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# The Chemistry of Comets

A. H. Delsemme

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# The chemistry of comets

By A. H. Delsemme

*Department of Physics and Astronomy, The University of Toledo, Toledo, Ohio 43606, U.S.A.*

In comets, most elements seem to be present in their cosmic abundances. This includes the metals whose abundances are the same as in chondrites, but also the light elements C, N, O, S that are the same as in the Sun; only hydrogen (and presumably helium and neon) is depleted by a factor close to 1000. In the bright comets of the 1970s, three-quarters of the cosmic abundance of carbon was found to be missing from the gaseous fraction. The missing carbon has now been found in Comet Halley: it was in the large organic fraction representing 33% of the cometary dust. A part of this fraction vaporizes slowly out of the dust grains: it is the origin of an extended source of gas discovered around the nucleus of Comet Halley. Water remains the major constituent being 80% of the volatile ices. Formic acid, formaldehyde, carbon dioxide and carbon monoxide explain together more than 13% of the rest of the volatiles. The last 7% include the parent molecules of the radicals excited by fluorescence and observed in the traditional spectra, like hydrogen cyanide HCN (for CN), probably acetylene $C_2C_2$ (for $C_2$) and cyclopropadiene $C_3H_2$ (for $C_3$). The inorganic fraction of the dust contains mainly silicates and some iron sulphide, whereas the organic fraction also contains unsaturated hydrocarbons and probably hydrogen cyanide, acetonitrile, aminoethylene, pyrrole, pyridine, pyrimidine and possibly purines including adenine. Some prebiotic precursors of the nucleic bases are present, but no traces of any amino acids have been found.

## 1. Introduction

Quantitative knowledge about cometary chemistry has essentially been derived from the bright comets of the 1970s and complemented by the wealth of information brought about by the flybys of Comet Halley during its 1986 passage. However, other historical comets have displayed enough diversity to suggest the existence of large physical and chemical differences.

Before discussing the chemical features of comets in general, it is worth considering whether the restricted amount of available data represents a fair sample for all comets. I have recently reviewed this particular matter (Delsemme 1988) and come to the conclusion that, in spite of their apparent diversity, comets represent a population of essentially homogeneous objects. I begin with a summary of this evidence.

## 2. Pristine comets are similar objects

Pristine comets show a rather narrow size distribution, with a mean diameter close to 10 km; however, they fragment and decay as soon as they enter the inner Solar System. After fragmentation, the size distribution becomes typical of a grinding process: the 10 km peak disappears and the number of fragments grows indefinitely for smaller and smaller sizes.

Surface decay of the cometary nuclei also changes the physical nature of a shallow outer layer, mostly by dust outgassing and, for shorter heliocentric distances, by dust sintering. The apparent diversity of the cometary population comes therefore more from the nucleus fragmentation and decay, than from any physical or chemical difference in the pristine stuff. A few examples of this fact are discussed hereafter.

## 3. Dust tails show grain sintering

The shape and the curvature of the dust tails ultimately depends on the size distribution of the dust grains. The primordial distribution consists of submicrometre particles, but it is changed by grain sintering at short heliocentric distances. Fragile grain clusters exist already at the low temperature of the icy conglomerate, but they fragment and scatter more or less easily after they have escaped into the coma. This was demonstrated by the *in situ* observations of Comet Halley by the *Vega* spacecraft (Simpson *et al.* 1986; Vaisberg *et al.* 1986). However, as soon as the clusters scatter into space, they reach quickly a temperature 20–30% higher than that of the black body (Hanner 1984). Hence at short heliocentric distances they are sintered by the solar heat before any possible splitting. This gives an interpretation of the fact that the r.m.s. diameter of dust in cometary tails grows steadily with shorter heliocentric distance (Delsemme 1982, 1988) (table 1). Of course, in the extreme case of Sun-grazing comets, grain vaporization may also considerably contribute to changing the grain-size distribution. Finally, striae observed in some dust tails have been explained by the belated splitting of grain clusters (Sekanina & Farrell 1980, 1982).

Table 1. Grain sizes (Finson–Probstein method)

| comet | Halley | Bennett | Arend–Roland | Seki–Lines |
|---|---|---|---|---|
| perihelion/AU | 0.59 | 0.54 | 0.32 | 0.03 |
| dust temperature/K | 520 | 540 | 700 | 2300 |
| size (r.m.s.)/μm | 1.2 | 1.0 | 2.8 | 13.3 |

## 4. Plasma tails are poor chemical indicators

The phenomenon that makes the plasma tail appear is the *confinement* (in a narrow magnetic tube induced by the solar wind) of a concentration of ions dense enough to make the tail visible. A simplistic theory shows that the intensity of the plasma tail varies with a rather large power ($n = 4$ to 5) of two parameters: the production rate of the neutral gases by the comet, and the inverse of its heliocentric distance (Delsemme 1988). The theory is reasonably well verified by the dependence on heliocentric distance observed for the plasma tail (Combi & Delsemme 1980) and also explains peculiarities and anomalies (Delsemme 1988) such as plasma tails observed at 5 AU, or vice versa the absence of a plasma tail for most of the short-period comets.

This clarifies an important point for comet chemistry: the highly variable neutral: ion ratio revealed by observations is an artifact sensitively dependent on a rather high power of (*a*) the size of the comet; (*b*) its heliocentric distance. For instance, for a *constant* CO/CN ratio, a doubling of the overall gas production multiplies the $CO^+/CN$ ratio by twenty. The observed ratio of two different ions also sensitively depends on heliocentric distance. In short, none of the observed ions can easily be used to clarify any of the quantitative chemical data from the cometary nucleus.

