

From interstellar dust to comets: the extended CO source in comet Halley

J. Mayo Greenberg and Aigen Li

Laboratory Astrophysics, University of Leiden, Postbus 9504, 2300 RA Leiden, The Netherlands
(mayo@rulhl1.LeidenUniv.nl; agli@strw.LeidenUniv.nl)

Received 11 September 1997 / Accepted 2 December 1997

Abstract. Some simple molecules in comet comae like CO, C₂, C₃, CN, H₂CO appear to be distributed in such a way that they are neither directly emitted from the nucleus surface nor created as daughter molecules from more complex gas phase species. The only remaining possible source is the organic component in comet dust. The requirements imposed on the comet dust grains by the distributed CO emission are that they be heated sufficiently to evaporate a large fraction of the more volatile fraction of the complex organic refractory molecules and that a large fraction of these contain CO groups. Inferring the *dust/gas* ratio within the mass limits from the comet dust size (mass) distribution obtained by the Giotto spacecraft for comet Halley, and assuming that the refractory organics remaining on the silicate cores are the heating agent by solar radiation in fluffy aggregates of interstellar core-mantle particles, the upper limits of the total amount of CO provided by dust can be approximately determined as a function of porosity. The resulting maximum CO production rate predicted by the comet dust model is significantly less than the observed distributed CO abundance. A possible solution lies in the fact that the dust to gas ratio has been underestimated in the dust size distribution employed here, by neglecting efficient dust fragmentation and sublimation in the innermost coma. On the other hand, it may not be impossible that the extended CO abundance was overestimated due to the crossing of dust jets, the time variation of the comet nucleus activity, and the anisotropic outgassing nature of the nucleus. At this point we can certainly say that, in order to obtain the observed distributed CO production rate from comet dust, it requires not only the organic refractory mantles and very high porosity, but also it seems that more heatable dust must be available than has been deduced from the space observation.

Key words: ISM: dust – comets: general – comets: individual: P/Halley

1. Introduction

When a comet approaches the Sun its volatile constituents are evaporated from the nucleus and move outward into the coma. The water group ions are by far the most abundant in the coma and it is generally believed that the source of H₂O is primarily the consequence of a direct outflow from the nucleus. An exception to this is that at large heliocentric distances prior to perihelion the H₂O source may be attributed to icy grains where the cometary activity is governed by the sublimation of molecules more volatile than H₂O. On the other hand, the radial distribution of many of the other molecular components of the coma, of which CO is the most abundant, indicates an extended source as well; i.e., the CO is produced not only directly from the nucleus but also from material which is moving outward from the nucleus. Eberhardt et al. (1987), using a spherically symmetric extended source function suggested that the nucleus rate of production of CO as a parent molecule in comet Halley was, relative to H₂O, $n(\text{CO})/n(\text{H}_2\text{O}) \leq 0.07$. They found that rather than falling off as $1/R^2$, the CO intensity shows an approximately exponential growth up to about 20000 km. The total derived production rate was $Q(\text{CO})/Q(\text{H}_2\text{O}) \leq 0.15$ from which it may be inferred that the extended source must account for $Q'(\text{CO})/Q(\text{H}_2\text{O}) \leq 0.08$. Eberhardt et al. (1987) speculated that the most likely extended source of the CO was some molecule evaporated from the organic component of the comet dust. Other molecules, like C₂, C₃, CN, H₂CO (Clairemidi et al. 1990; A'Hearn et al. 1986a, 1986b; Meier et al. 1993; Klavetter & A'Hearn 1994) in comet Halley and probably H₂CO in some other comets (e.g., Bockelée-Morvan & Crovisier 1992; Colom et al. 1992) also exhibit extended source distributions and are more than likely attributed as well to the organic fraction of the comet dust (Greenberg 1982a; Greenberg & Hage 1990).

Samarasinha & Belton (1994) have proposed an alternative description of the extended source distribution. Their description in terms of an extended collimated jet source originating in a vent rather than a spherically symmetric source leads to the suggestion that while only 1/3 of the CO is directly sublimated from the nucleus this leaves about 2/3 to be accounted for by the “effective” extended source function. They then conclude that

about 50% of this 2/3 “may be formed via photolysis of H₂CO while the *rest* (our italics) can be due to CO trapped in grain mantles and other C=O bearing molecules”. The question may be asked about what is the distributed source of H₂CO as well as the C=O bearing molecules? It appears that even if one attributes a significant fraction of the extended CO distribution to a collimation effect there still remains at least 1/3 to be accounted for as coming from the grain mantles; i.e., $Q'(CO)/Q(H_2O) \leq 0.05$.

The simulation by Samarasingha & Belton (1994) gave CO outflow velocities which appear to be incompatible with the terminal velocities of large dust grains (Finson & Probst 1968). However, if the dust grains are fluffy aggregates of interstellar dust particles as proposed by Greenberg & Hage (1990), their densities are such that the terminal velocities of a much larger fraction of the comet dust grain velocities are the same as that of the 0.1 μm grains in the Finson & Probst (1968) model which was stated as defining the largest mass for the terminal dust velocity. The density of the fluffy comet dust model required to provide the infrared emission is $\rho \leq 0.1 \text{ g cm}^{-3}$. At this density an area to mass ratio comparable to that for the 0.1 μm compact particles is achieved for masses $\sim 10^3$ times larger than that of 0.1 μm compact dust grains. Thus a much larger fraction of the McDonnell size distribution (McDonnell et al. 1991) may be considered as a source of the extended molecule distribution. But is even this large enough? The limit for $\rho = 0.1 \text{ g cm}^{-3}$ mass is still only 10^{-11} g .

The framework of the fluffy aggregate comet model is that comets are formed at very low temperature by aggregation of interstellar silicate core-organic refractory mantle particles with initial outer mantles of ices (Greenberg 1982b; Greenberg & Hage 1990). One of the observational supports of the model is that the in situ mass spectra of Halley dust with high dynamic range show that, except for the very small (attogram) grains (Utterback & Kissel 1990), neither pure organic (so-called “CHON”) nor pure silicate particles exist; instead, they are intimately mixed on a very fine scale in such a manner that they form the subunits with a core-mantle structure in the aggregates (Lawler & Brownlee 1992) as additionally reflected by the time-delay phenomenon in measuring the mass spectra (Kissel et al. 1986). An additional criterion required for the organic mantles of the interstellar dust in the comet dust aggregates is that the comet dust becomes hot enough to evaporate a significant portion of C=O bearing molecules. It was shown (Greenberg & Hage 1990; Greenberg & Shalabiea 1994; Greenberg & Li 1997) that to account for even $Q'(CO)/Q(H_2O) = 0.03$ may put further limitations on the density of comet dust than inferred from infrared emissivities. These calculations were only preliminary. We shall here attempt to put the result into much more quantitative terms. This will require more detailed calculations of the temperatures of comet dust as a function of porosity (density).

In Sect. 2 we illustrate the chemical composition of the organic refractory materials with emphasis on their potentiality as a CO source. The comet dust temperatures are calculated in Sect. 3 as a function of grain size (mass), porosity and the thickness of organic mantle. In Sect. 4 the volatility of the organics

containing CO groups is then used as a basis for providing upper size limits and lower porosity limits on the comet dust aggregates required to evaporate the organic mantle molecules in a manner consistent with the detected CO radial profile and in sufficient abundance with respect to H₂O. The possibility of the overestimation of the observed CO abundance in comet Halley is also discussed. The organic dust components as a source for other gas molecules such as C₂, C₃, CN etc. are briefly investigated in Sect. 5. Sect. 6 presents the conclusions.

2. Chemical composition of the interstellar organic refractory materials

It is now well established that, where volatile dust mantles like H₂O are not observed, as in the diffuse clouds, there is an equally ubiquitous solid organic material, mantling the silicate which is observed via its 3.4 μm absorption characteristic of CH stretches in CH₂ and CH₃ groups (Pendleton et al. 1994). The observational sources of information on the cometary organic refractory dust component are the mass spectrometry (Kissel & Krueger 1987). On the other hand chemical analysis and infrared spectra of laboratory organics are the most directly available. Before the interstellar dust aggregates into cometesimals it has an outer mantle of volatile ices with H₂O and CO being the dominant components (Greenberg 1982b). These outer mantle volatiles constitute the source of the direct nucleus emissions of H₂O and CO and will not primarily concern us here. What does concern us is the *chemical* composition of the *nonvolatile organics* and how their chemical components can react *within* the comet dust to provide a source of distributed CO molecules as the dust is heated.

