Section V The Cometary Coma

THE COMPOSITION OF COMETS¹

DIETER KRANKOWSKY Max-Planck-Institut für Kernphysik P.O. Box 103 980, 6900 Heidelberg, FRG

ABSTRACT. The chemical composition of gases in the coma of Comet Halley obtained from in situ and remote observations is reviewed. Water vapor with an abundance of approximately 80% by number is the dominant parent gas. Carbon monoxide is the second most abundant molecule, with about one-seventh of the water abundance. The other expected parent gases carbon dioxide, methane, and ammonia—contributed with at most a few percent to the coma gas. Molecular nitrogen is found to be a minor species, with an abundance of less than one percent. Formaldehyde is relatively abundant, with a few percent relative to water. Gas-phase isotope ratios of nitrogen, oxygen, and sulfur are found to agree with solar system values within experimental errors. Halley's hydrogen isotope ratio is comparable to the values found in other solar system objects poor in hydrogen, but distinctly different from the protosolar nebula and objects that accreted hydrogen in gaseous form. Carbon in the cyanide radical is enriched by 35% in ¹³C compared to the bulk solar system value that indicates the presence of non-homogenized interstellar carbon in Halley. Volatiles released from grains contribute noticeably to the coma gas. Complex organic molecules, inferred from various observations as constituents of the dust grains, are believed to be the origin of the distributed CO source, CN, and other jet structures in the coma.

1. Introduction

The missions of five spacecraft to Comet Halley in 1986 (*Nature*, 321, 1986) for the first time allowed a close-up view into and in situ measurements of the inner coma of a comet. Together with a wealth of Earth-bound and near-Earth-based observations, these measurements covered the entire range of the electromagnetic spectrum from the farultraviolet to radar wavelengths, providing the most complete set so far of compositional data of cometary volatiles and the only information on chemical properties of the dust obtained for an individual comet². Before, only Comet Kohoutek (1973 XII) was studied in a coordinated observational program, although the nine-month time for preparation did not allow for anything comparable to the Halley program. Furthermore, instrumental techniques, detectors, and space vehicles have since become mature and now permit observation of the coma at infrared and radio wavelengths.

Spectra in the visible (Arpigny *et al.* 1990), studied for decades, show the resonance fluorescence of sunlight by radicals and yield information on species like CN, NH, NH₂, C₂, and C₃. Their parent molecules constitute only a minute fraction of the volatile component

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²Early results have been presented on two conferences: Exploration of Halley's Comet, eds. B. Battrick, E.J. Rolfe, and R. Reinhard, ESA SP-250, 3 vols., 1986, and Diversity and Similarity of Comets, eds. E.J. Rolfe and B. Battrick, ESA SP-278, 1987.

of comets. Since the early 1970s, when ultraviolet (UV) spectroscopy of cometary comae from space vehicles started, the major volatile constituents of very many comets have been observed. The presumed dominant water is detectable by its dissociation products H, O, and OH. Carbon monoxide and its ion are detected directly, while carbon dioxide can only be observed through its metastable CO dissociation product or indirectly through the ion CO₂⁺. Other almost omnipresent signatures in the ultraviolet spectra are due to C, S, and CS. Major contributions to the UV spectroscopy of comets have been made by the International Ultraviolet Explorer (IUE) satellite, which obtained spectra of more than 30 comets (Feldman 1990). Although these comets have been very different with respect to their gas/dust ratio, gas production rate, and heliocentric distance and have been observed at different geometries, their ultraviolet spectra appear to be rather similar. Thus it has been argued (Feldman 1982, 1990) that the ultraviolet spectra suggest a common chemical composition and perhaps common origin of comets. Most of the parent progenitors of the atoms, radicals, and ions detected in the visible and ultraviolet spectra have no strong electronic transitions at these wavelengths. Parent molecules can only be observed in their vibrational transitions in the near and medium infrared or in their rotational transitions at far infrared and microwave wavelengths (Weaver et al. 1990). The rapid development in radio astronomy has added another important spectral window for the search for parent molecules (Crovisier and Schloerb 1990).

The following sections will concentrate on the chemical composition of the volatile component as observed in Halley. In a recent article by Whipple (1989), in which the developments in cometary science within the last thirty years are outlined, a modern bibliography on the subject can be found.