## 5. BRIGHTNESS LAWS ARE DRIVEN BY WATER SUBLIMATION

Cometary brightnesses are usually given in reduced magnitudes $H_1$ (that is, reduced to the geocentric distance $\varDelta = 1$ AU by $H_1 = H - 5 \lg \varDelta$). The dependence law on heliocentric distance is then given by:

$$H_1 = H_0 + 2.5n \lg r, \tag{1}$$

where $H_0$ is the absolute magnitude (the magnitude $H_1$ at heliocentric distance $r = 1$ AU) and $n$ is a numerical parameter. The diversity of the brightness laws for different comets is displayed by the values of $n$: its lower decile value is 2.1, its median 3.3 and its upper decile 6.2 (Delsemme 1988).

A fatal flaw of the parameter $n$ is its lack of physical meaning: for the same comet, it varies very much with heliocentric distance. In the diagram of $H_1$ against $\lg r$, the slope $n$ is often irregular because it is perturbed by outbursts, but it usually shows two discrete ranges: a steep slope ($n = 5$–$10$) near or beyond 3 AU, and a shallow one for distances smaller than 1.5 AU. The two slopes are explained by the vaporization theory (Delsemme 1982). They correspond respectively to the *radiative* régime and to the *vaporization* régime of the nucleus; they are conveniently separated by the distance $r_0$, the heliocentric distance at which vaporizations use only 2.5% of the solar heat absorbed by the nucleus.

In spite of its shortcomings, parameter $n$ of formula (1) has led Oort & Schmidt (1951) to a fruitful distinction among groups of dynamically different comets. The average value of $n$ is smallest (2.8) for the group of 'new' comets; it grows steadily for long-period (3.7), intermediate-period (3.8) and short-period comets (4.2). In the framework of the vaporization theory, the slow shift of $\bar{n}$ is interpreted (Delsemme 1974) by a fractionation induced by the early loss of the more volatile constituents; $r_0$ is being shifted to smaller values, bringing the steeper slope more and more into the range of the observations.

The distance $r_0$ is somewhat influenced by the sophistication of the vaporization model used; in particular, by the rotation rate of the nucleus, its polar inclination, its shape, its precession, the heat conductivity of its crust, the presence of an optically thick coma; however, the shift in $r_0$ induced by a reasonable variation of all these parameters remains moderate; the only parameter that can completely change the order of magnitude of $r_0$ is the chemical nature of the snows that drive the vaporizations. For instance, all other things being equal, $r_0 = 78$ AU for nitrogen, 38 AU for methane, 14 AU for formaldehyde, 8 AU for carbon monoxide and 2.5 AU for water (Delsemme 1982).

Because $r_0$ is so much more sensitive to the chemistry of the major volatile constituent than to any other physical parameter, $r_0$ can be used as an indicator of the nature of the material driving the vaporization. Although $r_0$ had not yet been defined in 1952, this was already the gist of the argument developed by Delsemme & Swings (1952) in favour of the existence of solid hydrates of gases (ionic hydrates and clathrates).

The values of $r_0$ have now been established for eleven comets (Delsemme 1985*a*) including a set of 'new' and quasi-new comets, in the hope of establishing the existence of very volatile constituents, that would be lost early as soon as comets are no more dynamically 'new'. To my surprise, all 'new' comets showed a value of $r_0$ consistent only with water ice or solid hydrates of gases (ionic or clathrate hydrates).

This constitutes the strongest argument so far for the presence of *water* in the solid phase (ice, snow or solid hydrates) as the major constituent of the volatile fraction of practically all cometary nuclei. The large amounts of H and OH released by the nucleus in the approximate ratio for water, in the comas of the bright comets of the 1970s, comes only as a confirmation that water is present, and not as a proof that water ice drives the sublimation of the nucleus.

## 6. Pristine nuclei are undifferentiated

I (Delsemme 1982) have listed circumstantial arguments that seem all to be in favour of undifferentiated nuclei. If the nuclei were radially differentiated, their decay with ageing or their fragmentation by splitting would sooner or later produce observable changes. However, all observations of cometary material that originated at different depths in the pristine nucleus, show the same properties, namely:

(*a*) the same dust-to-gas distribution pattern;
(*b*) the same spectral composition of the volatile;
(*c*) the same structural strength against fragmentation;
(*d*) the same vaporization pattern after fragmentation.

Of course, minor heterogeneities would not be observable below a certain size level that could probably be as large as 20–30 m. Besides, surface differentiation effects, that may pre-exist in 'new' comets because of their irradiation by galactic cosmic rays, can be considerably enlarged during perihelion passages by the outgassing of the surface layers and the sintering of dust into a crustal slag.

## 7. The dust:ice ratio

By definition, a 'primitive' mixture (Delsemme 1977) is a mixture where only hydrogen, helium and neon (that is, the most volatile gases) have been considerably depleted, whereas *all* the other elements have remained in proportion to their cosmic abundances. Standing in contrast with chondrites, carbon, nitrogen, oxygen and sulphur are not depleted in a 'primitive' mixture which contains all that can be condensed at a very low temperature, typically 30 K. In such a mixture, all metals including silicon, iron and magnesium are then assumed to be oxidized into silicates. The amount of oxygen used for that purpose depends somewhat on the nature of the silicates: the ratio of oxygen to metals may go from low (1.33) for olivine (in number of atoms) to high (1.80) for serpentine. Assuming that the rest of the oxygen is in the volatile ices (as well as C, N and S) then the primitive dust:ice mass ratio goes from 0.54 to 0.66, if Cameron's (1973) abundance table is used; it goes from 0.61 to 0.76 if we use strictly solar data (Ross & Aller 1976). Including possible uncertainties, the 'primitive' ratio remains in the range of $0.65 \pm 0.11$, if *all* the carbon is in volatile compounds (like $CH_4$, CO or $CO_2$). If three-quarters of the carbon is in refractory compounds, as was observed in the dust grains of Comet Halley, then the 'primitive' ratio becomes $1.10 \pm 0.22$. To summarize the situation, depending on where most organic molecules go (in the refractory dust or in the volatile ices), the 'primitive' dust:ice ratio may vary from 0.5 to 1.3.