In this work, the chemical characteristics of the laboratory organics – the residues of the photolysis of H₂O : CO : NH₃ = 5:5:1 mixtures at 10 K (Briggs et al. 1992) are taken as a first approximation to interstellar organic mantles (“first generation” organic refractory). The gas chromatograph mass spectrometer (GCMS) analysis of the soluble component shows that it consists in part of many prebiotically significant molecules, the most abundant having been determined to be approximately 7% ethylene glycol (HOCH₂CH₂OH), 30% glycolic acid (HOCH₂CO₂H), 21% 2-hydroxyacetamide (HCCH₂CONH₂), 3% urea (NH₂CONH₂), 6% glycerol (HOCH₂CH(OH)CH₂OH), 7% glyceric acid (HOCH₂CH(OH)CO₂H), and 19% glyceramide (HOCH₂CH(OH)CONH₂). Mass spectroscopic analysis of a residue has revealed masses up to ~ 1000 and identifications of both aliphatic and aromatic hydrocarbons have been obtained. Such masses appear to be present in all residues of similar mixtures. These results indicate the presence of highly unsaturated, aromatic hydrocarbons. This agrees qualitatively with what has been found for meteoritic material (Grady et al. 1983; Gilmour & Pillinger 1985) and cometary material (Kissel & Krueger 1987; Mukhin et al. 1989). The most refractory part of the organic residue material consists of relatively high molecular weight ($\geq 400 \text{ AMU}$) polymers, which have not yet been completely characterized.

The volatile part has also been studied by means of a gas collector (Mendoza-Gómez 1992). After the initial gas mixture ($\text{H}_2\text{O} : \text{CO} : \text{NH}_3 = 5:5:1$) was irradiated at 12 K, the sample was slowly warmed up, and the material coming off was trapped with a gas collector between given temperatures. It is interesting to note how little nitrogen is contained in the intermediate masses shown here compared with the compounds discussed earlier (Briggs et al. 1992). Coincidentally, nitrogen appears to be underabundant in comet volatiles (Wyckoff et al. 1991) and may possibly be embedded in the highly polymerized fraction which in our residue has not yet been analyzed. These results are consistent with comet origins as being the interstellar dust.

Comparison with comet Halley data shows a wide range of correspondences but the data is still incomplete. One basis for comparison can be made using the relative atomic compositions. This is being studied now both for the laboratory residues and the space irradiated residues discussed later in this section. A preliminary estimate of the relative atomic composition of the various laboratory residues of $\text{H}_2\text{O} : \text{CO} : \text{NH}_3 = 5:5:1$ is as follows:

- 1) Products evaporated and collected at $100\text{K} < T < 300\text{K}$ (Greenberg et al. 1993; Mendoza-Gómez 1992) — C : O : N : H = 1 : 1.2 : 0.03 : 1.4;
- 2) Organic residue material remaining at room temperature and analyzed by GCMS (Briggs et al. 1992) — C : O : N : H = 1 : 1.06 : 0.1 : 2.2;
- 3) Organic residue remaining at room temperature analyzed by mass spectroscopy [relatively more refractory than portion (2)] (Greenberg et al. 1993; Mendoza-Gómez 1992) — C : O : N : H = 1 : 0.06 : 0.001 : 1.1;
- 4) Unanalyzed organic residue (estimates based on the *overall* structure of the background mass spectra) — C : O : N : H = 1 : 0.06 : >0.001 : 1.1.

There have been no precise measurements of the relative amount of products 1, 2 and 3 but estimates have been made. From the surface appearance of the cold finger on which the residues have been created and which remain after various stages in the analysis procedures we have assumed roughly equal amounts of (1) and (2), and of (3) and (4). The molecules in (1) may be labeled as volatile (**V**) with respect to the temperatures at which Halley material was measured at about 1 AU; i.e., the dust at 1 AU has a temperature well above 300 K. Some of the organic residue molecules in (2) sublime at temperatures $\geq 350 - 400$ K which is required for them to be the possible sources of some of the CO in comet Halley as well as other molecules like C_2 and CN (Greenberg & Shalabiea 1994; Greenberg & Hage 1990; Greenberg, Singh & Almeida 1993). Some would remain solid at even higher temperatures (Sandford et al. 1991). At least approximately 1/2 of the mass of the molecules in (2) are required to provide the distributed source of CO in the comet Halley coma (Greenberg & Shalabiea 1994; Greenberg & Hage 1990). On this basis we assign 1/2 of (2) to the volatile category (**V**) and 1/2 to the refractory (**R**) category. The total volatile component is then estimated to be (1) + 1/2 (2) and the total refractory component is 1/2 (2) + (3) + (4). These

approximations lead to **V**: C:O:N:H = 1:1.2:0.05:1.7 and **R**: C:O:N:H = 1:0.6:>0.01:1.28. The *total* relative composition using equal masses of **V** and **R** as implied by Halley mass spectra is (**V**+**R**) = 1: 0.91: 0.03: 1.49. According to Krueger (private communication, based on Krueger & Kissel 1987) the stoichiometric distribution of elements in comet Halley mass spectra are as follow: dust = C:O:N:H \simeq 1:0.5:0.04:1 and PICCA gas = C:O:N:H \simeq 1:0.8:0.04:1.5 and, assuming equal amounts of gas and dust gives a *total* for the organics C:O:N:H = 1:0.6:0.04:1.2. It should be noted that the relative abundances for comet Halley dust are for the *organics* alone so that they are not to be directly compared with those in Jessberger & Kissel (1991) which include the *silicates* as well.

The comparison between the laboratory and comet Halley complex organics in terms of stoichiometric ratio is well within the expected errors described by Krueger (private communication) and Krueger & Kissel (1987). We have not yet answered the question of where the missing nitrogen is to be found but the overall consistency is reasonable. The $3.4 \mu\text{m}$ features in the infrared spectra of “first generation” laboratory residues although they bear a reasonably close resemblance to those of the interstellar dust, have not provided a really good fit (Pendleton et al. 1994). However, infrared spectra have been taken of laboratory residues exposed to long term solar ultraviolet irradiation equivalent to $\sim 10^6 - 10^7$ years in diffuse clouds where the volatile molecules are absent from the grain mantles. It is worthwhile noting that not only do their spectra more closely resemble those of interstellar dust in the $3.4 \mu\text{m}$ region than *any other* laboratory analogue refractory, but also their overall spectra bear a remarkably close resemblance to that of the organic component of the Murchison meteorite (Greenberg et al. 1995). As far as the $3.4 \mu\text{m}$ emission feature of comets is concerned, we should note that there is some controversy as to whether or how much is due to the organic refractory mantles or to gas phase molecules, e.g. methanol (Mumma et al. 1993; Bockelée-Morvan, Brooke & Crovisier 1995).

Adding up all the possible CO groups in the GCMS analyzed molecules gives a fraction by mass of ~ 0.16 of that component of the organic refractory. These compounds would be expected to have higher vapor pressures than the polymeric component. Whether the CO results from pyrolysis or photodissociation of the individual molecules is not considered here – only the maximum available CO. According to Kissel & Krueger (1987) only about 1/2 of the original comet organic refractory remains as a solid fraction of the comet dust, the rest appearing as part of the volatile coma molecules. For the dominant source of the distributed CO we shall estimate the lowest temperature at which the GCMS compounds evaporate and thus place some constraints on the properties of the comet dust aggregates.

