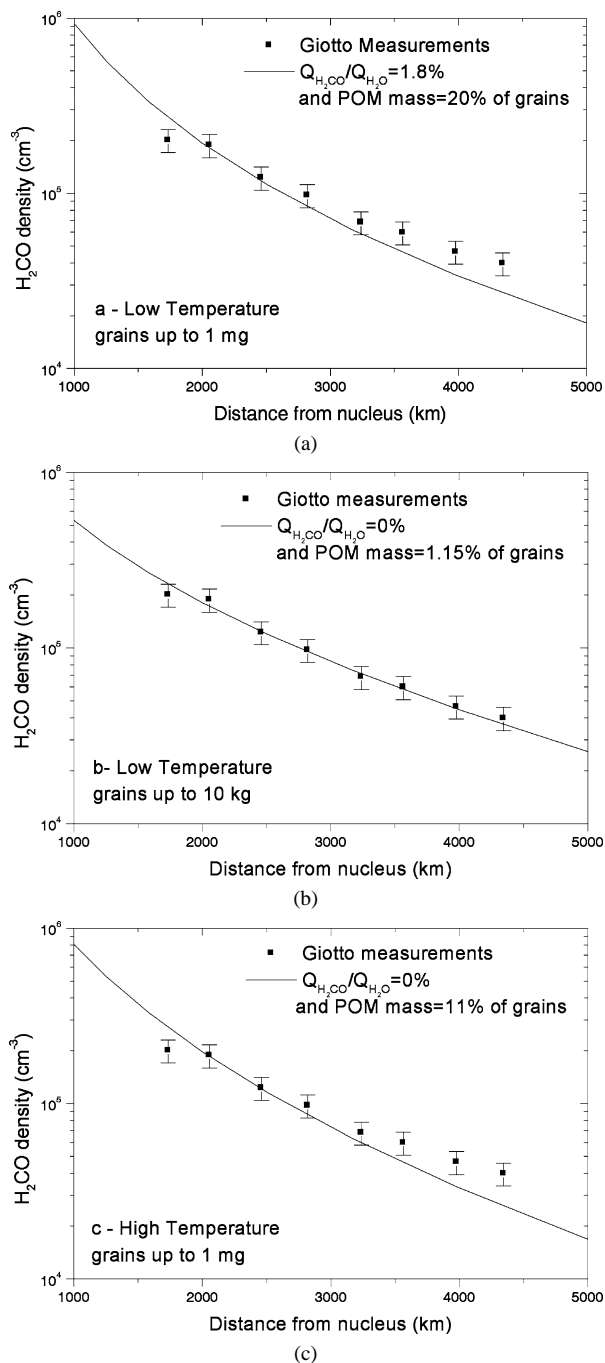


Fig. 5. Best fits for (a) $i = 1-29$ and (b) $i = 1-43$ with the low temperature model, and for (c) $i = 1-29$ with the high temperature model.

mass range for grains (classes 1 to 29), and as T_{grains} increases, the amount of POM estimated to obtain the best fit is less than for the low temperature case: 11% compared to 20%. This time, the best solution does not require any parent formaldehyde, but still, the fit to Giotto measurements is not really satisfying $S = 22\%$.

5.3. Intermediate model

Grain temperatures are actually between the two extremes previously presented. We propose now to discuss in further detail results obtained with our model for intermediate temperatures. Grain temperature depends not only on the amount of organic matter (which is the heating material), but also on the way it is mixed with silicates. We then consider three hypotheses:

- (1) Silicates and organics are entirely separated and there are pure organic grains. Then we can just consider the high temperature model, which is quite unrealistic.
- (2) Silicates and organics are homogeneously mixed. Then the temperature is an average of extreme values, dependent upon the relative amounts of both components. This assumption might be a better one, but still is far from being realistic.
- (3) Grains are a heterogeneous mixture of both components (organics may be a link between silicates to keep them together, they may wrap silicate cores, etc.). In this case the temperature of the organic component of grains is between cases (1) and (2).

Nevertheless those considerations are only speculations in comparison with what is known vs. assumptions. Despite all our attempts to reduce complexity of grains in order to calculate T in the model, one shall keep in mind that the temperature of *real* cometary grains may vary, *from grain to grain, even within the same size category*, between the two extremes.

Our intermediate model simulates case (2) above. With regard to our previous reservations and assumptions about temperature modeling, results should be interpreted as follows:

- We chose to run the model with 30% of amorphous carbon on grains. This is a lower limit of organic material required to heat the grain. Indeed, amorphous carbon,

whose properties are used to calculate T , is absorbing more solar photons than any organic compound that would actually be present on grains. Then, probably a higher organic content than 30% of aC is needed to reach the calculated temperature. Nothing more precise than only “more than 30% in mass of organics is needed” can legitimately be said about it. Greenberg (1998) estimates that about 40% of cometary grains are made of organics, consistent with our conclusion here.

- Taking into account that the mixture between silicates and organics is certainly not homogeneous; again more organics are needed to reach the temperature achieved by the model. This goes in the same direction as the previous point.
- Those assumptions do not affect the other free parameters of the model: Q_{H_2CO} , Q_{POM} .