The notion of 'primitive' ratio is useful because it sets limits for the dust:ice mass ratio in comets, if they condensed or accreted at a very low temperature from a reservoir of cosmic abundances and were never processed by heat later on. If they are heated during the course of their evolution, they lose more gas than dust; some of the gas may also get polymerized into dust. The result is the same: the dust:ice ratio becomes *larger* than the primitive ratio. This is likely to occur locally, in the outer layers of the nucleus, first after their irradiation with cosmic rays, second in the crustal slag after perihelion passage. Standing in contrast, it is extremely difficult to conceive any phenomenon that could produce the opposite, namely *diminish* the primitive ratio to a value lower than 0.5, by losing more refractory material than volatile material.

The actual dust:gas ratio of pristine comets is difficult to establish, in particular because of the surface decay of the nucleus. However, the interpretation of large brightness outbursts suggests the sudden blow off of a mantle of dust (Mendis & Brin 1977, 1978). I have reconstructed such an outburst from Finson & Probstein's (1968) data on Comet Arend-Roland. After the outburst, the dust:gas mass ratio seems to go back asymptotically to its steady-state value; for this reason it is believed that the steady state is representative of the inner composition of the nucleus. The best values for the dust:gas ratio have probably been reached by the Finson–Probstein method for two comets only (Delsemme 1982). They are $0.8 \pm 0.2$ and $0.6 \pm 0.4$ for comets Arend-Roland and Bennett respectively. Because of the error bars, the results are not essentially different and are consistent with a 'primitive' ratio in each case.

The *Vega* experiments have found 5–10 t $s^{-1}$ of dust and 30 t $s^{-1}$ of gas for the production rate of Comet Halley, but a Finson–Probstein study of the tail isophotes has shown that the dust:gas ratio during the flybys was far from the steady state (Barbieri *et al.* 1987; Fulle 1987; Fulle *et al.* 1987). At any rate, from the discrete data of the DIDSY (dust impact detection system) experiments, McDonnell *et al.* (1986) also suggest the existence of a large population of massive particles not taken into account in the production rate of dust found by the *Vega* experiment. Comet Halley's dust:ice ratio remains therefore remarkably consistent with a 'primitive' ratio.

Newburn & Spinrad (1985) have studied the dust:gas mass ratio in the coma of 17 comets. They find very low values, between 0.05 and 0.30. Of course a comet, even with a primitive ratio, may vaporize more gas than dust when not at a steady state; but this cannot last for a long time without choking the vaporization under a growing mantle of outgassed dust. On the other hand, it is unlikely that the 17 comets *all* showed lower values than the steady state. Newburn & Spinrad had to make many assumptions: an albedo of 0.05 for dust, a nominal expansion rate of 1 km $s^{-1}$ for gas, an assumption on the grain size distribution of the dust that they did not measure, because they did not use the Finson–Probstein method on the dust tail isophotes. Because in none of the cases the existence of a steady state was established either, no hard inconsistency has been found with a 'primitive' dust:ice ratio of 0.5 to 1.3 for the 17 comets in question.

## 8. NATURE OF THE DUST GRAINS

Before the flybys of Comet Halley, Brownlee's (1976) particles (collected by NASA's U2 plane in the upper atmosphere) were probably the most reliable source of information on the cometary grains. Their analysis suggested that they were very close to carbonaceous chondrites, with probably somewhat more carbon and sulphur. Typically, Brownlee's particles contained 5% C,† instead of 2.5% to 3.2% for the median carbonaceous chondrites.

However, the balance sheet for carbon in comets suggested that three-quarters of the cosmic carbon was still missing (Delsemme 1982). I therefore proposed that cometary dust could (before its entering the Earth's atmosphere) contain up to 30% carbon, to reach cosmic

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† In this paper all percentage compositions are by mass unless otherwise stated.

abundances. The PUMA (dust impact mass spectrometer) results of the *Vega* 1 flyby of Comet Halley have rather well supported this view (Kissel *et al.* 1986). The carbon content of the dust grains is within the error bars of the previous deduction (table 2).

TABLE 2. DUST IN COMET HALLEY: MEAN CHEMICAL COMPOSITION

(Interpreted from Kruegel & Kissel (1987).)

| organic 33% | | inorganic 67% | |
|---|---|---|---|
| unsaturated hydrocarbon | 16.0% | silicates | 51.5% |
| H,C+O | 5.2% | FeS (troilite) | 6.0% |
| H,C+N | 4.5% | C (graphite) | 3.0% |
| H,C+S | 1.8% | S (sulphur) | 1.0% |
| water | 5.5% | water | 5.0% |

The individual dust grains vary very much in mass and in composition. A chondritic silicate fraction without carbon seems to form the grain core, which is embedded in a variable amount of organic material. Most of the grains are from 0.2 to 1.0 μm in diameter, with a steep decrease in the number of larger size grains. Table 2 represents the *mean* composition averaged over 80 particles (Krueger & Kissel 1987). The organic fraction amounts to 33%; 3% reduced carbon, presumably graphite, it counted in the inorganic fraction; 11% water seems to be equally distributed in the two fractions. With this amount of carbon in the dust, the problem of the apparent carbon deficiency in comets (Delsemme 1982) seems to have completely vanished.