3. The comet dust temperatures

The temperature of the aggregated comet dust is a critical parameter for the determination of the CO emission rate. Following Greenberg & Hage (1990) we shall assume that dust which comes off the comet consists initially of aggregates of tenth

micron silicate core-organic refractory mantle interstellar dust grains from which the outer mantle of volatile components has evaporated. The temperature T_{cd} of comet dust with a size a was calculated on the basis of the dust energy balance between absorption and emission as following,

$$\int_0^{\infty} \pi a^2 Q_{abs}(a, \lambda) R(r, \lambda) d\lambda = \int_0^{\infty} \pi a^2 Q_{abs}(a, \lambda) 4\pi B(T_{cd}, \lambda) d\lambda \quad (1)$$

where $R(r, \lambda)$ is the solar radiation field where the comet is located (r); $B(T_{cd}, \lambda)$ is the Planck function; $Q_{abs}(a, \lambda)$ is the absorption efficiency which was obtained from Mie theory, assuming both the fluffy aggregates and the individual particles in the aggregates are spherical. We adopted the optical constants of interstellar silicates and organic refractories summarized in Li & Greenberg (1997). The composition of the interstellar silicates has been conjectured as most likely being that of an amorphous olivine $MgFeSiO_4$ (see Greenberg & Li 1996). We should note here the presence of the crystalline silicate component in comet dust. The crystalline silicate emission spectra have been detected in some comets (see Hanner et al. 1994 for a summary) including comet Halley and the recent exciting comet Hale-Bopp (Crovisier et al. 1997). Where and how the crystalline silicates are formed is not yet known but it seems to us that it is more than likely that the crystallization process occurred after comet formation and probably not until the comet dust is heated by the Sun (Greenberg et al. 1996). Although considerable work remains to be done on this subject we shall assume that the optical properties of amorphous olivine are of sufficient accuracy for the purpose of this work – calculating the comet dust temperatures.

The Maxwell-Garnett effective medium theory (Bohren & Huffman 1983) was applied twice to calculate the effective dielectric function first of the individual core-mantle particles and then of the aggregates (Greenberg & Hage 1990). Note, in addition to emission, evaporation also causes dust grains to lose energy. However, at ~ 1 AU, the evaporative cooling rate is much smaller than the radiative cooling rate (Lamy & Perrin 1988) therefore the evaporation term is not included in Eq. 1. Since the relatively more volatile fraction of the organics can no longer contribute to the dust mass or to the dust heating we shall consider a range of possible ratios of organic (**or**) to silicate (**si**) masses with the minimum being $m_{or}/m_{si} = 0$ (pure silicates) and the maximum being 1. These results are presented Fig. 1 for a number of different porosities. It is apparent that the grain temperature increases with increasing porosity, and with decreasing size. The dust grains become hotter as the organic refractory mantles become thicker.

For the size distribution of the comet dust we use that of McDonnell et al. (1991) as a starting point. However, it is important to keep in mind that the McDonnell size distribution was derived on the basis of an extrapolation of the spacecraft measurements which were available from 2×10^5 km to 600 km away from the nucleus. With the neglect of dust fragmentation, the extrapolation to the nucleus surface by McDonnell et al.

(1991) may result in an underestimation of the weight of larger dust grains and thereby an underestimation of the total dust mass in the inner coma region. The effect could be significant, if it is true, as argued by various authors that, the fragmentation processes are most efficient in the innermost coma (Keller et al. 1990; Konno et al. 1993; Goidet-Devel et al. 1997). Such effect will ultimately be taken into account.

4. The nature of the distributed CO source

Up to now we have described the relevant characteristics of comet dust as a potential source for the extended CO. In this section we are going to account for the in situ CO data quantitatively or semi-quantitatively and thus place constraints on the nature of comet dust. It is organized as following: we first revisit the Giotto NMS CO intensity (spatial) profile (Eberhardt et al. 1987) and rederive a source strength profile from which the scale length of the source will be obtained; we then approximately calculate the corresponding critical temperatures at which the comet dust aggregates satisfy the scale length and thus the source strength profile condition. Comparing the critical temperatures with the calculated dust temperatures (see Sect. 3), we can constrain the upper limits of the sizes (masses) and the lower limits of the porosities of the comet dust particles whose temperatures are still higher than the critical temperatures so that they can still act as a source for the extended CO. Finally, we estimate the upper limit of the total amount of CO which can be provided by dust and discuss its implications. For simplicity, we first only consider dust with equal mass for the silicate core and the organic refractory mantle. The effects caused by varying mantle thickness will be discussed later.

4.1. The strength profile of the extended CO source

The in situ radial profile of the CO intensity multiplied by the square of the radial distance from the nucleus (R) detected by the Giotto NMS (Eberhardt et al. 1987) apparently shows an almost linear increase from 10^3 km, the closest distance where the NMS detection was available, up to ~ 13500 km, a distance where the intensity times R^2 reaches its maximum and becomes almost constant beyond that point. The presence of an extended source is obvious. To a good approximation, we represent the observation of Eberhardt et al. (1987) by two linear functions, as plotted in Fig. 2a, they are well within the observational uncertainties. With the assumption of spherically symmetrical outflow, we then convert the intensity profile into the CO production rate (relative to H_2O) $Q(CO, R)/Q(H_2O)$, adopting a scale length of 7.5×10^5 km, 3.9×10^4 km for CO, H_2O respectively. The radial CO production rate profile, as presented in Fig. 2b, shows that the total CO production rate $Q(CO)/Q(H_2O)$ is about 15%, with $\approx 6\%$ from the direct sublimation of volatiles in the nucleus, leaving $\approx 9\%$ attributed to the extended source. The strength of the extended CO source, as derived from the production rate profile and depicted in Fig. 2c, is similar to the one obtained by Eberhardt et al. (1987), except the source strength profile peaks at ~ 6000 km in this work rather than ~ 9000 km

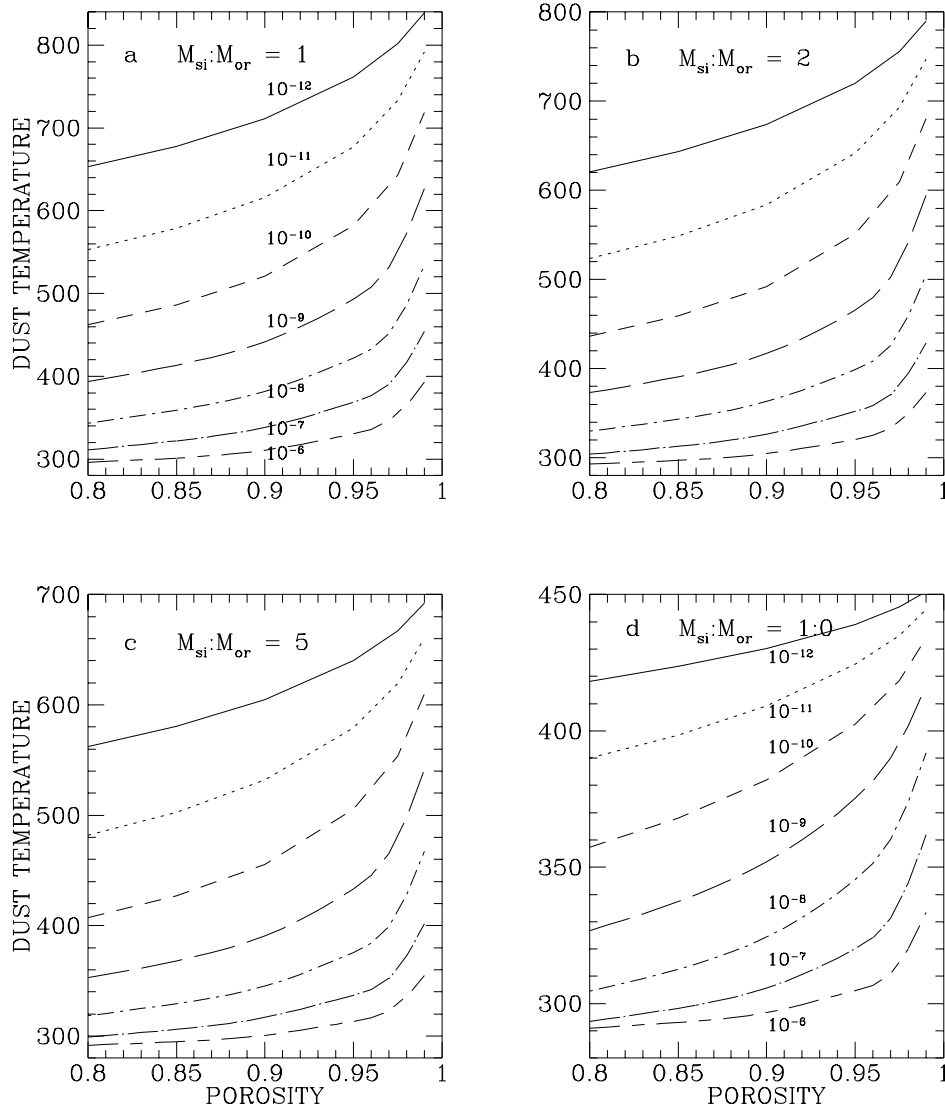


Fig. 1. Temperatures of porous aggregates of tenth micron silicate core-organic refractory mantle particles as a function of porosity at 1 AU. The lines in each set correspond to (from top downward) 10^{-12} g, 10^{-11} g, 10^{-10} g, 10^{-9} g, 10^{-8} g, 10^{-7} g, 10^{-6} g.

in Eberhardt et al. (1987). This is mostly due to the different saturation positions adopted (~ 13500 km in this work, rather than ~ 20000 km in Eberhardt et al. 1987). As will be shown later, the effects on the final results caused by this difference are minor.