Results are shown in Table 8 and Fig. 6. According to this model: $0 < Q_{H_2CO} < 7.14 \times 10^{27} \text{ s}^{-1}$, $0.79\% < Q_{POM} < 20\%$. The best fit to Giotto measurement in all our simulations ($S = 6\%$) is achieved for this intermediate temperature model when only grains up to 1 g are incorporated into our calculations. One can consider this assumption as an attempt to take into account that the total amount of grains is not well constrained for grains above 10 mg, and that production of H_2CO from the bulk of large grains is probably limited by diffusion throughout the surface of the large grains.

5.4. Discussion

Results obtained with the Halley-like dust model are summarized in Fig. 7. Our knowledge of the total amount of grains, and their composition (and hence their temperature), provides only a range of results between extreme cases, rather than a firm conclusion. No relevant result is obtained at high temperature with the full range of grains, those ones being too hot and too abundant to fit observations. Three other cases are slightly out of the limits we set ($S < 15\%$), those are the cases including the small range of grains at low and high temperatures, and the one with the full range of grains for intermediate temperature. Removing these cases, production of parent formaldehyde from the nucleus is estimated to be between 0 and 1.2%, and the amount of POM between 0.8 and 20% relative to the total mass of grains. This large range reflects our lack of strong constraints on grain parameters. In terms of the low amount of POM, and good fit to Giotto measurements, the best results are obtained if we consider a lot of cold grains ($Q_{POM} = 1\%$ and $S = 7\%$) and for the middle case with intermediate T and intermediate amount of grains ($Q_{POM} = 4\%$ and $S = 6\%$). This last result is probably the most realistic since it is obtained with “average” cometary grain conditions. We choose this case to discuss in further detail the contribution of grains to the overall coma composition. Figure 8 presents the percentage of POM lost from grains as a function of their size (i.e., temperature) and their distance from the nucleus. It shows

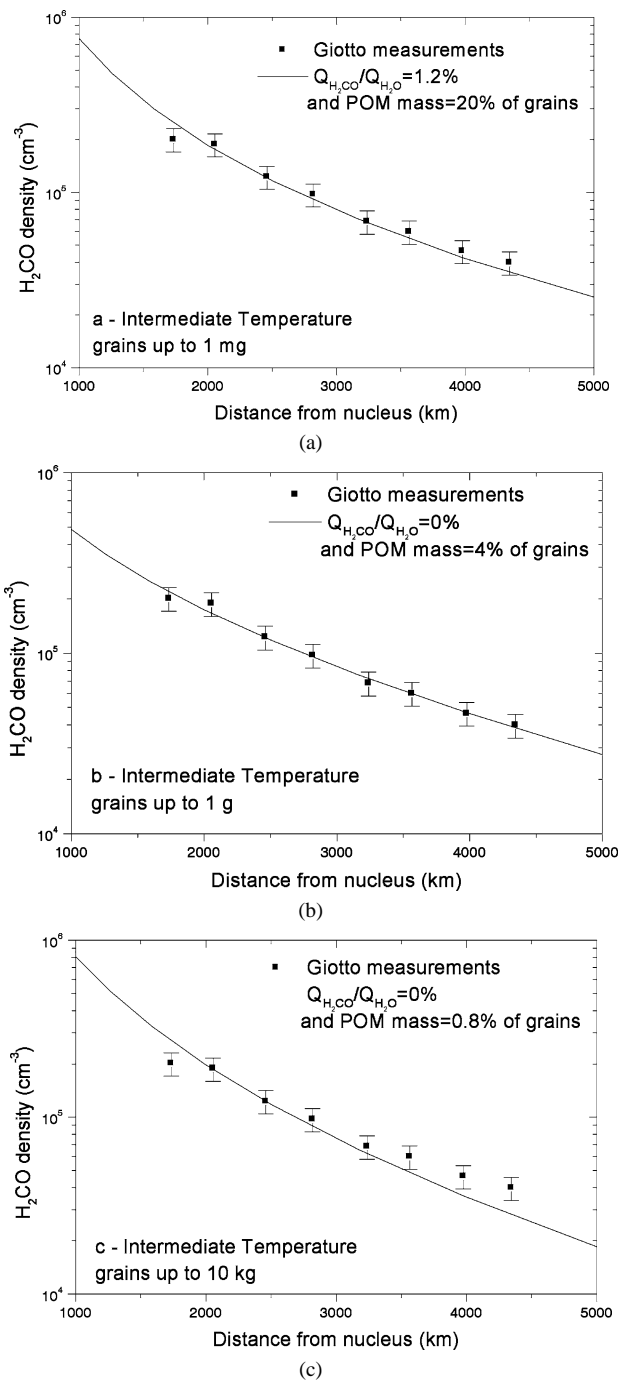


Fig. 6. Best fits for (a) $i = 1-29$, (b) $i = 1-35$, and (c) $i = 1-43$ with the intermediate temperature model.