The inorganic fraction (6.7%) contains 51.5% silicates (mainly of magnesium and iron), 6% troilite FeS, 3% carbon, 1% sulphur, 5.5% water.

The organic fraction (33%) contains 16% hydrocarbons with a H/C ratio close to 0.67 suggesting unsaturated hydrocarbons such as $C_3H_2$; there are also 5.2% of oxygen-containing species, probably formic acid and formaldehyde in about equal amounts; then, 4.5% of nitrogen-containing species, a mixture of hydrogen cyanide, acetonitile, aminoethylene, pyrrole, pyridine, pyrimidine (50 coincidence pairs in mass spectra); purines and adenine are also present in several grains, whereas there is no indication for amino acids; finally, there is 1.8% of sulphur-containing species. Some molecules contain several oligo elements; amino methanol seems to be present, as well as some oxygen atoms that seem to be occasionally exchanged by sulphur atom.

Some important conclusions that may be connected to the problem of the origin of life on the Earth are:

(1) the prebiotic molecules HCN, $H_2CO$ and $H_2O$ are present;
(2) the precursors of the nucleic bases (purines and pyrimidines) are present;
(3) the amino acids are absent.

Let us finally remark that the high impact velocity of the grains (78 km $s^{-1}$) on the neutral mass spectrometer must have destroyed a certain amount of large molecules; in particular, large condensed heterocycles tend to be destroyed by a high momentum transfer.

Thanks to the large amount of organic material in the dust of Comet Halley, there is no doubt now that the abundance of all elements, including the light elements C, N, O, S, are about in cosmic proportions in this comet (at the exception of H, and presumably He and Ne, depleted by a factor of about 1000). The same situation is likely to exist in other comets (Delsemme 1982).

Another important conclusion is the presence of a large fraction of rather volatile molecules in the CHON particles: 15–30% of the so-called 'dust' is probably formed with 'icy' molecules that may be almost as volatile as, and even possibly more volatile than water; therefore they must vaporize according to the 'icy grain halo' model described by Delsemme & Miller (1971). In particular, their decay may explain the existence of an extended source of some of the gaseous species observed around the nucleus, and extending into the coma.

For example, formaldehyde has been observed in the CHON particles; its mass seems to represent several percent of the total dust. Formaldehyde is more volatile than water; it has also been identified in the gaseous coma; its photodissociation by the solar light takes place in a few thousand seconds; its branching ratio into CO plus other fragments ($H_2$ or $H+H$) is 69%; however, it can be freed by grains with a lifetime of a few ten thousands of seconds and it can explain the observed extended source of CO.

## 9. ORIGIN OF THE DUST IN COMETS

Some cometary grains contain metals or silicates only, some other grains contain a silicate core plus a variable mantle of organic molecules; finally the CHON grains do not contain metals at all, only organic molecules. The grains – most in the 0.2 to 1.0 μm range – are sufficiently different chemically to imply that they were condensed at different places and brought together (before or during accretion) by a process comparable by all means to a sedimentation. This is rather similar to the carbonaceous chondrites which also contain a mixture of fine grains of different origin, namely a high-temperature and a low-temperature fraction. The most plausible place for this sedimentation to happen has been described in models of the solar nebula; when the turbulence subsides because mass transfer to the protosun has stopped, then rings of dust separate from the gas and sediment from various distances in the nebula, into its equatorial plane, preparing the stage for the accretion of planetesimals. In this scenario, the dust of carbonaceous chondrites has sedimented in the outer asteroid ring and the frosty and icy cometary dust has sedimented between Jupiter and Neptune's distances. The recent observations of the chemical diversity of the dust in Comet Halley seems to be consistent with such a scenario; recent proposals that reconsider alternate origins for comets may have difficulties to explain the chemical diversity of their dust grains.

## 10. NATURE OF THE VOLATILE FRACTION

There is a deep similarity in the spectra of many comets in the visible region and the beginning of the ultraviolet region (Swings & Haser 1957). Many early differences were shown to come from observational artifacts (spectral and spatial dispersion, sensitivity limits of the photographic plate, etc.).

Feldman (1982) expressed the same remark for the vacuum ultraviolet region, suggesting that there might be a deep similitude in the composition of most comets.

Delsemme (1982) established that comets Bennett 1970 II, Kohoutek 1973 XII and West 1796 VI were similar in many respects. After careful discussion, the elemental ratios of H, C, N, O, S in their volatile fraction were found to be close enough to be incorporated into a single model, representing 'the average bright comet of the 1970s'. The final model is given in table 3 (after a slight revision (Delsemme 1985*b*)).

It is worth mentioning that the elemental ratios of Comet Kohoutek were oscillating wildly;

Table 3. Light elements in some bright comets: mean abundances in volatile fraction

(All elements are normalized to oxygen = 1.00.)

| element | bright comets (Delsemme 1985*b*) | Comet Halley (this work) |
|---|---|---|
| H | 1.8±0.4 | 1.8±0.4 |
| C | 0.20±0.10 | 0.20±0.05 |
| N | 0.10±0.05 | 0.10±0.05 |
| O | 1.00 | 1.00 |
| S | 0.003±0.0015 | 0.01±0.005 |

the observations had picked up epochs close to two outbursts and far from steady state. It was, however, possible to make use of the observations. An outburst propagates in a few days into the coma; the H atoms had been produced an average of eleven days earlier than the OH radicals observed simultaneously. Correcting for the delays damped the spurious fluctuations due to the outbursts and yielded a ratio H/OH = 1.8±0.8 for the same production epoch of H and OH. In the same way, when C and O were corrected for the two different ionization lags of two days and five days respectively, the C/O ratio yielded an average of 0.22±0.06 for Kohoutek (close to 0.21±0.03 for Comet West), making the two spurious ratios of 0.08 (5 January) and 0.58 (8 January) disappear. This example has been discussed in detail to show that early differences came more from deficiencies in the models than from actual compositional differences.