The behavior of the strength profile can be well understood in terms of the evaporation of dust grains. The first increase may result from the sequential fragmentation of the original larger dust grains lifted off the nucleus. The fragmentation leads to an increase of the amount of smaller particles which can be heated sufficiently to sublimate and thus produce CO. Since the total amount of larger dust particles and their CO compounds are not infinite, the presence of a maximum CO source strength is expected at a certain position of the coma, after which a decrease occurs due to the gradual depletion of larger grains and the depletion of the CO containing compounds, and finally the CO source goes bankrupt. It is interesting to note that the position where the source strength peaks is almost identical to the position where the dust fragmentation ends (Goidet-Devel et al.

1997). However, it is more likely that the fragmentation occurs mainly in the innermost coma. The actual scale length of the extended CO source should be determined by the combination of the fragmentation time scale together with the dust evaporation rate and the photodissociation rate of the parent molecules of CO. A discussion of this in detail is beyond the scope of this article. As a first approximation, it is reasonable to assume a scale length of ≈ 13500 km for the extended CO source from the CO intensity profile and from the radial distribution profile of the CO production rate.

4.2. The critical temperatures of comet dust

The scale length of the extended CO source implies that the dust grains which make a contribution to the distributed CO have already offered all of their CO and/or CO containing parent molecules within a distance R away from the nucleus smaller than the scale length, i.e., $R \leq 13500$ km. Since the distributed CO is dominantly contributed by the relatively volatile fraction

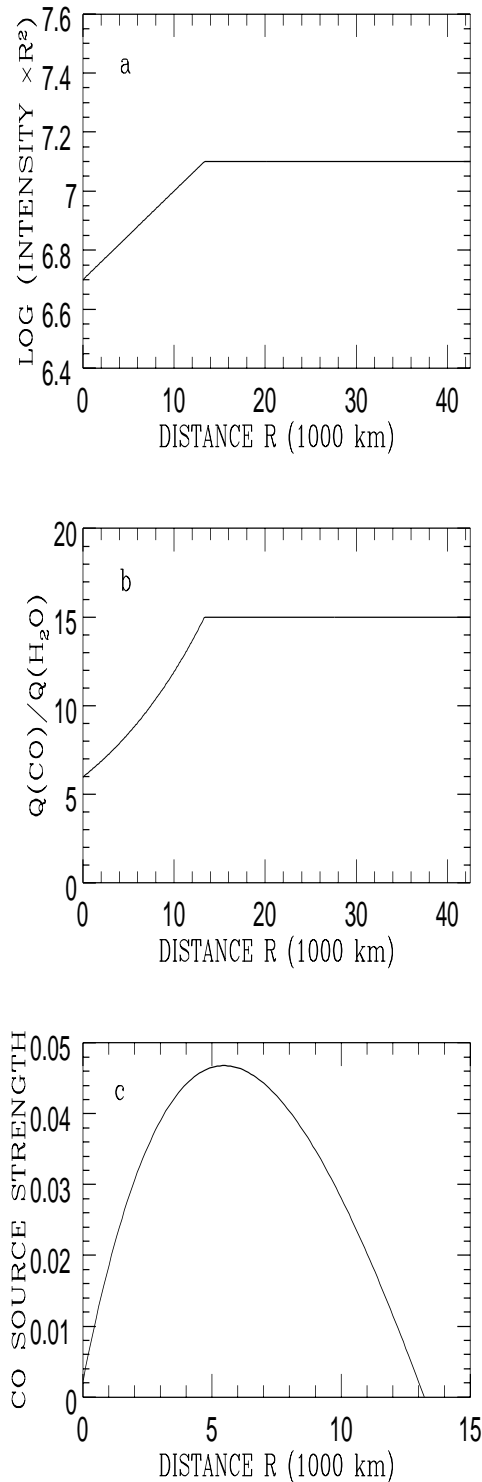


Fig. 2. The source of the extended CO molecule. a: The CO intensity times the square of the distance from the nucleus is shown as a function of the distance. The observational data of Eberhardt et al. (1987) are approximated by two linear functions here. b: The CO production rate relative to H₂O (in per cent). c: The radial profile of the extended CO source strength (in arbitrary units).

of the organic refractory mantle, as discussed in Sect. 2, we can assume that the CO contributing dust grains lose their volatile organic mantle within the scale length of the CO source. This requires that these grains should be heated sufficiently so as to be hot enough and evaporate rapidly enough. Since the dust temperatures are a function of size and porosity, as illustrated in Fig. 1, it is obvious that, within a dust size distribution, only the smaller size portion is able to meet the requirements. In order to obtain the total amount of CO which can be provided by comet dust it is necessary to determine the maximum size (mass, m_{\max}^{CO}) of dust which still can evaporate its volatile organic refractory mantle within the scale length. Thus we need to calculate the “critical temperature” of dust with a certain size (mass) and porosity – the lowest temperature at which the dust is still able to do such a job. For convenience, we define a notation $m_{\text{dust}}^{\text{CO}}$ for the integrated total dust mass up to m_{\max}^{CO} , the maximum size (mass) of dust which still can evaporate its volatile organic refractory mantle within the scale length since this term will be frequently referred to later.

The critical temperature is dependent on the grain size, porosity and its evaporation rate. With the lack of detailed data on the specific chemical composition, and with the lack of detailed knowledge on the vaporization process of the organic refractory, it is impossible to precisely determine the vaporization rate and thus the lifetime of comet dust. As a first approximation, following Lamy & Perrin (1988), we calculate the vaporization rate and the residence time scale of the volatile organic refractory and then derive the critical temperature as a function of dust size and porosity. The sublimation enthalpy, approximated by the bending energy, is taken to be 30 kcal/mole (Wallis et al. 1987; Lamy & Perrin 1988). The resulting critical temperatures are presented in Fig. 3 as a function of grain porosity for a variety of grain sizes (masses). From Fig. 3 we can see that the critical temperatures decrease with the increase of porosity and with the decrease of grain size. This is easy to understand because, for the grains with the same mass, the total surface area exposed to the solar irradiation is proportional to $(1-P)^{2/3}$ where P is porosity. Thus the more fluffy the grain the faster its evaporation, leading to a lower critical temperature. For grains with same porosity P , the smaller ones take a shorter time to evaporate, therefore the critical temperatures are lower for smaller grains. The size and porosity dependent evaporation rate naturally explains the wide range of the C/R values (the carbon to rock-forming elements ratios) as shown by the Halley dust mass spectra and the asymmetric shape of the C/R ratio histogram (Lawler & Brownlee 1992): the fact that smaller grains more easily lose their organic mantles leads to the steeper distribution for low-carbon particles and the flatter distribution for high-carbon particles.