that if POM is released entirely from small and large grains within 10^3 km, grains with a size of order $10 \mu\text{m}$ (the coldest ones) can contribute to an extended source of POM up to 10^5 km from the nucleus. Figure 9 shows the contribution of grain size to the extended formaldehyde. No contribution for grains below $1 \mu\text{m}$ is shown, because all polyoxymethylene is released before 1000 km from the nucleus, because the temperature of these grains is larger than for bigger grains. Their contribution is not displayed on the figures due to scale

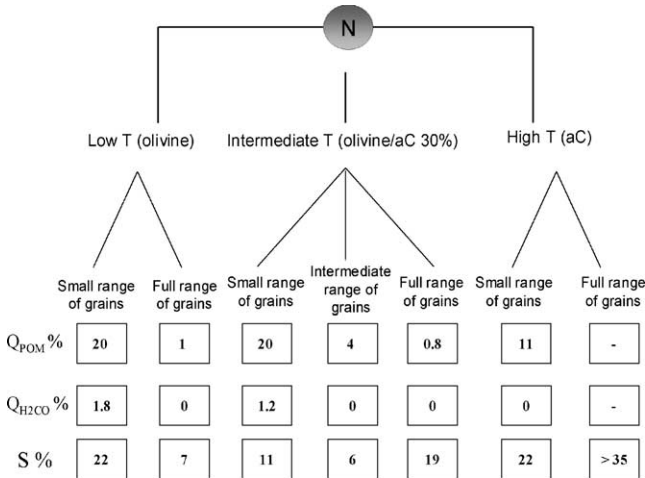


Fig. 7. Summary of results calculated with our model including both photo- and thermal-degradations of POM. From the nucleus (*N*) 3 grain temperature hypotheses are considered (aC: amorphous carbon). Grains incorporated into our calculations are: up to 1 mg for the small range (*i* = 1–29), up to 1 g for the intermediate range (*i* = 1–35), up to 10 kg for the full range (*i* = 1–43). Results for the best fit obtained are displayed below each case. Q_{POM} is the percentage in mass of POM in the refractory component of grains. Q_{H_2CO} is the ratio to water of parent formaldehyde, and σ is the divergence between our results and Giotto measurements estimated with a 35 percent error bars.

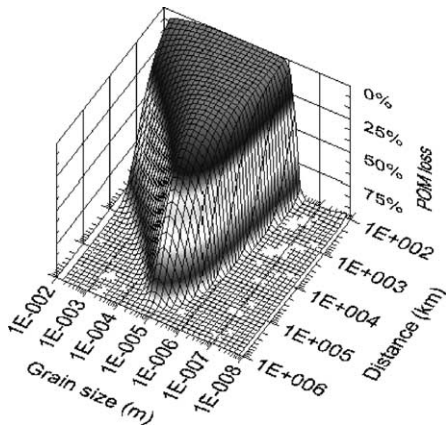


Fig. 8. Intermediate temperature and intermediate range of grains. Fraction of the total amount of POM lost by degradation as a function of grain size and distance from the nucleus.

factors, and for better clarity of the 3D graphs. For such small grains, one can see (Fig. 10) that the thermo degradation scale length is less than 100 km.

Figure 10 also shows that thermal degradation dominates the whole grain size distribution except on a range between 1 to 10 microns. For this last population the degradation is dominated by photolysis up to distances larger than 10^5 km from the nucleus. In the region covered by the Giotto measurements (1500 to 4500 km for nucleus), the production of the extended source of H_2CO is dominated by the thermal degradation of POM on the larger grains.

Figure 11 shows the discrepancy between our model and Giotto measurements (measured as a function of S) vs.

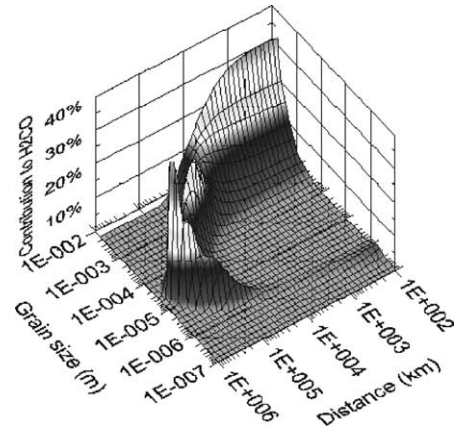


Fig. 9. Intermediate temperature and intermediate range of grains. Contribution to the production of extended formaldehyde in the coma as a function of grain size and distance from the nucleus.

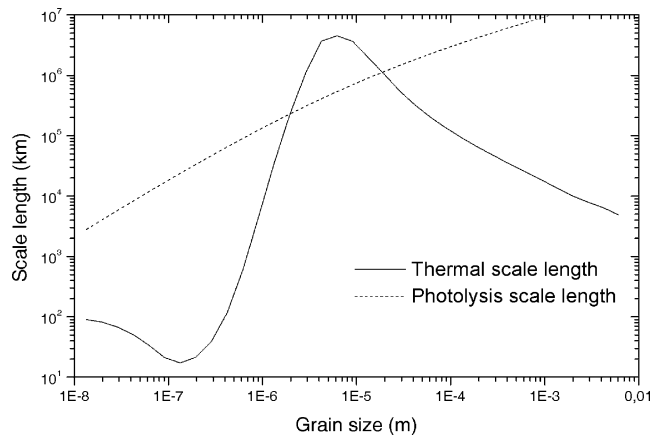


Fig. 10. Scale lengths for photo- and thermal-degradation of POM (l_p and l_t) as a function of the grain size.