The complete quantitative molecular analysis of the volatile fraction remains, however, a difficult feat, because the number of species involved remains uncertain, and the excitation mechanisms that bring different molecules into visibility in the spectra remain intricate. As far as the traditional bands observed in the visual are concerned, spectral differences from comet to comet are small and concentrate around the same 'normal' ratios; for instance, $C_3/CN = 0.2$ and $C_2/CN = 1.5$ (Cochran 1987).

The situation is somewhat different in the vacuum ultraviolet region, where major carbon compounds seem to be variable in some comets. Festou (1984) has mentioned the diversity of the CO/OH ratio in comets Kohoutek 1973 XII, West 1976 VI and Bradfield 1979 X. The interpretation of the two outbursts of Comet Kohoutek given in the previous paragraph is convincing enough not to attach any significance at the spurious value 0.58; but the very low value of CO/OH = 0.044 of Comet Bradfield has not been explained. It could come, either from the same type of fluctuation out of steady state, or from genuine elemental differences.

Woods *et al.* (1986) suggests that the variability of the $CO/H_2O$ ratio is large: they quote 27% for West, 18% for Halley and 1% for Bradfield. Of course they recognize that the differences do not necessarily reflect intrinsic compositional differences between comets, but may come from deficiencies in the models used to interpret the observations.

## 11. The CO distribution in Comet Halley

Many observations have been collected on or near the dates of the Comet Halley flybys. For this reason, the CO distribution in Comet Halley needs a separate discussion. Not surprisingly, important discoveries come from the flybys themselves. Eberhardt *et al.* (1986) report that the *Giotto* neutral-gas mass spectrometer has discovered the existence in the coma of a large source of CO extending up to 15000 km from the cometary nucleus. Independently, Krueger & Kissel (1987) have discovered the existence of a large organic fraction, containing in particular formaldehyde $H_2CO$ and formic acid $HCO{\cdot}OH$, in the dust grains analysed by the dust-impact gas spectrometer PUMA of the *Vega* 1 spacecraft. Although the two groups have not yet mentioned the correlation between these two discoveries, I shall verify in §12 that the photodissociation of $H_2CO$ and of $HCO{\cdot}OH$ from the volatile fraction of the grains explains quantitatively the origin of the extended source of CO. Other explanations proposed already in the literature do not seem therefore to be justified.

From Eberhardt *et al.* (1986, figure 2), the point CO source represents 40% and the extended source 60% of the total CO flux. Eberhardt *et al.* give a *total* production of $CO/H_2O = 10 \pm 5\%$, because other molecular fragments might contribute to the 28 u peak. Because $N_2$ is the major other contributor to the peak, we have used the feedback of the very low evaluation of the total elemental N coming from other data (table 3); this suggests that the actual value of $CO/H_2O$ lies in the upper range of Eberhardt *et al.* limits, and can be reasonably represented by $CO/H_2O = 13 \pm 3\%$.

The other source of information on CO comes from the vacuum ultraviolet spectra. Festou *et al.* (1986) report $CO/OH = 10 \pm 5\%$; however, because of the discovery of formic acid whose photodissociation represents another source of OH, we must remain aware more than ever that OH is not an automatic measure of $H_2O$. The $C/O = 10\%$ reported by Steward from the *Pioneer Venus* spacecraft should not be construed as an identical result to that of Festou *et al.* The carbon resonance line used for the previous ratio represents only a fraction close to one-half of the total carbon, because the rest has remained in ionized $CO^+$ blown away at a large velocity by the solar wind.

Finally, Woods *et al.* (1986) give $CO/H_2O = 20 \pm 5\%$ on 26 February 1986, and $17 \pm 4\%$ on 13 March; only the latter is close enough to the *Giotto* flyby to be compared and used here. We conclude this discussion by adopting:

$$CO/H_2O = 13 \pm 3\%$$

as the only possible value of the ratio which is reasonably consistent with all observations, including vacuum ultraviolet as well as mass spectra.

## 12. DUST CONTRIBUTION TO THE VOLATILE FRACTION

The large organic fraction of 33% of the dust, found in the grains of Comet Halley, brings new problems and new vistas related to the interface between dust and volatiles.

First, the organic fraction cannot be completely refractory, otherwise it would have survived the entry into the upper atmosphere and would therefore still be present in the pores of the Brownlee's particles. The interpretation of Krueger & Kissel's (1988) data yields a total carbon content of 25% compared with 5% in Brownlee's (1976) particles. The missing 20% carbon cannot be too volatile either, otherwise it would have vaporized into the coma before being detected by the *Giotto*'s neutral mass spectrometer. Table 2 suggests that it is combined with about 10% of H, O, N and that the fraction represents a total of 30% of the dust; in particular, 5.2% of the dust seem to come from two major constituents: formic acid and formaldehyde.

Assuming a 'primitive' dust:ice mass ratio of 1.10 (see §7), we have an amount of $CO/H_2 = 0.07$ that will be released in an extended source by a two-step process:

(*a*) vaporization of the CHON grains or CHON mantles, compatible with a characteristic lifetime of about $2 \times 10^4$ s;

(*b*) photodissociations of formic acid and formaldehyde into CO plus other molecular fragments, with a shorter lifetime, about $5 \times 10^3$ s for $H_2CO$, $2 \times 10^3$ s for $HCO \cdot OH$, from their cross sections and the solar flux.