4.3. The total amount of CO from dust and its implications

Now we compare the calculated comet dust temperatures with the critical temperatures, through which we can place some constraints on dust size and porosity. Fig. 3 shows the calculated comet dust temperatures as well as the critical temperatures as

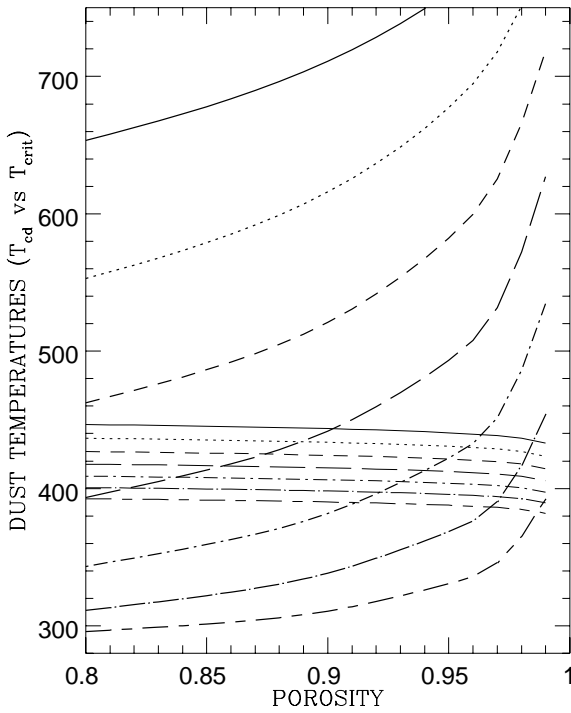


Fig. 3. Comparison of the calculated comet dust temperatures (thick lines, cf. Fig. 1a) with the estimated critical temperatures (thin lines) at 1 AU as a function of grain sizes (masses) and porosities (only for $m_{\text{or}}/m_{\text{si}} = 1$). The lines in each set correspond to (from top downward) 10^{-12} g, 10^{-11} g, 10^{-10} g, 10^{-9} g, 10^{-8} g, 10^{-7} g, 10^{-6} g.

a function of porosity for a range of grain sizes (masses). It can be seen from Fig. 3 that, all dust grains smaller than 10^{-10} g are hotter than their corresponding critical temperatures in the porosity range, $P > 0.80$. For those with a mass of 10^{-9} g, the lower limit of their porosity is $P \simeq 0.86$; namely, in order to evaporate all of their CO and/or CO containing compounds within the scale length (13500 km), they can not be more compact than $P \simeq 0.86$; for 10^{-8} g, $P \geq 0.95$; for 10^{-7} g, $P \geq 0.98$; for 10^{-6} g, even $P \simeq 0.99$ is not high enough. Since in the dust size distribution (McDonnell et al. 1991), the bulk of the mass of dust (and thereby of CO) resides in the larger particles, the constraints on the larger grains (as large as possible) are more useful and more suitable. For example, although for the grains with a mass of 10^{-12} g, the porosity need not be very high in order to satisfy the critical temperature condition, they only constitute a minor portion in the total dust mass and thus contribute little to the observed CO compared to the larger grains (say, 10^{-6} g). It is also noteworthy that the $10 \mu\text{m}$ silicate emission feature predicted by such small grains is too sharp compared to the observation (Greenberg & Hage 1990). Furthermore, we know that dust grains as large as 10^{-6} g exist in the outer coma, even beyond 8300 km, since they have been detected by the spacecrafts Vega 1 and Vega 2 (Mazets et al. 1987).

Now the question is how much CO can be provided by dust? We can estimate the total amount of CO contributed by dust grains in the coma from the following equation

$$Q'(\text{CO})/Q(\text{H}_2\text{O}) = \frac{m_{\text{CO}}}{(m_{\text{or}})_{\text{V}}} \frac{(m_{\text{or}})_{\text{V}}}{m_{\text{or}}} \frac{m_{\text{or}}}{m_{\text{dust}}} \frac{m_{\text{dust}}}{m_{\text{gas}}} \frac{m_{\text{gas}}}{m_{\text{H}_2\text{O}}} \quad (2)$$

where $m_{\text{CO}}/(m_{\text{or}})_{\text{V}}$ is the mass fraction of CO in the volatile part of the organic refractory; $(m_{\text{or}})_{\text{V}}/m_{\text{or}}$ is the mass ratio of the volatile organic refractory component to the full whole organic mantle; $m_{\text{or}}/m_{\text{dust}}$ is the mass fraction of the organic mantle in an individual dust particle; $m_{\text{dust}}/m_{\text{gas}}$ is the mass ratio of dust to gas, approximated by the dust to gas production rate; $m_{\text{gas}}/m_{\text{H}_2\text{O}}$ is the mass fraction of water vapor in the gas (the entire range of volatile molecules including CO, CO_2 , H_2CO , CH_3OH , CH_4 , NH_3 etc. as well as H_2O). Based on the discussions in the preceding sections, we adopt $m_{\text{CO}}/(m_{\text{or}})_{\text{V}} = 16\%$, $(m_{\text{or}})_{\text{V}}/m_{\text{or}} = 1/2$, $m_{\text{or}}/m_{\text{dust}} = 1/2$ (i.e., $m_{\text{or}}/m_{\text{si}} = 1$). The interstellar dust aggregated comet nucleus model gives $m_{\text{gas}}/m_{\text{H}_2\text{O}} \simeq 1.4$ (Greenberg 1998). The question now is what is the possible dust to gas production rate $m_{\text{dust}}/m_{\text{gas}}$? Note here m_{dust} is actually $m_{\text{dust}}^{\text{CO}}$, the integrated total dust mass up to $m_{\text{max}}^{\text{CO}}$ (see the definition in Sect. 4.2). As discussed in Sect. 4.2, for a given grain porosity, the upper limit of grain size (mass, $m_{\text{max}}^{\text{CO}}$) can be provided by the critical temperature constraint. On the other hand, for a given dust mass, the dust to gas production rate can be inferred from the McDonnell size distribution (see Fig. 14 of McDonnell et al. 1991). Thus, substituting the inferred $m_{\text{dust}}/m_{\text{gas}}$ value into Eq. 2, we can obtain the maximum CO production rate $Q'(\text{CO})/Q(\text{H}_2\text{O})$. Fig. 4 presents the maximum CO production rate predicted from the comet dust model as a function of porosity. As expected the $Q'(\text{CO})/Q(\text{H}_2\text{O})$ value increases with the grain fluffiness. For the case of $P = 0.80$ ($m_{\text{max}}^{\text{CO}} \simeq 5 \times 10^{-10}$ g), $Q'(\text{CO})/Q(\text{H}_2\text{O})$ is $\simeq 0.53\%$, while for $P = 0.99$ ($m_{\text{max}}^{\text{CO}} \simeq 3 \times 10^{-7}$ g), $Q'(\text{CO})/Q(\text{H}_2\text{O})$ reaches $\simeq 1.3\%$, increasing by a factor of > 2 . However, the predicted absolute value is still well below the detected number.

Since what is of interest here is the upper limit of the total amount of CO, we should take all possible dust sources into consideration. In other words, when we integrate the CO production over a size distribution within which all the particles satisfy the critical temperature condition, we should integrate up to the largest grains since the dust mass is concentrated in larger grains. Therefore, our attention should be concentrated on the largest grains. As discussed before, grains larger than 10^{-6} g are certainly too large (too cold) to evaporate their organic mantle within the scale length limit, while, even for $m_{\text{max}}^{\text{CO}} = 10^{-6}$ g, the aggregates have to be extremely fluffy: $P > 0.99$, in order to be acceptably heated. Furthermore, using the McDonnell size distribution (McDonnell et al. 1991) gives only $m_{\text{dust}}/m_{\text{gas}} \approx 0.25$ ($m_{\text{max}}^{\text{CO}} = 10^{-6}$ g), so that the maximum ratio of CO to gas production rate provided by this range of dust masses is only $Q'(\text{CO})/Q(\text{H}_2\text{O}) \approx 1.4\%$ – much less than the observed value of 9% . As a matter of fact, in order to fully account for the observed CO, $Q'(\text{CO})/Q(\text{H}_2\text{O}) \approx 0.09$, a dust to gas production rate as high as 1.6 ($m_{\text{dust}}^{\text{CO}}/m_{\text{gas}} \approx 1.6$) is required. According to the McDonnell size distribution, a dust to gas production rate

$m_{\text{dust}}^{\text{CO}}/m_{\text{gas}} = 1.6$ corresponds to a maximum dust size (mass) of $m_{\text{max}}^{\text{CO}} \approx 1.9 \times 10^{-2}$ g, in other words, all dust grains up to $m = 1.9 \times 10^{-2}$ g should be heated sufficiently to evaporate all of their available CO bearing organics. Obviously, such giants ($m \leq 1.9 \times 10^{-2}$ g) will never be so hot!