2. Coma Composition and Parent Molecules

The chemical composition of the gas in the coma is different from the composition of the volatiles in the nucleus. Photoprocesses, as well as the chemical reactions between neutrals, and between neutrals and ions, can lead to substantial alterations of the molecular composition of the expanding gas in the coma. Expansion velocities are typically on the order of 1 km/s, and hence a molecule takes 3 hours to reach a distance of 10,000 km. For some species, lifetimes against photodissociation are much shorter. Spectroscopic composition measurements, depending on the strength of the investigated lines, often cover a substantial radial range. It is then necessary to make appropriate corrections for the change in the chemistry occurring in this distance range, in order to obtain the composition at the nuclear surface. These corrections are facilitated if radial profiles can be obtained which can be fitted to the theoretical models, such as the Haser model (Haser 1957, 1966), or the more sophisticated vectorial model (Combi and Delsemme 1980, Festou 1981). Measurements closer to the nucleus than 10^4 km are difficult, however, and the radial resolution obtainable is often only a few thousand kilometers.

In situ neutral mass spectrometer (NMS) measurements on board Giotto, which made the closest approach to Halley's nucleus, were obtained to a distance of $\sim 1,000$ km from the nucleus. Still, at such a far range, very reactive molecules or species with a lifetime much smaller than 1,000 s were not observable by the instruments. This limitation can cause considerable uncertainty in deducing the chemical composition at the nucleus from the measurements in the coma. For instance, from the in situ measurements, it will probably not be possible to decide whether S₂ (lifetime ≈ 350 s), discovered by A'Hearn *et al.* (1983) in Comet IRAS-Araki-Alcock (1983 VII), is a possible precursor of the relatively abundant neutral and the ionized sulfur observed by the Giotto instruments.

2.1. WATER VAPOR

Water has been expected to be the major volatile species, because its dissociation products dominate the ultraviolet spectra of comets. But unquestioned direct observation before Halley was not available. The tentative identification of water in Comet Bradfield (1974 III) by its 1.35-cm line at radio wavelengths by Jackson *et al.* (1976) was challenged by Crovisier *et al.* (1981) and by Hollis *et al.* (1981). Searches for the 1.35-cm line in other comets gave negative results, except for Comet IRAS-Araki-Alcock (1983 VII), where apparently this line was detected by Altenhoff *et al.* (1983). Similarly, efforts to identify water ice were not conclusive. Reports of the detection of H₂O absorption at $3 \mu m$ (Campins *et al.* 1983, Hanner 1984) were questioned by A'Hearn *et al.* (1984). However, observational evidence for water ice in Comet Kohoutek (1973 XII) and in Comet P/Schwassmann-Wachmann 1 was claimed by Crifo (1983) and Hartmann and Cruikshank (1983), respectively.

The first definite detection of water vapor in a comet by remote observation was achieved on December 22 and 24, 1985 (Mumma *et al.* 1986), when nine infrared spectral lines of the ν_3 band (2.65 μ m) were found in the coma of Halley's Comet by a Fourier transform spectrometer on board the NASA-Kuiper Airborne Observatory. From these data and later observations, production rates, spatial distribution, and outflow velocities of H₂O were derived (Weaver *et al.* 1986). Water was also detected by the infrared spectrometer (IKS) on the VEGA 1 spacecraft (Combes *et al.* 1986, 1988) on March 6 by observing the ν_3 band at 2.65 μ m and from the three-channel spectrometer (TKS) on VEGA 2 (Krasnopolsky *et al.* 1986) on March 9 by utilizing the 1.38- μ m band. The first in situ measurement of water vapor in a cometary coma was obtained from the NMS experiment on board the European Space Agency's Giotto spacecraft on March 13, 1986, when it flew past the nucleus of Halley's Comet at a distance of about 600 km (Krankowsky *et al.* 1986). These data established that H₂O is the most abundant volatile, with 80% by number.

The IUE satellite observatory provided monitoring of the water production of Halley during the period from September 1985 to July 1986, except for a two-month period between January and March, when the solar elongation angle to the comet was too small. The H₂O gas production rates as a function of the heliocentric distance of Halley were retrieved from the fluorescent emission of OH (0-0 band) from IUE data (Festou *et al.* 1986, Feldman *et al.* 1986b). Pre- and post-perihelion observations of the OH emission are also available from the Soviet ASTRON satellite (Boyarchuk *et al.* 1987). These data are complemented by the production rates obtained from the H I Lyman- α measurements of the Pioneer Venus Orbiter ultraviolet spectrometer (Stewart 1987) and the Dynamics Explorer-1 satellite (Craven and Frank 1987). The water production rates from the various observations are in reasonable agreement.