The CO flux produced by the extended source, as observed by mass spectrometry of the neutral gas, is $(13 \pm 4)\,\% \times 0.6 = (8 \pm 2)\,\%$ of $H_2O$, in reasonable agreement with the 7% deduced from the vaporization of the CHON grains.

I conclude that the release and photodissociation of formic acid and formaldehyde, that represent more than 5% by mass of the dust, can explain the total amount of CO released in an extended source of 15000 km around the nucleus, as observed by the neutral mass spectrometer of *Giotto*.

We can generalize the previous approach and predict that the CHON grains are the source of other volatile species. A major one is hydrogen cyanide HCN; HCN was already deduced to be the parent molecule of CN by quantitative arguments (Delsemme & Combi 1980). Because it is present in the CHON grains (Krueger & Kissel 1988), its slow release explains the persistence of the spiral-shaped CN jets observed in the coma of Comet Halley by A'Hearn *et al.* (1986). It can also be expected that CHON-type grains may play an important role in the exchange of matter between volatile dust and gas. During perihelion passage, their thermal evolution in the cometary mantle from volatile compounds (like formaldehyde) into stable dust (polyformaldehyde) could explain:

(*a*) a slow evolution towards less gas and more dust (a larger and larger dust:ice mass ratio);

(*b*) a slow transfer of carbon from gas to dust;

(*c*) the disappearance of an excess source of carbon in the coma of evolved comets;

(*d*) a reduction of the C/O ratio in the coma of evolved comets, depending on their perihelion distance and the number of their previous passages;

(*e*) the claimed 'puzzle' of the carbon abundance in the coma.

## 13. ELEMENTAL BALANCE SHEET OF COMET HALLEY

The first task for an elemental balance sheet is to establish the elemental ratios that must be satisfied.

### 1. $H/O = 1.8 \pm 0.4$

Steward (1987) gives a constant $H/O = 1.4$ for 17 days, from the *Pioneer Venus* data on and after perihelion. The $H/O = 1.4$ is very close to the $H/O = 1.5$ that Delsemme (1982) had found for the average in the bright comets of the 1980s. However, he revised this value upward to 1.8 because it is the minimal value consistent with all the data *and* with the elemental balance sheet (Delsemme 1985*b*). For Comet Halley, such a revision is also needed for the same reasons. The 1.4 value would imply an amount of $CO + CO_2$ at least as large as 30% of $H_2O$, an amount inconsistent with the data of the mass spectrometry from *Vega* and *Giotto* as well as with the ultraviolet data of the IUE and the *Pioneer Venus*.

### 2. $C/O = 0.20 \pm 0.05$

The reasons for accepting this C/O value have been discussed above; it is consistent with $CO/H_2O = 0.13 \pm 0.05$ (which includes an extended source of CO, as established by the discussion of § 11), because there is also $CO_2/H_2O = 0.035$ (Krankovski *et al.* 1986) and we can accept $(CN + C_2 + C_3)/H_2O = 0.035$ from the traditional spectra. The large $CO_2^+$ ion source observed in an outburst (Feldman *et al.* 1986) is also consistent with the $CO_2$ amount; all what it requires is an effective ionization source. The 0.20 ratio for C/O is consistent with the resonance lines of the *Pioneer Venus* data (Steward 1987), because the $CO^+$ fraction blown away at high speed by the solar wind is not entirely counted in the atomic carbon detected by *Pioneer Venus*.

### 3. $N/O = 0.1 \pm 0.05$

This N/O value is derived from the sum of the CN, NH, $NH_2$ and $N_2^+$ observed in the traditional visual and near-ultraviolet spectra, and is consistent with the upper value for $N_2$ given at mass-spectrometer peak 28 of Eberhart *et al.* (1986).

### 4. $S/O = 0.001 \pm 0.005$

Feldman *et al.* (1987) give $CS_2/H_2O$ varying from 5 to $10 \times 10^{-4}$ (discounting some outbursts) from September 1985 to July 1986; Festou *et al.* (1986) also give the same limits for a much shorter period close to the epoch of the *Giotto* passage. The adopted $S/O = 10^{-3}$ takes the existence of $S_2$ into account, as well as that of the ions $HCS^+$ and $CH_2SH^+$ (Krankovski *et al.* 1986).

### 5. *Balance sheet of the elements*

The balance sheet of the elements given in table 4 uses the elemental ratios for cometary dust given by Krueger & Kissel (1988) from data on 80 dust particles that hit the impact mass spectrometer on board the *Vega* 1 spacecraft. The columns for the cometary gas have been derived from table 3, itself coming from the previous discussion. Finally, the gas columns of table 4 have been normalized to the dust columns by using the dust:gas mass ratio of 1.10, derived from the fact that the dust is quasi-chondritic, but contains three-quarters of the total

TABLE 4. ELEMENTAL ABUNDANCES IN COMET P/HALLEY

(Abundances in dust from Krueger & Kissel's (1987) impact mass spectrometer on board *Vega* 1; abundances in gas from this paper; dust gas mass ratio = 1.1 (see text). Data in atom numbers are normalized to silicon = 1.00.)