One may suggest H_2CO (Meier et al. 1993), and possibly C_3O_2 (Huntress et al. 1991), or POM (polyoxymethylene, see Huebner 1987), CH_3OH , CO_2 etc. as additional sources. However, as shown by Meier et al. (1993), the NMS detected H_2CO can not come directly from the nucleus, instead, it must also be attributed to an extended source, most probably the dust grains themselves. Abundance considerations may rule out the POM assumption (Krankowsky & Eberhardt 1990) although laboratory ultraviolet photoprocessing of certain ice mixtures indeed leads to the formation of POM (Bernstein et al. 1995). The C_3O_2 proposition (Huntress et al. 1991) was questioned by Crovisier et al. (1991) based on the fact that the rather weak $4.45 \mu\text{m}$ feature (the ν_3 band of C_3O_2) in comet Halley indicates a very low C_3O_2 production rate ($Q(\text{C}_3\text{O}_2)/Q(\text{H}_2\text{O}) \approx 0.0011$) and thus C_3O_2 may be excluded as a significant contributor to the distributed CO (however, see Allen 1991). As far as CH_3OH and CO_2 are concerned, their scale lengths ($\sim 3.9 \times 10^4$ km for CH_3OH and $\sim 2.5 \times 10^5$ km for CO_2 , assuming a gas outflow velocity of 0.5 km/s and adopting the photodestruction rates listed in Table 5 of Crovisier 1998) show that neither CH_3OH nor CO_2 can contribute to the distributed CO observed by Giotto.

It seems that the dust explanation encounters a severe problem in fully accounting for the large number of CO molecules. A likely solution to this problem may be that the dust to gas production rate ($m_{\text{dust}}/m_{\text{gas}}$) was underestimated in McDonnell et al. (1991). The dust size distribution, on which the dust to gas ratio was derived, was obtained by extrapolating the measurements made from beyond 600 km to the nucleus surface. However, it has been well established that dust fragmentation occurred in the coma (in particular, in the near-nucleus inner coma) both observationally (Vaisberg et al. 1986) and theoretically (Keller et al. 1990; Konno et al. 1993; Oberc 1996; Goidet-Devel et al. 1997; etc.). Note that the bulk of the dust mass is concentrated in larger grains so that the extrapolation could substantially underestimate the dust mass. Indeed, the intermediate and large mass profiles obtained by the dust impact detection system (DIDSY) on board the Giotto spacecraft, near its closest encounter, show a steeper than $1/R^2$ (R is the distance from the Halley nucleus) flux dependence at $R < 2000$ km (McDonnell et al. 1986). The resulting total dust mass is very sensitive to the cumulative mass index as well as the largest grain size (mass). Furthermore, after the larger particles rapidly fragment into smaller ones (Konno et al. 1993), the smaller ones could sublimate quickly so that they could have not been detected by the spacecrafts beyond 600 km (for Giotto), 8890 km (for Vega 1), and 8030 km (for Vega 2). Moreover, the maximum liftable grain size adopted by McDonnell et al. (1991) could also be questionable since the more porous the aggregate, the higher the maximum liftable dust mass (Gombosi 1986). The fact that the actual density is much lower than the one adopted by McDonnell et al. (1991) could underestimate the maximum liftable

grain size and thereby underestimate the global dust to gas production rate. Therefore it is reasonable to believe that the dust to gas release rate may have been underestimated, in particular, in the smaller size range. Here we shall not quantitatively investigate the radial dependence of the dust to gas production rate further, due to the lack of full knowledge of the comet nucleus surface activity, dust fragmentation, etc. We note here that it is possible that there still exist a certain number of larger grains ($m \leq 10^{-6}$ g) beyond the CO source scale length (~ 13500 km) and these dust grains are still fragmenting into smaller ones which are hot enough to evaporate their volatile organic mantle and hence add some CO. However, since the largest dust grains which constitute the bulk of dust mass have already finished fragmenting within the inner coma, say, 6000 km away from the nucleus surface (e.g., Goidet-Devel et al. 1997), the total CO from the fragmented grains beyond the scale length is negligible, so that the CO intensity times R^2 stays constant up to the very outer coma where the photodissociation of CO can not be neglected any more.

An alternative solution lies in the observed CO abundance itself. In deriving the CO production rate for the distributed component, two basic assumptions were made: the outflow of gas and dust in the coma from the nucleus is *spherically symmetrical* and *temporally invariant*. However, if Giotto crossed several dust jets and/or gas jets which contain enhanced CO and H_2CO (but not H_2O) at a distance where the distributed CO source peaks, then the previously derived CO production rate for the distributed component could have been overestimated. In addition, the outgassing in comet Halley is highly anisotropic since a large fraction of its nucleus surface was covered by inert crust materials. Thus the temporal invariant assumption may not be valid. Based on their hydrodynamic simulation, Crifo & Rodionov (1997) showed that the spatial variation of the CO abundance may be explained in terms of the different CO production rate of the night-side outer coma with the day-side outer coma. According to them, no distributed CO sources, either grains or parent molecules, are required.

In the above discussions, we have only considered the case with equal average mass for the silicate core and the organic refractory mantle ($m_{\text{or}}/m_{\text{si}} = 1$). As dust grains flow out from the nucleus, their mantles gradually get eroded through evaporation. Thus there exists the possibility that, within a size distribution, the mass fraction of the mantle also has a wide range of values, ranging from 1/2 (or a bit higher), the original value (Kissel & Krueger 1987; Krueger & Kissel 1987), to 0. As shown in Sect. 3, the grain temperature decreases with the reduction of the mantle thickness. Thus, in order to satisfy the critical temperature condition, the constraint is even more restrictive: the comet dust should be either smaller or more fluffy than their counterparts with the same mass but thicker interstellar dust mantles. As illustrated in Fig. 4, the maximum CO production rates $Q'(\text{CO})/Q(\text{H}_2\text{O})$ contributed by dust for $m_{\text{or}}/m_{\text{si}} = 1/2$ and $m_{\text{or}}/m_{\text{si}} = 1/5$ are much less than those for $m_{\text{or}}/m_{\text{si}} = 1$.

The scale length of the extended CO source adopted here is 13500 km, smaller than the one (20000 km) adopted by Eberhardt et al. (1987). Although we consider 13500 km as more

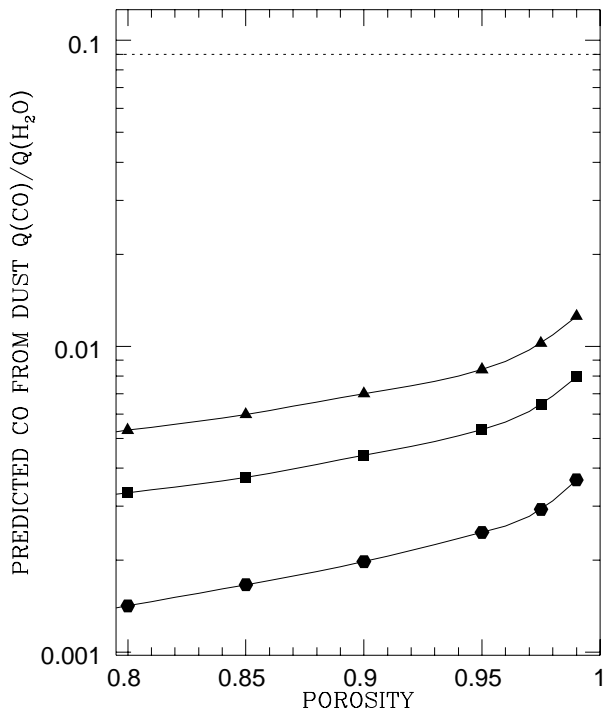


Fig. 4. The maximum CO production rate provided by comet dust as a function of grain porosity. Triangles – $m_{or}/m_{si} = 1$; squares – $m_{or}/m_{si} = 1/2$; hexagons – $m_{or}/m_{si} = 1/5$. The dotted line gives the observed abundance of distributed CO.

reasonable if one takes the scatter of the data beyond 15000 km into account, the number 20000 km of Eberhardt et al. (1987) is also within the observational uncertainties and thus we can not exclude it. We have also tried a case with 20000 km as the scale length and found that the corresponding critical temperature constraint could be relaxed a little. However, the general conclusion, i.e., that the dust should be very fluffy, was not affected. For example, the porosity constraint now becomes: for $m_{max}^{CO} = 10^{-9}$ g, $P \geq 0.84$; for $m_{max}^{CO} = 10^{-8}$ g, $P \geq 0.94$; for $m_{max}^{CO} = 10^{-7}$ g, $P \approx 0.98$; for dust grains with a mass higher than 10^{-6} g, they are still too cold to evaporate.