From the Lyman- α measurements, obtained by the ultraviolet imager on board the Suisei spacecraft, a periodic breathing of the hydrogen coma has been derived by Kaneda *et al.* (1986). Outbursts of water from the surface has been suggested by the authors as the possible cause. The Suisei data have been criticized by Feldman (1990), who pointed out that the rapid time variability is not confirmed by the Lyman- α observations by IUE.

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2.2. CARBON MONOXIDE

The second most abundant gas in the coma of Halley is CO, as found by the in situ mass spectra of the NMS experiment on Giotto (Eberhardt et al. 1986a, 1987a). At distances between 20,000 and 50,000 km, CO's abundance is 15% relative to water, dropping to 7% at a distance of 1,000 km from the nucleus. This can be understood in terms of an extended source of CO in the coma (Eberhardt et al. 1987a) contributing about half the amount of the measured CO. Carbon monoxide was also measured by ultraviolet spectrometers on two sounding rockets (Woods et al. 1986) and verified as the second most abundant gas in Halley. On February 26, 1986, a relative abundance of $(20\pm5)\%$ was found. The data obtained on March 13, 1986, gave a CO gas production rate relative to H_2O of $(17\pm4)\%$ in very good agreement with the value from the NMS experiment, thus confirming the assumption that the 28-amu/e mass spectral peaks are mostly due to CO. The radial brightness profiles from the rocket flights also seem to suggest the presence of a source of CO in addition to the nucleus. Marginal detections of CO were also reported by Combes etal. (1986, 1988) from the infrared experiment IKS aboard the VEGA 1 spacecraft and by Festou et al. (1986) from IUE observations, where estimates for CO gas production rates relative to H_2O range from 10% to 20%, in agreement with the Giotto and rocket results. In comparison, a 27% CO abundance relative to H₂O was found for Comet West (1976 VI) (Feldman and Brune 1976, Feldman 1978), whereas Comet Bradfield (1979 X) contained only ~ 1% CO (Weaver 1981).

2.3. CARBON DIOXIDE

In P/Halley, carbon dioxide was detected for the first time in a comet, although the bands of CO_2^+ in ion tails of comets (Festou *et al.* 1982) have suggested its presence. The IKS instrument on VEGA 1 derived, in a first analysis of the ν_3 band at 4.3 μ m, an abundance of 1.5% relative to H₂O (Combes *et al.* 1986), which was revised to 2% by Moroz *et al.* (1987). Most recently, Combes *et al.* (1988) obtained from the same data a CO_2 abundance of 2.7% relative to water. From the radial density profile of the mass peak at 44 amu/e, measured by the NMS experiment on Giotto, an upper limit of 3.5% relative to water was found, allowing for the possible contributions of other species such as CS and C_3H_8 to the 44-amu/e mass peak (Krankowsky *et al.* 1986). Carbon dioxide is abundant in comets. It contributes to the carbon inventory in the volatile fraction and, as suggested by Feldman *et al.* (1986a), could be responsible, due to its high volatility, for outbursts observed at large heliocentric distances.

2.4. METHANE

Methane has been considered as another carbon-bearing parent molecule in models of comet formation. Originally suggested by Wurm (1943) for a scenario in which comets formed in the neighborhood of the giant planets, methane has also been included at various abundance levels in early models that attempted to link comets to the interstellar clouds (Mitchell *et al.* 1981, Biermann *et al.* 1982, Yamamoto *et al.* 1983). A search for CH₄ in Comet Halley on March 20, 1986, utilizing the Fourier Transform Spectrometer on the NASA-Kuiper Airborne Observatory, resulted in an upper limit for the gas production rate of 4×10^{28} molecules s⁻¹ (Drapatz *et al.* 1986), corresponding to less than 4% relative to H₂O. The evaluation of the CH₄ abundance from the neutral gas spectra of the NMS experiment on Giotto is difficult because of possible confusion with the dissociation fragments from H_2O , possibly NH_3 , and heavier molecules that lead to interference in the mass range 12 to 16 amu/e. So far, only an upper limit of 7% for the volume mixing ratio relative to water has been published by Krankowsky *et al.* (1986). An estimate of the CH₄ abundance can be obtained from the in situ ion composition measurements. The relative abundance of ion mass peaks in the range of 12 to 19 amu/e measured by the ion mass spectrometer (IMS) experiment has been used by Allen *et al.* (1987) to derive a CH₄ gas production rate of 2% relative to H₂O by modeling the photo- and ion-chemistry in the inner coma.