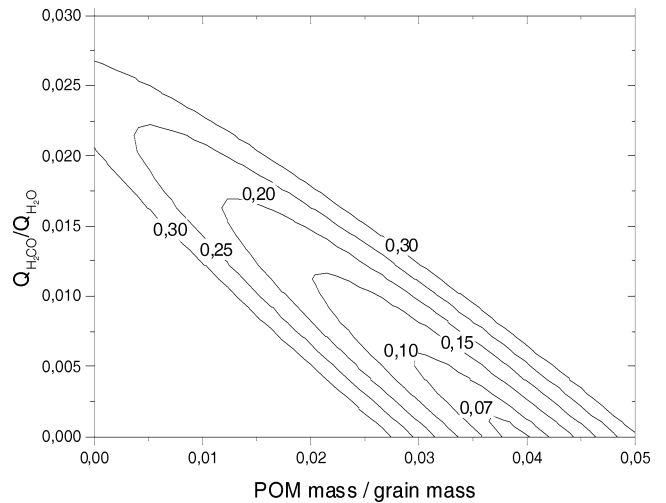


Fig. 11. Intermediate temperature and intermediate range of grains. Projected difference between model and Giotto observations (S) as a function of Q_{POM} (% POM in grains) and Q_{H_2CO} (% H_2CO/Q_{H_2O}). Only solutions with $S < 30\%$ are displayed.

Q_{POM} (% POM in grains) and $Q_{\text{H}_2\text{CO}}$ (% $Q_{\text{H}_2\text{CO}}/Q_{\text{H}_2\text{O}}$). The best solution (already presented above) is shown at the bottom and on the right of the figure: no parent formaldehyde and 4% of POM. However, the graph shows that the range of solutions for which $S < 15\%$ is rather well constrained regarding the amount of POM: $3.5\% \lesssim Q_{\text{POM}} \lesssim 4.5\%$. It also shows that some parent formaldehyde $0\% < Q_{\text{H}_2\text{CO}} < 1.2\%$ can be emitted from the nucleus. We think unlikely for H_2CO not to be present at all as a parent molecule. This compound has been detected in the interstellar medium in the gas phase (Snyder et al., 1969) as well as in the solid phase (Keane et al., 2001), moreover it is easily synthesized when ice mixtures containing $\text{H}_2\text{O} + \text{CO}$ or CH_3OH are photolyzed (Allamandola et al., 1988; Bernstein et al., 1995) or irradiated with protons (Moore et al., 1991, 1996; Hudson and Moore, 1999). H_2O , CO , and CH_3OH are among the most abundant molecules detected in comets, and are known to be parent molecules (at least partially, in the case of CO (DiSanti et al., 1999)). Native formaldehyde has also been detected in comets through high resolution near-IR spectroscopy (see for example the case of 153P/Ikeya Zhang, C/1999 H1 (Lee) and C/2001 A2 (Linear) (DiSanti et al., 2002a, 2002b)). In Comet Hale-Bopp, formaldehyde molecular abundance is estimated to be 1.1% in the coma assuming an extended source (Bockelée-Morvan et al., 2000), with a contribution of the nucleus not exceeding 6% (Wink et al., 1999). This implies that the parent H_2CO is present at a level of at most $\sim 0.1\%$. Therefore, even if Halley and Hale-Bopp abundances are not necessarily similar, we think that a more realistic solution for our model is to consider a fraction of a percent for parent H_2CO , and less than 4% in mass of POM. For example, in Fig. 11, we can see that $S \sim 10\%$ with $Q_{\text{H}_2\text{CO}} = 0.5\%$ and $Q_{\text{POM}} \sim 3\%$. As mentioned earlier in this paper, from Bernstein et al. (1995) and Greenberg (1998), values up to 8% in mass of POM-like polymers can be reached in comets through irradiation of ice mixtures. Higher values may also be reached when ices containing H_2CO and NH_3 are submitted to thermal processes. Hence, our estimate of the amount of POM is quite consistent with previous estimates based on observations and laboratory work.

6. Conclusion

The distribution of formaldehyde in Comet Halley, as reported in Meier et al. (1993), has not been satisfactorily explained, either as a parent molecule released from the nucleus, or as a daughter product of any known parent gaseous cometary compound. Based on in-situ measurements and laboratory work on cometary ice analogs, it is now established that cometary grains are probably composed of a mixture of inorganic (silicates) and organic (high molecular weight molecules) material. We propose that refractory organic molecules can be slowly degraded by solar UV pho-

tons and/or heat and that they release volatile fragments in the coma.