| element | atomic mass | cometary dust number | cometary dust mass | cometary gas number | cometary gas mass | cometary totals number | cometary totals mass | cometary totals number | cometary totals mass |
|---|---|---|---|---|---|---|---|---|---|
| H | 1.0 | 7.80 | 7.8 | 21.86 | 21.9 | 29.66 | 29.7 | 48.4 % | 5.3 % |
| C | 12.0 | 6.00 | 72.0 | 2.42 | 29.1 | 8.42 | 101.1 | 13.7 % | 18.1 % |
| N | 14.0 | 0.20 | 2.8 | 1.21 | 16.9 | 1.41 | 19.7 | 2.3 % | 3.6 % |
| O | 16.0 | 6.50 | 104.0 | 12.12 | 194.1 | 18.62 | 298.1 | 30.4 % | 53.4 % |
| S | 32.0 | 0.50 | 16.0 | 0.12 | 3.8 | 0.62 | 19.8 | 1.0 % | 3.5 % |
| Mg | 24.3 | 0.70 | 17.0 | — | — | 0.70 | 17.0 | 1.1 % | 3.0 % |
| Si | 28.0 | 1.00 | 28.0 | — | — | 1.00 | 28.0 | 1.6 % | 5.0 % |
| Fe | 55.9 | 0.70 | 39.1 | — | — | 0.70 | 39.1 | 1.1 % | 7.0 % |
| Al + Na | ⟨25⟩ | 0.07 | 1.7 | — | — | 0.07 | 1.7 | 0.1 % | 0.3 % |
| Ca, Cr, Mn, Ni | ⟨50⟩ | 0.08 | 4.0 | — | — | 0.08 | 4.0 | 0.1 % | 0.7 % |
| totals | — | 23.55 | 292.4 | 37.73 | 265.8 | 61.28 | 558.2 | 99.9 % | 99.9 % |

carbon of the comet, itself representing a nominal three-quarters of the cosmic carbon abundance.

Table 5 compares the elemental abundances in Comet Halley with the solar and chondritic abundances. It is now quite clear that, except for hydrogen depleted by a factor of almost 900, all the abundances of the light elements in Comet Halley are within the error bars of solar abundances. The slight carbon deficiency may come from the variable $CO^+$ fraction blown away by the solar wind, hence not counted in its entirety in the atomic carbon line of the IUE. The big carbon deficiency reported for other comets has disappeared entirely, mainly because of the large amount of carbon now detected in the dust.

TABLE 5. COMPARISON OF ELEMENTAL ABUNDANCES IN ATOM NUMBERS

(Data from Mason (1971) are rounded averages; see his pp. 22, 83, 96 and 138.)

| element | solar (Cameron 1981) | Comet Halley (1986 passage) | chondrites (Mason 1971) CI | CM | CV, CO |
|---|---|---|---|---|---|
| H | 26600.0 | 30.0 | 2.0 | 1.0 | 0.10 |
| C | 11.7 | 8.1 | 0.7 | 0.4 | 0.08 |
| N | 2.3 | 1.4 | 0.05 | 0.04 | 0.01 |
| O | 18.4 | 18.8 | 7.5 | 5.3 | 4.10 |
| S | 0.5 | 0.6 | 0.5 | 0.2 | 0.12 |
| Si | 1.0 | 1.0 | 1.0 | 1.0 | 1.00 |

## 6. *Discussion of a heuristic model for volatile molecules*

Table 6 displays a heuristic model for the volatile molecules present in the nucleus of Comet Halley. Each line of the table represents the contribution of each molecule to the elemental abundances. The sum of each column gives a number proportional to the abundance of a particular element. The amounts of each molecule have been adjusted to keep them in quantitative agreement with the known molecular abundances; some adjustments, within the known error bars, have been used to keep as much as possible the elemental abundances (the sum of each column) in proportion to the elemental abundance ratios of table 3.

TABLE 6. CHEMICAL COMPOSITION OF THE VOLATILE FRACTION OF COMET HALLEY

| parent | % | H | C | O | N | S |
|---|---|---|---|---|---|---|
| $H_2O$ | 80 | 160 | — | 80 | — | — |
| $H_2CO_2$ | 4.5 | 9 | 4.5 | 9 | — | — |
| $H_2CO$ | 4 | 8 | 4 | 4 | — | — |
| $CO_2$ | 3.5 | — | 3.5 | 7 | — | — |
| $CO$ | 1.5 | — | 1.5 | 1.5 | — | — |
| $CH_4$ | 1.0 | 4 | 1 | — | — | — |
| $C_2H_2$ | 1.5 | 3 | 3 | — | — | — |
| $C_3H_2$ | 0.2 | 0.4 | 0.6 | — | — | — |
| $N_2H_4$ | 0.2 | 0.8 | — | — | 0.4 | — |
| HCN | 1 | 1 | 1 | — | 1 | — |
| $N_2$ | 0.5 | — | — | — | 1 | — |
| $H_4C_5N_4$ | 0.5 | 2 | 2.5 | — | 2 | — |
| $NH_3$ | 1.0 | 3 | — | — | 1 | — |
| $S_2$ | 0.2 | — | — | — | — | 0.4 |
| $H_2S$ | 0.2 | 0.4 | — | — | — | 0.2 |
| $CS_2$ | 0.2 | — | 0.2 | — | — | 0.4 |
| totals: | 100 | 189.2 | 21.8 | 101.5 | 5.4 | 1.0 |

ratios: H/O = 1.86; C/O = 0.21; N/O = 0.05; S/O = 0.01.

The building of such a balance sheet for the elements remains difficult because of the large number of simultaneous constraints which are sometimes self-contradictory. For instance, the known production rates for water and for oxygen-bearing compounds are in contradiction with the *Pioneer Venus* data that give H/O = 1.4. It is impossible to achieve a H/O ratio smaller than 1.8 (the ratio adopted in table 3) and it remains a feat to come close to it in table VI, because most other molecules add at least two hydrogen atoms per oxygen atom.