Ground-based infrared spectroscopy of the ν_3 band of CH₄ around 3.3 μm between March 15 and April 8, 1986, has yielded marginal estimates for the CH₄ production rate (Kawara *et al.* 1988). Methane production rates of 0.2% to 1.2% relative to water have been derived, using assumed rotational temperatures of 50 to 200 K. Observations of the (0-0) band of CH by optical spectroscopy (Wyckoff *et al.* 1988) have shown that, in addition to CH from photodissociation of CH₄, other parent molecules originating from the nucleus or CH produced in an extended source contribute to the observed CH, which prevents the CH₄ abundance from being derived. Therefore, the amount of methane in Halley is difficult to determine at present.

2.5. AMMONIA

Ammonia is a candidate parent molecule in comets and a possible progenitor of the observed NH and NH₂ radicals. Together with N₂, ammonia is considered to be an important source of the cosmochemically abundant element nitrogen in the volatiles of comets. The distribution of nitrogen between ammonia and molecular nitrogen is indicative of the environment where comets formed (see, e.g., Prinn and Fegley 1989). Ammonia was marginally detected by direct observation at radio wavelengths in Comet IRAS-Araki-Alcock (1983 VII) (Altenhoff *et al.* 1983). From the NMS experiment on Giotto, an upper limit of 10% for the volume mixing relative to H₂O has been reported (Krankowsky *et al.* 1986). Similar to the case for CH₄, improved estimates are obtained through modeling using the mass spectral data of the ion mass spectrometer on Giotto. Limits, determined from the IMS data inside the contact surface, on the NH₃ production rate relative to H₂O are 1% to 2% (Allen *et al.* 1987).

This derivation of the NH₃ abundance has been criticized by Marconi and Mendis (1988). Their main point is that the NH₃ abundance required to fit the Giotto IMS ion composition data can be drastically reduced by increasing the value used for the UV flux (which is responsible for ionizing H₂O) by a factor of ten over what Allen *et al.* (1987) assumed in their model. Such an increase in UV flux will also slightly decrease the photodestruction lifetime of H₂O. As derived from a first interpretation of the Giotto NMS measurements (Krankowsky *et al.* 1986), the shorter H₂O lifetime—4.4 × 10⁴ s, compared with the generally accepted value of 6.6×10^4 s for 0.9 AU from Huebner and Carpenter (1979)—was taken as circumstantial evidence for an elevated UV flux during the Giotto encounter. However, the lifetime of water derived from the NMS Giotto measurements has been recalculated recently (Krankowsky and Eberhardt 1990), to be 5.6×10^4 s, by taking into account the radial variation of the Giotto flyby geometry. The new value of the water photodestruction lifetime agrees within 10% with the theoretical value of 6.2×10^4 s at 0.9 AU on March 13, 1986 derived from a recent study of the photodissociation of water

(Crovisier 1989), where a dependence of the photodestruction rate on the solar UV flux as characterized by the 10.7-cm solar index has been included.

From three independent spectrophotometric observations of NH₂ in the visible, Wyckoff *et al.* (1989b) derived for Halley a low NH₃ abundance of 0.002 ± 0.001 relative to water. Wyckoff *et al.* also reported NH₃/H₂O ratios for P/Borrelly (~ 0.002), for Hartley-Good (~ 0.0002), and for Thiele (~ 0.001). Recently, Tegler and Wyckoff (1989) recalculated the NH₂ fluorescence efficiencies and revised the relative NH₃ abundance in Halley to 0.005 ± 0.002. Fabry-Perot observations of NH₂ yielded an NH₃ abundance of 0.001 (Magee-Sauer *et al.* 1988). Using the fluorescence efficiencies of Tegler and Wyckoff, the Fabry-Perot data suggest an NH₃ abundance of 0.004 relative to water (Magee-Sauer *et al.* 1989). However, as Magee-Sauer *et al.* (1989) have mentioned, taking into account $K''_{a} = 1$ levels, which have not been sampled by the (0,8,0) band in their observation, would increase the derived NH₃ abundance by a factor of two, according to Arpigny (1989). There is little doubt that NH₃ is present in Comet Halley. The concentration is still rather uncertain.