We present new equations to model the distribution of daughter molecules as a function of distance from nucleus, when such compounds are released from a parent in the solid phase on grains: by photodegradation, thermal degradation, or a combination of both processes. Based on quantitative measurements of the production of formaldehyde from polyoxymethylene, we show that the degradation of this polymer is so far the best interpretation for formaldehyde measurements in Comet Halley. Because of the large number of uncertain parameters (mostly grains distribution and temperature) we cannot derive a sharp estimate of the amount of POM on cometary grains. Nevertheless, according to our different hypotheses, $1\% \lesssim Q_{\text{POM}} \lesssim 20\%$ in mass of grains, with a nominal value of about 3 to 4%, and a related mixing ratio for parent formaldehyde between 0 to 1.2%, with a nominal value of a few tenths of a percent. Both nominal values are quite realistic if one refers to previous estimates based on observations and laboratory work (Bernstein et al., 1995; Greenberg, 1998; Bockelée-Morvan et al., 2000). Without being a definitive evidence for the presence polymers in comets, we conclude that the presence of POM-like polymers in the solid state on cometary grains is to date the best interpretation of observations that have remained puzzling for a long time.

This study will be extended to new measurements on Comet Hale-Bopp, in order to validate our hypothesis. This future work will require further theoretical developments of our approach and is in progress. (For Comet Hale-Bopp we deal with ground based observations, and we can both study the distribution of formaldehyde in the coma and its production as a function of heliocentric distance.) New laboratory work is also in progress to minimize the uncertainty in the kinetic constants for the degradation of the POM we use for the experimental part of this study. New quantitative measurements will also be undertaken with different kinds of POM-like polymers, different structures, synthesis procedures, etc. The sensitivity of our results to those new data will have to be checked. But the final step towards the identification of the parent molecule of formaldehyde in comets will be its in-situ detection, probably thanks to the Rosetta mission.

A main conclusion of this study is that we can no longer neglect the contribution of the refractory organic component of cometary grains to the composition of the gaseous coma. Other molecules or radicals present unexplained extended sources in comets, for example: CN (Klavetter and A'Hearn, 1994), HNC (Irvine et al., 1998a; Rodgers and Charnley, 1998, 2001), and CO (DiSanti et al., 1999). There are a few candidates to explain the origin of CN or HNC: hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$), HCN polymers, but only a few preliminary experimental results have been published so far (Cottin et al., 2002; Fray et al., Experimental study of the degradation of polymers. Application to the origin of extended sources in cometary atmospheres, sub-

mitted for publication). More laboratory work is needed to include their degradation parameters in our model to conclude whether they are good candidates or not. Coma chemistry involving volatiles can also be evoked to explain the production of HNC in some cases (Irvine et al., 1998a, 1998b). CO is a more complex case. The total amount of CO (nucleus + extended) is 24% in Hale–Bopp: about one half is produced by an extended source and the other half is from nucleus (DiSanti et al., 1999). So far no mechanism can account such a production in the coma. Even if photodegradation of POM yields a small amount of CO (about the same order of magnitude than for H₂CO (Cottin et al., 2000)), no CO is produced by thermal degradation, which is the dominant degradation mechanism of POM for most of grains. Also, if extended CO in Hale–Bopp originated from POM photodegradation, then one should expect extended formaldehyde production to at least equal that for CO, and more probably be larger by perhaps as much as one or two orders of magnitude. This would result in more H₂CO than CO in the coma, which is not the case. This suggests that POM cannot be the main precursor for carbon monoxide. An experimental study of CO release by photodegradation or thermal degradation of refractory material obtained after energetic processing of ice mixtures should be undertaken in order to determine if a CO extended source can also originate from the slow degradation in the coma of other high molecular weight molecules. The diversity of the molecular composition of comets has been established. Henceforth, complex processes are likely to occur in the coma and multiphase chemistry (solid/gas) has to be included in our attempts to model its chemistry. The case of the extended source of formaldehyde and polyoxymethylene is certainly only one example among others, and its generalization requires new experimental developments. The approach presented in this paper offers a new insight to try to unravel the nature of the complex organic components of comets, which is critical to understand the chemical evolution of material from the interstellar medium to the Solar System.