Since the exact composition of the organic refractory component, the detailed vaporization process, the precise mechanism on how CO is produced from grains (either from the direct sublimation from grains or from the photodissociation of parent molecules released from the grains) are all poorly known, it is difficult to determine an accurate evaporation rate and to strictly constrain the critical temperature. The calculation carried out by Lamy & Perrin (1988) and by ourselves, is based on the assumption that CO is directly sublimated from the grain mantle or comes from its parent molecules which have been quickly photodissociated on the mantle so that the photodissociation time scales of its parents do not need to be taken into account. The actual process could be different, for example, the presence of the non-nucleus H₂CO indicates that the CO containing complex molecules may have not been completely dissociated in the mantle but are more probably first released from

the mantle and then fragment into daughter molecule species. However, Combi & Fink (1997) argue that a direct release from the mantle rather than from a released parent molecule is more favorable based on an extensive investigation of the C₂ spatial distribution of a set of comets. We stress that our modeling on the mantle vaporization is a rough approximation. A more realistic model should simultaneously consider the dust fragmentation, the evaporation of dust mantle, and the release and photodissociation of its parent molecules (even grandfather molecules). The lack of appropriate data on these restricts us from a detailed investigation. In any case, an upper limit on grain temperature can not exceed ~ 500 K, otherwise the organic residues can not survive as shown by laboratory experiments (Greenberg & d'Hendecourt 1985). It is interesting to note that our results are approximately consistent with those of Wallis et al. (1987) for kerogen, the insoluble components of organic residues on earth (see Table 1 in Wallis et al. 1987) which they considered as an analog to the organic material in carbonaceous chondrites and interstellar grains. In summary, we conclude that our simple approach to the critical temperature and to the grain evaporation process is certainly qualitatively suitable, if not completely quantitative, for deducing the general capability of the comet dust aggregates to thermally dissociate and provide a potential source for the distributed cometary gas species.

5. Organic mantle as a source for other gas species

The radial profile of H₂CO determined from measurements made by the NMS on board Giotto indicates an extended source (Meier et al. 1993) which could also come from the evaporation of the organic mantle. In addition to CO and H₂CO, the organic mantle could also contribute to the cometary C₂, C₃, CN etc. molecules. UV irradiation of ice mixtures analog to interstellar ices indeed clearly indicates the formation of C \equiv N, C₂, C₃ containing complex molecules (Briggs et al. 1992; Bernstein et al. 1995). On the other hand it is proposed that the gas molecules C₂H₂ and C₂H₆ recently detected in comet Hyakutake and comet Hale-Bopp could also be responsible for C₂ through a three-generation photodissociation process (Sorkhabi et al. 1997). The spatial profiles of C₂ in the inner coma of comets ($< 10^4$ km) including comet Halley show a flatter distribution than can be predicted by direct outflow from the nucleus or by a two-generation photodissociation model. A recent investigation by Combi & Fink (1997) further showed that a three-generation model, with the physically suitable eject velocities of daughter fragments included, also could not improve the fit. Instead, they found that the model with C₂ directly released from grains can better explain the heliocentric distance dependence as well as the flat spatial profile. Thus they concluded that “it appears that C₂ can be produced predominantly from the vaporization (or thermal dissociation) of small superheated (~ 500 K) CHON grains” (cf. Combi & Fink 1997). It is likely that the C₂ containing compounds are mostly concentrated in the more refractory fraction of the mantle compared to the CO compounds (Briggs et al. 1992). This is qualitatively consistent with the results of Combi & Fink (1997) that the scale

length of the C₂ source is much larger than that of the extended CO source. Note the observed abundance of the C₂ radical is much less than that of CO. In order to identify the C₂ origin, much work on the heliocentric distance variation as well as the spatial radial distribution of C₂ in the coma remains to be done.

An extensive long-term narrow-band photometry survey of 85 comets made by A'Hearn and his colleagues showed that CN is predominantly produced from the dust grains in the coma, and C₂ is produced partially from the dust grains and partially directly from the nucleus (A'Hearn et al. 1995). However, this does not mean that the refractory organics are solely responsible for the CN radical. At large heliocentric distance (r_H) where the comet dust grains are too cold to sublimate, the CN bearing molecules, sublimated from the volatile ice mantles coated on the silicate core-organic refractory mantle particles, such as HCN, HNC, HC₃N, CH₃CN etc. which have been seen in comets are responsible for CN. It is not surprising that, in comet Hale-Bopp, in the heliocentric distance range $2.9 \text{ AU} < r_H < 4.6 \text{ AU}$, HCN alone can explain the observed CN, no additional sources being required (Rauer et al. 1997). A direct proof of dust grains as a source for CN, C₂ and C₃ is the detection of the CN, C₂, C₃ jets in comet Halley at 1 AU (A'Hearn et al. 1986a, 1986b; Clairemidi et al. 1990). The large spatial extension and the long temporal endurance of these jets could only be understood in terms of a dust origin for the jets, otherwise the jets (with a gaseous origin) will quickly diffuse due to the collisions between the molecules. A detailed modeling of the CN jets by Klavetter & A'Hearn (1994) indeed led to a dust origin.

6. Conclusion

The organic refractory interstellar dust grain mantles studied by laboratory analog methods appear to provide a reasonable match to the stoichiometric distribution of the elements observed in comet Halley dust mass spectra. The volatility and the CO-producing ability of comet dust are discussed. Although the exact chemical composition of the organic refractory material and the precise mechanism of how CO is produced from dust mantles are still poorly known, the upper limits of the total amount of CO provided by dust can be approximately determined as a function of porosity based on the constraint provided by the dust thermal properties, assuming that the laboratory organics are representative of comet dust organics in terms of the mass fraction containing CO groups. We found that the maximum CO production rate predicted by the comet dust model is much less than the observed abundance of distributed CO if the commonly accepted McDonnell comet dust size distribution is employed. While the McDonnell size distribution was derived on the basis of the in situ detection within the zone from 600 km to 20,000 km away from the comet Halley nucleus, in the light of efficient dust fragmentation and sublimation in the innermost coma, the dust to gas ratio could have been underestimated in the McDonnell size distribution. It is also possible that the CO production rate for the distributed component derived from observation was overestimated by using a spherically symmetrical

distribution which does not take into account the possible contamination caused by jets and the anisotropic outgassing. At this point no firm conclusions regarding the accurate grain porosity and size can be drawn, but it is obvious that, in order to maximize the theoretical CO production rate provided by comet dust, the organic refractory mantle and high porosity are required.

Acknowledgements. This work was supported in part by NASA grant NGR 33-018-148 and by a grant from the Netherlands Organization for Space Research (SRON). We thank Dr. W.A. Schutte for his helpful suggestions on the grain vaporization. One of us (AL) wishes to thank Leiden University for an AIO fellowship and the World Laboratory for a scholarship. AL also thanks Prof. G.V. Coyne, S.J. for his kind support in participating in the Vatican Observatory summer school. We thank Dr. J. Crovisier for useful suggestions.