2.6. MOLECULAR NITROGEN

The significance of the abundance of N_2 in relation to the abundance of NH_3 in comets has been mentioned in the preceding section. Non-equilibrium models of the solar nebula (Lewis and Prinn 1980) and chemical models of dense interstellar clouds (Prasad and Huntress 1980) suggest N_2 as the major chemical form of nitrogen, whereas NH_3 is favored in solar nebula equilibrium models (Lewis 1972). Molecular nitrogen has not been detected in cometary spectra before P/Halley, although the N_2^+ ion was observed (Fowler 1910, Swings and Page 1948). In a preliminary evaluation of neutral mass spectral peaks at 28 amu/e from the Giotto NMS experiment, Eberhardt et al. (1986a, 1987a) derived an upper limit of 10% for the N_2 gas production rate relative to H_2O . An improved upper limit for the N₂ abundance comes from ion composition data. From the ion spectrum obtained by the Giotto IMS experiment, in the distance interval from 1.1×10^5 to 1.7×10^5 km, an abundance of less than 10% for N_2^+ relative to CO⁺ ions was deduced (Balsiger *et al.* 1986). With a CO abundance of 20% as measured by the ultraviolet spectrometer on the rocket flight of February 26, 1986 (Woods *et al.* 1986), an upper limit of 2% for the N_2 has been deduced by Allen et al. (1987). Ground-based emission spectra of molecular ions in the visible provided for a still lower estimate of the N_2 abundance in Comet Halley. Using the measured column density ratio N_{π}^{+}/CO^{+} and taking into account the measured $CO/H_{2}O$ ratio, Wyckoff and Theobald (1989) deduced an N₂ abundance of 4×10^{-4} relative to water.

2.7. FORMALDEHYDE

When formaldehyde was detected (Snyder *et al.* 1969) in the interstellar gas by radio astronomy, unsuccessful searches began for H₂CO in comets. At optical wavelengths, several features observed in the spectra from Comet IRAS-Araki-Alcock (1983 VII) were tentatively attributed to H₂CO (Cosmovici and Ortolani 1984). In Halley, the infrared instrument IKS on VEGA 1 detected spectral features in the 3.2 to 3.7 μ m range which were identified as being due to formaldehyde (Combes *et al.* 1986, 1988). The H₂CO production rate relative to H₂O was estimated to be $\leq 4\%$. Observations of the radio emission of H₂CO at 6-cm wavelength yielded a H₂CO production rate of about 1.5% relative to water (Snyder *et al.* 1989). There is an indication in the data that H₂CO, in addition to its release from the nucleus, also originated from an extended source in the coma. Reanalyzing the infrared spectrum of the IKS experiment on VEGA 1, Mumma and Reuter (1989) retrieved an H₂CO abundance of $(4.5 \pm 0.5)\%$ relative to water. This value agrees with a preliminary estimate obtained from an analysis of the radial profile of the ion with mass 30 amu/e (interpreted as H₂CO⁺) from the Giotto NMS experiment, resulting in an abundance of ~ 4.5%. The derived radial density profile of H₂CO seems to suggest a distributed source (Krankowsky *et al.* 1990). In infrared spectra obtained from the ground, Knacke *et al.* (1986) and Danks *et al.* (1987) found features that they attributed to the ν_1 and ν_5 bands of H₂CO, whereas such features were not seen in the spectra measured by Baas *et al.* (1986) and Wrickramasinghe and Allen (1986). Recently, formaldehyde has been observed in Comet Machholz (1988j) with a production rate a factor of ten larger than that in Halley (Snyder *et al.* 1990).

2.8. HYDROGEN CYANIDE AND METHYL CYANIDE

Spectral lines of the CN radical are among the most prominent signatures at optical wavelengths in comets. Hydrogen cyanide has been expected to be one of the possible parent molecules of CN. Its detection by radio astronomy was claimed for the first time in Comet Kohoutek (1973 XII) (Huebner et al. 1974). Then for many years searches for HCN in other comets by radio spectroscopy were not successful or gained marginal results (see Winnberg et al. 1987). Three groups (Schloerb et al. 1986, Despois et al. 1986, Winnberg et al. 1987) have detected HCN in Halley, with an abundance of about 0.1% that of water. In effect, HCN is one of the best monitored parent molecules in Halley, with the HCN production rate following closely the dust and gas activity. Comparison with the CN production suggests that HCN is an important parent for CN, although indications hint that it is not the only parent (Schloerb et al. 1987, Despois et al. 1986). The 28-amu/e peak in the ion spectra from the Giotto IMS experiment interpreted as being mainly due to protonated hydrogen cyanide H_2CN^+ has been utilized to derive HCN abundances by photochemical modeling (Ip et al. 1990). An upper limit of 2×10^{-4} relative to H₂O has been obtained. This value is about four times lower than the value from radio observations. Ip et al. suggested that these data could indicate a minor contribution of HCN to CN in the coma of Halley. Detection of methyl cyanide (CH₃CN) was claimed in Kohoutek (1973 XII) (Ulich and Conklin 1974) but never confirmed. Searches for methyl cyanide and cyano-acetylene (HC₃N), possible parents for the CN radical observed in Halley, resulted in upper limits only, which are on the order of 10^{-3} relative to water (Bockelée-Morvan *et al.* 1986).