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References

- Allamandola, L.J., Sandford, S.A., Valero, G.J., 1988. Photochemical and thermal evolution of interstellar/precometary ice analogs. *Icarus* 76, 225–252.
- Arpigny, C., 1994. Physical chemistry of comets: models, uncertainties, data needs. *AIP Conf. Proc.* 312, 205–238.
- Bernstein, M.P., Sandford, S.A., Allamandola, L.J., Chang, S., Scharberg, M.A., 1995. Organic compounds produced by photolysis of realistic interstellar and cometary ice analogs containing methanol. *Astrophys. J.* 454, 327–344.
- Bessel, M.S., Wickramasinghe, N.C., 1975. Polyoxymethylene polymers as interstellar grains. *Mon. Not. R. Astron. Soc.* 170, 11P–16P.
- Biver, N., 1997. Molécules mères cométaires : observations et modélisations. Thesis. Université Paris VII, France.
- Biver, N., Bockelée-Morvan, D., Crovisier, J., Colom, P., Henry, F., Moreno, R., Paubert, G., Despois, D., Lis, D.C., 2002. Chemical composition diversity among 24 comets observed at radio wavelengths. *Earth Moon Planets* 90, 323–333.
- Biver, N., 13 colleagues, 1999. Spectroscopic monitoring of Comet C/1996 B2 (Hyakutake) with the JCMT and IRAM radio telescopes. *Astron. J.* 118, 1850–1872.
- Biver, N., 12 colleagues, 2000. Spectroscopic observations of Comet C/1999 H1 (Lee) with the SEST, JCMT, CSO, IRAM, and Nançay radio telescopes. *Astron. J.* 120, 1554–1570.
- Bockelée-Morvan, D., Crovisier, J., Colom, P., Despois, D., 1994. The rotational lines of methanol in Comets Austin 1990 V and Levy 1990 XX. *Astron. Astrophys.* 287, 647–665.
- Bockelée-Morvan, D., Wink, J., Despois, D., Biver, N., Colom, P., Crovisier, J., Gerard, E., Lellouch, E., Jorda, L., 1998. Interferometric imaging of molecular lines in Comet Hale–Bopp. *Bull. Am. Astron. Soc.* 30, 31.02.
- Bockelée-Morvan, D., 17 colleagues, 2000. New molecules found in Comet C/1995 O1 (Hale–Bopp). Investigating the link between cometary and interstellar material. *Astron. Astrophys.* 353, 1101–1114.
- Boice, D.C., Huebner, W.F., Sablik, M.J., Konno, I., 1990. Distributed coma sources and the CH₄/CO ratio in Comet Halley. *Geophys. Res. Lett.* 17, 1813–1816.
- Combes, M., 16 colleagues, 1988. The 2.5–12 μm spectrum of Comet Halley from the IKS–VEGA experiment. *Icarus* 76, 404–436.
- Combi, M.R., Delsemme, A.H., 1980. Neutral cometary atmospheres. I. An average random walk model for photodissociation in comets. *Astrophys. J.* 237, 633–640.
- Cooke, A., Wickramasinghe, N.C., 1977. Polyoxymethylene co-polymers on grains. *Astrophys. Space Sci.* 50, 43–53.
- Cottin, H., Gazeau, M.C., Raulin, F., 1999a. Cometary organic chemistry: a review from observations, numerical and experimental simulations. *Planet. Space Sci.* 47, 1141–1162.
- Cottin, H., Gazeau, M.C., Doussin, J.F., Raulin, F., 1999b. S.E.M.A.Ph.Or.E COMETAIRE, a tool for the study of the photochemical decomposition of probable cometary large organic molecules. First application: polyoxymethylene. *Phys. Chem. Earth C* 24, 597–602.
- Cottin, H., Gazeau, M.C., Doussin, J.F., Raulin, F., 2000. An experimental study of the photodegradation of polyoxymethylene at 122, 147 and 193 nm. *J. Photochem. Photobiol.* 135, 53–64.
- Cottin, H., Szopa, C., Moore, M.H., 2001a. Production of hexamethylenetetramine in photolyzed and irradiated interstellar cometary ice analogs. *Astrophys. J. Lett.* 561, L139–L142.
- Cottin, H., Gazeau, M.C., Bénilan, Y., Raulin, F., 2001b. Polyoxymethylene as parent molecule for the formaldehyde extended source in Comet Halley. *Astrophys. J.* 556, 417–420.
- Cottin, H., Gazeau, M.C., Chaquin, P., Bénilan, Y., Raulin, F., 2001c. Experimental and theoretical studies on the gas/solid/gas transformation cycle in extraterrestrial environments. *J. Geophys. Res. (Planets)* 106, 33325–33332.