The only three molecules that are the exception are CO, $CO_2$ and $H_2CO_2$. However, the ratio $CO_2/H_2O$ has been measured and cannot be changed beyond its error bars. $H_2CO_2$ formic acid and $H_2CO$ formaldehyde, discovered in the organic fraction of the dust grains, are volatile enough to be counted in the volatile fraction: formaldehyde is much more volatile than water, and formic acid has almost exactly the same vapour pressure as water (it boils at 101 °C). Both have been assumed to be the parent molecules for the extended source of CO that has been observed, because both photodissociate in times shorter than the vaporization of grain clusters. A larger amount of formic acid would undoubtedly improve the H/O ratio, therefore an amount somewhat larger than 4.5% would be beneficial to the balance of table 6.

The total production of CO has been set at 10% of the volatiles, that is, 12.5% of the production of water; $CO_2$ is set at 3.5% of the volatiles (or 4.2% of water). The total production rate of $(CO+CO_2)$ has been pushed to the maximum compatible with the errors bars of the observations to keep both H/O and C/O within reasonable limits.

Acetylene $C_2H_2$ is assumed to be the source of $C_2$, and $C_3H_2$ the source of $C_3$; $C_3H_2$ has now been shown to be abundant in interstellar space. Hydrogen cyanide is the source of CN, as established by quantitative arguments by Delsemme & Combi (1980). Finally, the normal ratios $C_2:C_3:CN = 1.5:0.2:1$ (Cochran 1987) have been adopted here.

The number of sulphur molecules (Feldman *et al.* 1987: Krankovski *et al.* 1986) is small enough not to interfere very much with the H and the C balance sheet. A more serious problem might turn out in the nitrogen balance. Hydrazine $N_2H_4$ is the probable source of $NH_2$ (Delsemme 1975), whereas $NH_3$ does not seem to be very abundant: a bonus for the balance sheet because it introduces much hydrogen and no oxygen. It is also difficult to introduce more than 1% of $N_2$ as suggested by the small production rate of $N_2^+$.

It is interesting to note that neither $N_2$ nor CO can be very abundant in a nucleus whose temperature is driven by the vaporization of water ice; this is because of the very large vapour pressure of $N_2$ and of CO. Even their clathrates have high dissociation pressures. Incidentally, the assumption that carbon monoxide can form a clathrate with water has been recently confirmed by D. W. Davidson (1986, personal communication); it has a dissociation pressure of $1.26 \times 10^3$ Pa at 273 °K; it lies therefore between the oxygen and the nitrogen clathrates in stability.

The observed presence of purine $H_4C_5N_4$, in the organic fraction of the dust, must not be taken at its face value in table 6. It has been used here as a symbol and a reminder that we may still have several unknown organic compounds in the dust that might dissociate or vaporize into the coma.

Altogether, our understanding of the volatile fraction has considerably improved with Comet Halley. The major recent achievement is, of course, the understanding that a very large fraction of the dust is volatile enough to be the origin of an extended source of gas in the inner coma.

## 14. Isotopic ratios

Before Comet Halley, the only isotopic ratio approximately measured in comets was $^{12}C/^{13}C$, but the error bars were so large that it was impossible to say whether it was really different from 89, the terrestrial ratio.

With the flybys of Comet Halley, the situation has changed. Eberhardt *et al.* (1986) report that the Giotto neutral mass spectrograph gives a D/H ratio between 60 and 480 p.p.m., implying that the cometary deuterium is enriched by a factor of at least three with respect to interstellar hydrogen, or to hydrogen in Jupiter and Saturn. A comparable enrichment occurs in terrestrial water, suggesting that water on the terrestrial planets can be of cometary origin, an idea that was proposed earlier by models of the accretion of the planets from the solar nebula.

Eberhardt *et al.* (1987) also report $^{18}O/^{16}O = (23 \pm 6) 10^{-4}$ in Comet Halley, agreeing within the error limits, with the average Solar System value of $20 \times 10^{-4}$. Although we still miss many data, nothing has been found yet that would not be consistent with the cometary material originating from the same original reservoir as the rest of the Solar System.

## 15. Conclusions

Comets seem to represent a population of rather homogeneous objects. In particular, their original size distribution peaks at a mean diameter of the order of 10 km. Evolved comets only, have fragmented into smaller pieces during their decay. Cometary dust grains seem to be made of clusters of extremely fine particles (0.2–1.0 μm) sintered by heat at a variable degree during their perihelion passages. The plasma tails of comets cannot be used as a good indicator of their chemistry because they are too sensitive to scaling factors. The brightness laws of comets seem to be driven only by the sublimation of water ice or at least of gas hydrates of the clathrate type. Pristine nuclei are likely to be radially undifferentiated. Only their crustal surface must be outgassed and sintered by the heat of perihelion passages.

Comet Halley is confirmed to be in the same general class as the bright comets of the 1970s. Its elemental analysis, taking gas and dust into account, seems to have solved one of the major puzzles of comet chemistry: contrarily to earlier suspicions, carbon was not depleted; with an organic fraction of 33 % in the cometary dust, the carbon of Comet Halley is close to cosmic abundances, as well as all other elements including N, O, S, but at the exclusion of hydrogen (and presumably of helium and neon) who is depleted by a factor close to 1000 (nominally, 900 in Comet Halley, if one takes into account the unexpected presence of hydrocarbons in the dust).

Taken into account what we did not know about dust, the bright comets of the 1970s must be rather similar chemically to Comet Halley. In particular, their dust: ice mass ratio is likely to be a 'primitive' mixture and as such, is likely to be between 0.5 and 1.3.

Isotopic ratios rather point to a Solar System origin. The deuterium enrichment is consistent with that of the water in our oceans.

More than ever, comets appear to be made of a pristine material older than the planets, preserved in its primitive state by the very deep cold of interstellar space and able to give us information about the chemistry of the early solar nebula.

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