2.9. SULFUR AND HYDROCARBONS

The radical CS has been seen in many cometary spectra since its detection in Comet West (1976 VI) (Smith *et al.* 1980). Observations of CS in Comet IRAS-Araki-Alcock (1983 VII) by the IUE satellite have demonstrated that the short-lived (scale length \approx 300 km) parent of CS (scale length \approx 100,000 km) is the molecule CS₂ (Jackson *et al.* 1986). The IUE satellite monitored the CS production rate in Halley (Feldman *et al.* 1987). A uniform decrease in the production rate toward larger heliocentric distances was found. At the time of the spacecraft encounters at 0.9 AU, the CS production rate was ~ 0.1% that of water, which is essentially the production rate of the parent CS₂ from the nucleus. Wallis and Krishna Swamy (1987) have claimed the detection of the sulfur dimer S₂—strongly disputed by Feldman (1990)—in IUE spectra from Halley with a mixing ratio of ~ 0.001. Also, Kim and A'Hearn (1990) have reported a possible indentification of S₂ in Halley. Thus, after A'Hearn *et al.* (1983) discovered the molecule S₂ in Comet IRAS-Araki-Alcock with an abundance of $\sim 0.05\%$ relative to OH, the possible detection of S₂ in Halley could indicate that S_2 is a common species in comets. CS_2 hardly photodissociates into S_2 ; therefore S_2 is likely a parent molecule (A'Hearn and Feldman 1984), generally not observed in spectra owing to its short photodestruction lifetime (≈ 350 s at 0.9 AU). The implications of the presence of S_2 in cometary nuclei are significant for the origin of cometary matter. As A'Hearn and Feldman have pointed out, it is unlikely that solid S_2 has formed by gas phase condensation, which produces primarily other sulfur compounds. Possibly surface reactions on grains and irradiation have played a role in the formation of S_2 . Furthermore, S_2 must have been preserved at temperatures below 30 K according to laboratory experiments by Greenberg et al. (1986). These facts are taken as arguments that interstellar matter is preserved in cometary nuclei. A tentative identification of the sulfur compound OCS in Halley has been claimed by Combes et al. (1988) on the basis of a marginal feature at 4.85 μ m in the spectra from the IKS infrared spectrometer on VEGA 1. For the abundance relative to water, an upper limit of < 0.01 has been given. A radio search at millimeter wavelengths resulted in an upper limit of < 0.06 for the relative abundance of OCS in Halley (Bockelée-Morvan et al. 1986, 1987).

A strong and broad emission feature at 3.2 to 3.5 μ m detected by the IKS experiment on VEGA 1 has been attributed to the C-H stretch in saturated and unsaturated hydrocarbons (Combes *et al.* 1986, 1988; Encrenaz *et al.* 1988). For the origin of this emission, hydrocarbons in the gas phase, polycyclic aromatic hydrocarbons (PAH), and organic mantles of small grains have been considered. If the observed emission is due to solids or PAH, then the carbon production rate has been estimated to be at the percent level or less relative to water (Combes *et al.* 1988). For gaseous fluorescence a similar production rate for carbon was quoted originally (Combes *et al.* 1986). However, in the meantime, the authors have corrected this value upward by almost a factor of 100 (Combes *et al.* 1988). Such a high carbon production rate is not supported by the in situ gas and ion measurements in the coma of Comet Halley. Likely the emission is predominately from solids, with only small contributions from gas fluorescence. A summary of the parent molecules definitely detected in Comet Halley is shown in Table 1.

3. Grains as a Source of Coma Gas

Gas jets were discovered in the visible molecular emission bands of the radicals CN and C₂ in narrow-band filtered images of Comet Halley by A'Hearn *et al.* (1986a, b). These jets, seemingly independent from those in the continuum reflected from the dust, extended to projected distances of more than 50,000 km and persisted for several weeks. It was estimated that as much as half the amount of CN observed in the coma by Millis and Schleicher (1986) could be produced within the jets. A'Hearn and co-workers linked the observed gas jets to submicron dust particles and argued that the radicals observed in the jets were produced by the photodissociation of the parent molecules on the grain surface or from the short-lived parents released from the grains into the gas phase. The mass loss rate of the dust required to support the observed amount of the radicals in jets was estimated to be only a small fraction of the total mass loss rate of the dust from the comet (McDonnell *et al.* 1987, Mazets *et al.* 1986). The CHON particles, which are composed primarily of C, H, O, and N and which were detected by the particle impact analyzer experiments (PIA and PUMA) on the Giotto and VEGA spacecraft (Kissel *et al.* 1986), were suggested as candidate grains. Analyzed dust particles in the micrometer to submicrometer range were