- Cottin, H., Bachir, S., Raulin, F., Gazeau, M.C., 2002. Photodegradation of hexamethylenetetramine by VUV and its relevance for CN and HCN extended sources in comets. *Adv. Space Res.* 30, 1481–1488.
- Crifo, J.F., 1988. Cometary dust sizing: comparison between optical and in-situ sampling techniques. *Part. Part. Syst. Char.* 5, 38–46.
- Crifo, J.F., 1991. Hydrodynamic models of the collisional coma. In: Newburn, R.L., Neugebauer, M., Rahe, J. (Eds.), *Comets in the Post-Halley Era*. Kluwer, Dordrecht, pp. 937–989.
- Crifo, J.F., 1994. Elements of cometary aeronomy. *Current Science* 66, 583–602.
- Crifo, J.F., 1995. A general physicochemical model of the inner coma of active comets. I. Implications of spatially distributed gas and dust production. *Astrophys. J.* 445, 470–488.
- Crifo, J.F., Rodionov, A.V., 1997. The dependence of the circumnuclear coma structure on the properties of the nucleus. I. Comparison between a homogeneous and an inhomogeneous spherical nucleus, with application to P/Wirtanen. *Icarus* 127, 319–353.
- Crovisier, J., 1994. Photodestruction rates for cometary parent molecules. *J. Geophys. Res.* 99, 3777–3781.
- Crovisier, J., Bockelée-Morvan, D., 1999. Remote observations of the composition of cometary volatiles. *Space Sci. Rev.* 90, 19–32.
- Dello Russo, N., DiSanti, M.A., Mumma, M.J., Magee-Sauer, K., Rettig, T.W., 1998. Carbonyl sulfide in Comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp): evidence for an extended source in Hale-Bopp. *Icarus* 135, 377–388.
- DiSanti, M.A., Mumma, M.J., Dello Russo, N., Magee-Sauer, K., Novak, R., Rettig, T.W., 1999. Identification of two sources of carbon monoxide in Comet Hale-Bopp. *Nature* 399, 662–665.
- DiSanti, M.A., Dello Russo, N., Magee-Sauer, K., Gibb, E.L., Reuter, D.C., Mumma, M.J., 2002a. CO, H₂CO, and CH₃OH in Comet 2002 C1 Ikeya-Zhang. In: *Proceedings of Asteroids, Comets, Meteors—ACM 2002*, International Conference. In: *ESA SP*, vol. 500, pp. 571–574.
- DiSanti, M.A., Dello Russo, N., Magee-Sauer, K., Gibb, E.L., Reuter, D.C., Xu, L.-H., Mumma, M.J., 2002b. A comparison of the volatile carbon-oxygen chemistry in several Oort cloud comets. *Bull. Am. Astron. Soc.* 34, 855.
- DiSanti, M.A., Mumma, M.J., Dello Russo, N., Magee-Sauer, K., Griep, D.M., 2003. Evidence for a dominant native source of carbon monoxide in Comet C/1996 B2 (Hyakutake). *J. Geophys. Res. (Planets)* 108, 15.
- Dole, M., 1973. Polyoxymethylene. In: Dole, M. (Ed.), *The Radiation Chemistry of Macromolecules*, Vol. II. Academic Press, pp. 187–194.
- Eberhardt, P., 1999. Comet Halley's gas composition and extended sources: results from the neutral mass spectrometer on Giotto. *Space Sci. Rev.* 90, 45–52.
- Eberhardt, P., 10 colleagues, 1987. The CO and N₂ abundance in Comet P/Halley. *Astron. Astrophys.* 187, 481–484.
- Fink, U., DiSanti, M.A., 1990. The production rate and spatial distribution of H₂O for Comet P/Halley. *Astrophys. J.* 364, 687–698.
- Fischer, V.H., Langbein, W., 1967. Strahlungsinduzierte Reaktionen in Polyoxymethylen. *Kolloid Z. Z. Polym.* 216–217, 329–336.
- Goldanskii, V.I., 1977. Mechanism for formaldehyde polymer formation in interstellar space. *Nature* 268, 612–613.
- Greenberg, J.M., 1982. What are comets made of? A model based on interstellar dust. In: Wilkening, L.L. (Ed.), *Comets*. Univ. of Arizona Press, Tucson, pp. 131–163.
- Greenberg, J.M., 1998. Making a comet nucleus. *Astron. Astrophys.* 330, 375–380.
- Greenberg, J.M., Li, A., 1998. From interstellar dust to comets: the extended CO source in Comet Halley. *Astron. Astrophys.* 332, 374–384.
- Haser, L., 1957. Distribution d'intensité dans la tête d'une comète. *Bull. Acad. Roy. Belgique* 43, 740–750.
- Hudson, R.L., Moore, M.H., 1999. Laboratory studies of the formation of methanol and other organic molecules by water + carbon monoxide radiolysis: relevance to comets, icy satellites, and interstellar ices. *Icarus* 140, 451–461.
- Huebner, W.F., 1987. First polymer in space identified in Comet Halley. *Science* 237, 628–630.
- Huebner, W.F., Boice, D.C., Sharp, C.M., 1987. Polyoxymethylene in Comet Halley. *Astrophys. J. Lett.* 320, 149–152.
- Huebner, W.F., Keady, J.J., Lyon, S.P., 1992. Solar photo rates for planetary atmospheres and atmospheric pollutants. *Astrophys. Space Sci.* 195, 1–294.
- Irvine, W.M., 16 colleagues, 1996. Spectroscopic evidence for interstellar ices in Comet Hyakutake. *Nature* 383, 418–420.