References

- A'Hearn, M.F., Hoban, S., Birch, P.V., Bowers, C., Martin, R. & Klinglesmith, D.A., 1986a, *Nature* 324, 649
- A'Hearn, M.F., Hoban, S., Birch, P.V., Bowers, C., Martin, R. & Klinglesmith, D.A., 1986b, in: *Proc. 20th ESLAB Symposium on the Exploration of Halley's Comet*, ESA SP-250, II, p.438
- A'Hearn, M.F., Millis, R.L., Schleicher, D.G., Osip, D.J. & Birch, P.V., 1995, *Icarus* 118, 223
- Allen, M., 1991, *Nature* 354, 272
- Bernstein, M.P., Sandford, S.A., Allamandola, L.J. & Chang, S., 1995, *ApJ* 454, 327
- Bockelée-Morvan, D. & Crovisier, J., 1992, *A&A* 264, 282
- Bockelée-Morvan, D., Brooke, T.Y. & Crovisier, J., 1995, *Icarus* 116, 18
- Bohren, C.F. & Huffman, D.R., 1983, *Absorption and Scattering of Light by Small Particles*, Wiley, New York
- Briggs, R., Ertem, G., Ferris, J.P., Greenberg, J.M., McCain, P.J., Mendoza-Gómez, C.X. & Schutte, W., 1992, *Origins of Life & Evolution of the Biosphere* 22, 287
- Clairemidi, J., Moreels, G. & Krasnopolsky, V.A., 1990, *Icarus* 86, 115
- Colom, P., Crovisier, J., Bockelée-Morvan, D., Despois, D. & Paubert, G., 1992, *A&A* 264, 270
- Combi, M.R. & Fink, U., 1997, *ApJ* 484, 879
- Crifo, J.F. & Rodionov, A.V., 1997, *Icarus*, submitted
- Crovisier, J., Encrenaz, T. & Combes, M., 1991, *Nature* 353, 610
- Crovisier, J., Leech, K., et al., 1997, *Science* 275, 1904
- Crovisier, J., 1998, in: Greenberg, J.M. (ed.), *Formation and Evolution of Solids in Space*, Kluwer, in press
- Delsemme, A.H. & Miller, D.C., 1971, *Planet. Space Sci.* 19, 1259
- Eberhardt, P., Krankowsky, D., Schulte, W., Dolder, U., Lammerzahl, P., Berthelier, J.J., Woveries, J., Stubbemann, U., Hodges, R.R., Hoffman, J.H. & Illiano, J.M., 1987, *A&A* 187, 481
- Finson, M.L. & Probst, R.F., 1968, *ApJ* 154, 327
- Gilmour, I. & Pillinger, C.T., 1985, *Org. Geochem.*, 8, 421
- Goidet-Devel, B., Clairemidi, J., Rousselot, P. & Moreels, G., 1997, *Icarus* 126, 78
- Gombosi, T.I., 1986, in: *Proc. 20th ESLAB Symposium on the Exploration of Halley's Comet*, ESA SP-250, II, p.167
- Grady, M.M., Wright, I.P., Fallick, A.E. & Pillinger, C.T., 1983, in: *Proc. 8th Symp. Antarctic Meteorites*, p.289
- Greenberg, J.M., 1982a, Laboratory dust experiments – tracing the composition of cometary dust, in: Gombosi, T.I. (ed.) *Cometary Exploration II*, Central Res. Inst., Hungarian Acad. Science, p.23

- Greenberg, J.M., 1982b, What are comets made of – a model based on interstellar dust, in: Wilkening, L. (ed.), *Comets*, University of Arizona Press, p.131
- Greenberg, J.M. & d’Hendecourt, L.B., 1985, in: Klinger, J., Benest, D., Dollfus, A. & Smoluchowski, R. (eds.), *Ices in the Solar System*, Dordrecht Reidel, p.185
- Greenberg, J.M. & Hage, J.I., 1990, *ApJ* 361, 260
- Greenberg, J.M., Singh, P.D. & de Almeida, A.A., 1993, *ApJ* 414, L45
- Greenberg, J.M., Mendoza-Gómez, C.X., de Groot, M.S. & Breukers, R., 1993, Laboratory dust studies and gas-grain chemistry, in: Millar, T.J. & Williams, D.A. (eds.), *Dust and Chemistry in Astronomy*, IOP publ. Ltd., p.265
- Greenberg, J.M. & Shalabiea, O.M., 1994, Comets as a reflection of interstellar medium chemistry, in: Milani, A., di Marino, M. & Cellino, A. (eds.), *Asteroids, Comets, Meteors*, Kluwer, p.327
- Greenberg, J.M., Li, A., Mendoza-Gómez, C.X., Schutte, W.A., Gerakines, P.A. & de Groot, M., 1995, *ApJ* 455, L177
- Greenberg, J.M., Li, A., Kozasa, T. & Yamamoto, T., 1996, On the crystalline silicate component of comet dust, in: Gustafson, B.A.S. & Hanner, M.S. (eds.), *Physics, Chemistry, and Dynamics of Interplanetary Dust*, ASP Conference Series, Vol. 104, 497
- Greenberg, J.M. & Li, A., 1996, *A&A* 309, 258
- Greenberg, J.M. & Li, A., 1997, in: Schmitt, B., de Bergh, C. & Festou, M. (eds.), *Solar System Ice*, Chapter 13, in press
- Greenberg, J.M., 1998, *A&A* 330, 375
- Hanner, M.S., Lynch, D.K. & Russell, R.W., 1994, *ApJ* 425, 274
- Huebner, W.F., 1987, *Science* 237, 628
- Huntress, Jr. W.T., Allen, M., Delitsky, M., 1991, *Nature* 352, 316
- Jessberger, E.K. & Kissel, J., 1991, in: Newburn, R.L., Neugebauer, M. & Rahe, J. (eds.), *Comets in the Post-Halley Era*, Kluwer, Dordrecht, p.1075
- Keller, H.U., Marconi, M.L. & Thomas, N., 1990, *A&A* 227, L1
- Kissel, J., Brownlee, D.E., Büchler, K., et al., 1986, *Nature* 321, 336
- Kissel, J. & Krueger, F.R., 1987, *Nature* 326, 755
- Klavetter, J.J. & A’Hearn, M.F., 1994, *Icarus* 107, 322
- Konno, I., Huebner, W.F. & Boice, D.C., 1993, *Icarus* 101, 84
- Krankowsky, D. & Eberhardt, P., 1990, in: Mason, J. (ed.), *Comet Halley: Investigation, Results, and Interpretations*, Ellis Horwood Ltd., Chichester, England, p.273
- Krueger, F.R. & Kissel, J., 1987, *Naturwissenschaften* 74, 312
- Lamy, P.L. & Perrin, J.-M., 1988, *Icarus* 76, 100
- Lawler, M.E. & Brownlee, D.E., 1992, *Nature* 359, 810
- Li, A. & Greenberg, J.M., 1997, *A&A* 323, 566
- Mazets, E.P., Sagdeev, R.Z., Aptekar, R.L., et al., 1987, *A&A* 187, 699
- McDonnell, J.A.M., Kissel, J., Grün, E., et al., 1986, in: Proc. 20th ESLAB Symposium on the Exploration of Halley’s Comet, ESA SP-250, II, p.25
- McDonnell, J.A.M., Lamy, P.L. & Pankiewicz, G.S., 1991, in: Newburn, R.L., Neugebauer, M. & Rahe, J. (eds.), *Comets in the Post-Halley Era*, Kluwer, Dordrecht, p.1043
- Meier, R., Eberhardt, P., Krankowsky, D. & Hodge, R.R., 1993, *A&A* 277, 677
- Mendoza Gómez, C.X., 1992, Complex irradiation products in the interstellar medium, PhD thesis, Leiden University
- Mukhin, L.M., Dikov, Y.P., Evlanov, E.N., Fomenkova, M.N., Nazarov, M.A., Priludsky, O.F., Sagdeev, R.Z. & Zubkov, B.U., 1989, in: *Lunar Planetary Science Conf. XX*, Houston, Texas, p.733
- Mumma, M.J., Stern, S.A. & Weissman, P.R., 1993, Comets and the origin of the solar system: Reading the Rosetta stone, in: Levy, E.H., Lunine, J.I. & Matthews, M.S. (eds.), *Planets and Protostars III*, University of Arizona Press, Tucson, p.1177
- Oberc, P., 1996, *Icarus* 124, 195
- Pendleton, Y.J., Sandford, S.A., Allamandola, L.J., Tielens, A.G.G.M. & Sellgren, K., 1994, *ApJ* 437, 683
- Rauer, H., Arpigny, C., Boehnhardt, H., et al., 1997, *Science* 275, 1909
- Rickman, H., 1991, in: Newburn, R.L., Neugebauer, M. & Rahe, J. (eds.), *Comets in the Post-Halley Era*, Kluwer, Dordrecht, p.733
- Samarasinha, N.H. & Belton, M.J.S., 1994, *Icarus* 108, 103
- Sandford, S.A., Allamandola, L.J., Tielens, A.G.G.M., Sellgren, K., Tapia, M., & Pendleton, Y.J. 1991, *ApJ* 371, 607
- Sorkhabi, O., Blunt, V.M., Lin, H., et al., 1997, *Planet. Space Sci.* 45, 721
- Vaisberg, O., Smirnov, V. & Omelchenko, A., 1986, in: Proc. 20th ESLAB Symposium on the Exploration of Halley’s Comet, ESA SP-250, II, p.17
- Wallis, M.K., Rabilizirov, R. & Wickramasinghe, N.C., 1987, *A&A* 187, 801
- Wyckoff, S., Tegler, S.C. & Engel, L., 1991, *ApJ* 368, 279
- Utterback, N.G. & Kissel, J., 1990, *AJ* 100, 1315