Species	Gas Production Rate Relative to H ₂ O (by number)	Instrumental Technique							
CΟ	0.07^{1}	Giotto NMS, gas spectra ²							
	$0.17 \cdots 0.20^3$	Rocket UV experiment ⁴							
	0.15 ³	Giotto NMS, gas spectra ²							
CO ₂	< 0.035	Giotto NMS, gas spectra ⁵							
	0.027	Vega IKS, IR spectra ⁶							
CH ₄	< 0.07	Giotto NMS, gas spectra ⁵							
	$\overline{<}$ 0.04	KAO, IR spectra ⁷							
	$\sim 0.02^{8}$	Giotto IMS, ion spectra ⁹							
	$0.002 \cdots 0.012$	IR spectra, ground based ¹⁰							
NH ₃	< 0.1	Giotto NMS, gas spectra ⁵							
-	$0.01 \cdots 0.02^8$	Giotto IMS, ion spectra ⁹							
	$0.004 \cdots 0.008$	Optical spectroscopy ^{11,12}							
N ₂	< 0.1	Giotto NMS, gas spectra ²							
-	< 0.02 ⁸	Giotto IMS, ion spectra ⁹							
	~ 0.0004	N ⁺ ₂ spectrophotometry ¹³							
H ₂ CO	0.045	Vega IKS, IR spectra ¹⁴							
-	0.015^{3}	VLA, radio wave ¹⁵							
HCN	~ 0.001	Millimeter spectra ^{16,17,18}							
	$\sim 0.0002^{8}$	Giotto IMS, ion spectra ¹⁹							
¹ Released from	n nucleus.	¹¹ Tegler and Wyckoff (1989).							
² Eberhardt et	al. (1986b, 1987b).	¹² Magee-Sauer et al. (1989).							
³ Released from	n nucleus and extended source.	¹³ Wyckoff and Theobald (1989).							
⁴ Woods et al.	(1986).	¹⁴ Mumma and Reuter (1989).							
⁵ Krankowsky	et al. (1986).	¹⁵ Snyder et al. (1989).							
⁶ Combes et a	. (1988).	¹⁶ Despois <i>et al.</i> (1986).							
⁷ Drapatz et a	<i>l.</i> (1986).	¹⁷ Schloerb et al. (1986).							
⁸ Inferred from	n models of coma.	¹⁸ Winnberg <i>et al.</i> (1987).							
⁹ Allen et al. (1987).	¹⁹ Ip et al. (1990).							
¹⁰ Kawara et d	ul. (1988).	- 、 /							

Table 1. Abundances of Probable Parent Molecules in the Coma of Comet Halley

found to be composed essentially of two components, a silicate-like and a refractory organic fraction, in proportions varying from particle to particle (Kissel *et al.* 1986, Clark *et al.* 1986, Jessberger and Kissel 1990). A quantitative study of photosputtering from CHON grains and of the spatial development of trace gas jets as possible mechanisms for the gas jet formation seemed to suggest the feasibility of both processes to produce gas jets (Combi 1987).

The idea of grains releasing gas into the coma has been strengthened by the discovery of an extended source of CO in the coma (Eberhardt *et al.* 1986a, 1987a). At a distance of 1,000 km, a CO gas production rate of 7% relative to H₂O was found, increasing to 15% at 20,000 km. The radial distribution of the extended CO source was calculated, and the maximum of CO gas production was found at ~ 9,000 km. Micron-sized dust particles of the CHON type were proposed as a source for the additional CO. It has been noted that Vaisberg *et al.* (1986) observed a distinct variation of the grain size distribution with distance from the nucleus. Small grains become overabundant, and the relative abundance of the medium-sized grains seems to decrease with increasing distance. The depletion starts near the nucleus ($R \leq 10,000$ km), with grains in the 10^{-14} to 10^{-13} g range. This has been interpreted as the result of fragmentation of larger grains. Aggregate particles seem to lose their interstitial material and eventually break up into very small grains (Eberhardt *et al.* 1986a, 1987a). This process proceeds faster with smaller grains, and the lifetime of the aggregates should increase with their size. Once the breakup begins, additional surfaces of volatile material will be exposed, leading to an enhancement of the gas production. The shape of the source function and the location of the maximum at ~ 9,000 km is in qualitative agreement with the results of Vaisberg *et al.* (1986).