- Irvine, W.M., Bergin, E.A., Dickens, J.E., Jewitt, D., Lovell, A.J., Matthews, H.E., Schloerb, F.P., Senay, M., 1998a. Chemical processing in the coma as the source of cometary HNC. *Nature* 393, 547–550.
- Irvine, W.M., Dickens, J.E., Lovell, A.J., Schloerb, F.P., Senay, M., Bergin, E.A., Jewitt, D., Matthews, H.E., 1998b. Chemistry in cometary comae. *Faraday Discussion* 109, 475–492.
- Keane, J.V., Tielens, A.G.G.M., Boogert, A.C.A., Schutte, W.A., Whittet, D.C.B., 2001. Ice absorption features in the 5–8 μ m region toward embedded protostars. *Astron. Astrophys.* 376, 254–270.
- Kissel, J., Krueger, F.R., 1987. The organic component in dust from Comet Halley as measured by the PUMA mass spectrometer on board Vega 1. *Nature* 326, 755–760.
- Klavetter, J.J., A'Hearn, M.F., 1994. An extended source for CN jets in Comet P/Halley. *Icarus* 107, 322–334.
- Lis, D.C., Keene, J., Young, K., Phillips, T.G., Bockelée-Morvan, D., Crovisier, J., Schilke, P., Goldsmith, P.F., Bergin, E.A., 1997. Spectroscopic observations of Comet C/1996 B2 (Hyakutake) with the Caltech Submillimeter Observatory. *Icarus* 130, 355–372.
- Lisse, C.M., A'Hearn, M.F., Hauser, M.G., Kelsall, T., Lien, D.J., Moseley, S.H., Reach, W.T., Silverberg, R.F., 1998. Infrared observations of comets by COBE. *Astrophys. J.* 496, 971.
- McDonnell, J.A.M., Lamy, P.L., Pankiewicz, G.S., 1991. Physical properties of cometary dust. In: *Comets in the Post-Halley Era*, Vol. 2. Kluwer, Dordrecht, pp. 1043–1073.
- Meier, R., Eberhardt, P., Krankowsky, D., Hodges, R.R., 1993. The extended formaldehyde source in Comet P/Halley. *Astron. Astrophys.* 277, 677–691.
- Mitchell, D.L., Lin, R.P., Carlson, C.W., Korth, A., Rème, H., Mendis, D.A., 1992. The origin of complex organic ions in the coma of Comet Halley. *Icarus* 98, 125–133.
- Möller, G., Jackson, W.M., 1990. Laboratory studies of polyoxymethylene: application to comets. *Icarus* 86, 189–197.
- Moore, M.H., Tanabé, T., 1990. Mass spectra of sputtered polyoxymethylene: implications for comets. *Astrophys. J.* 365.
- Moore, M.H., Khanna, R., Donn, B., 1991. Studies of proton irradiated H₂O + CO₂ and H₂O + CO ices and analysis of synthesized molecules. *J. Geophys. Res.* 96, 17541–17545.
- Moore, M.H., Ferrante, R.F., Nuth, J.A.I., 1996. Infrared spectra of proton irradiated ices containing methanol. *Planet. Space Sci.* 44, 927–935.
- Mount, G.H., Rottman, G.J., 1981. The solar spectral irradiance 1200–3184 Å near solar maximum. *J. Geophys. Res.* 86, 9188–9193.
- Mumma, M.J., Reuter, D.C., 1989. On the identification of formaldehyde in Halley's comet. *Astrophys. J.* 344, 940–948.
- Rabek, J.F., 1995. *Polymer Photodegradation: Mechanisms and Experimental Methods*. Chapman & Hall, London.
- Rodgers, S.D., Charnley, S.B., 1998. HNC and HCN in comets. *Astrophys. J. Lett.* 501, L227–L230.
- Rodgers, S.D., Charnley, S.B., 2001. On the origin of HNC in Comet Lee. *Mon. Not. R. Astron. Soc.* 323, 84–92.
- Roessler, K., Sauer, M., Schulz, R., 1992. Gaseous products from VUV photolysis of cometary solids. *Ann. Geophys.* 10, 226–231.
- Schutte, W.A., Allamandola, L.J., Sandford, S.A., 1993a. Formaldehyde and organic molecule production in astrophysical ices at cryogenic temperatures. *Science* 259, 1143–1145.
- Schutte, W.A., Allamandola, L.J., Sandford, S.A., 1993b. An experimental study of the organic molecules produced in cometary and interstellar ice analogs by thermal formaldehyde reactions. *Icarus* 104, 118–137.
- Shalaby, S.W., 1979. Radiative degradation of synthetic polymers: chemical physical, environmental, and technological considerations. *J. Polymer Sci.: Macromol. Rev.* 14, 419–458.

- Snyder, L.E., Buhl, D., Zuckerman, B., Palmer, P., 1969. Microwave detection of interstellar formaldehyde. *Phys. Rev. Lett.* 22, 679.
- Snyder, L.E., Palmer, P., Pater, I.d., 1989. Radio detection of formaldehyde emission from Comet Halley. *Astron. J.* 97, 246–253.
- Vanysek, V., Wickramasinghe, N.C., 1975. Formaldehyde polymers in comets. *Astrophys. Space Sci.* 33, L19–L28.
- Wink, J., 10 colleagues, 1999. Evidence for extended sources and temporal modulations in molecular observations of C/1995 O1 (Hale-Bopp) at the IRAM interferometer. *Earth Moon Planets* 78, 63.
- Woon, D.E., 1999. Ab initio quantum chemical studies of reactions in astrophysical ices 1. Aminolysis, hydrolysis, and polymerization in H₂CO/NH₃/H₂O ices. *Icarus* 142, 550–556.