Further support for such a mechanism comes from the analysis of the measured distribution of H_2CO in the coma (Snyder *et al.* 1989, Krankowsky *et al.* 1990). Both independent data sets seem to require the existence of an extended source of H_2CO in Halley's coma. The chemical nature of the material in the grains releasing CO, CN, and H_2CO or the short-lived parent of these species is, at present, uncertain. The proposed photolyzed outer mantle of interstellar grains (Greenberg 1982) could be the source of evaporating organic molecules, including CO or a parent of it. In interstellar clouds, CO is condensing directly on the grain surfaces as solid CO (Lacy *et al.* 1984), which requires temperatures as low as 17 K (Léger 1983). Laboratory irradiation with UV of CO, NH₃, and other ice mixtures has shown that molecules containing cyano (C \equiv N) groups are formed, and that these reaction products have much lower vapor pressure and are not lost even at temperatures as high as 150 K (Lacy *et al.* 1984). From IR absorption spectra, Lacy *et al.* conclude that formation of molecules, containing the cyano group, also occurs on the interstellar grains. The observation for the presence of relatively unaltered interstellar grains in the nucleus.

Interpreting spectra obtained by the positive ion cluster analyzer (PICCA) experiment on the Giotto spacecraft, Huebner (1987) and Mitchell *et al.* (1987) proposed the existence of polymerized formaldehyde $((H_2CO)_n)$, also known as polyoxymethylene (POM), in dust grains of Halley. They argued that impact or photodissociation will disintegrate POM into compounds that consist of alternating methylene (CH₂) and atomic oxygen units, which were presumably detected as ions by the PICCA instrument (Korth *et al.* 1986, Mitchell *et al.* 1986). Decomposition of POM was proposed as the mechanism for the extended source of CO and as the source for H₂CO. The affinity of POM to silicates and graphite suggests POM as the interstitial glue of the CHON dust particles, bonding submicron grains into larger particles which disintegrate when the glue has evaporated. As discussed above, this process could then explain the observed change in the dust particle size distribution around 10,000 km from the nucleus (Vaisberg *et al.* 1986). Other polymers containing atomic nitrogen or cyanide radicals could represent the source for the observed CN jets.

The mass ratio of POM to dust was estimated to be ~ 0.02 at 10,000 km, assuming a dust-to-gas mass ratio of 0.3 (Mitchell *et al.* 1987). The revised dust-to-gas mass ratio of ~ 1 of McDonnell *et al.* (1987)—with an extrapolation of the size distribution to onekilogram particles—lowers the POM to dust mass ratio to ~ 0.006. However, in order to account for the CO released from grains, a CO production rate relative to H₂O of ~ 8% is required (Eberhardt *et al.* 1987a). This number translates into a mass ratio of CO to dust of ~ 0.1 (dust/gas ≈ 1 assumed). The POM/dust ratio would have to be higher than 0.1, as only a fraction of the POM dissociates into CO. This is not only in disagreement with the estimate of the mass ratio of POM to dust, but also means that a very substantial fraction of the grains would have to evaporate, although the evaporated grains are not necessarily included in the dust production rate, as this rate is based partly on dust densities measured at distances > 8,000 km.

Therefore, despite the fact that POM offers an attractive qualitative explanation, a severe mass balance problem seems to exist. This argument is fairly insensitive to the assumed dust/gas mass ratio, which can only increase noticeably when the number of large dust particles in the size distribution, not measured by the dust detectors on VEGA and Giotto, is increased. However, such particles contribute little to the presumed gas release. A solution to the mass balance problem could lie at the opposite end of the dust size distribution. If very many particles with masses $\ll 10^{-17}$ g have been present in the coma, they would have escaped detection by the dust detectors. Indications for the existence of very many particles in the mass range of 10^{-17} to 10^{-20} g are in the quasi-noise events found in non-triggered spectra of the PUMA particle impact analyzer on the VEGA spacecraft (Sagdeev *et al.* 1989, Kissel 1989, private communication).

A puzzling recent discovery (Kim *et al.* 1989) is that the spectral features of NH in the (0-0) band observed in Halley almost totally fluoresce with negligible contributions from collisions. This indicates that NH exists mainly at distances from the nucleus larger than 30,000 km. The authors conclude that NH cannot be a direct dissociation product from NH₃. Other, more complex molecules and dust grains are proposed as possible sources.

Irrespective of the chemical nature of the CN-, CO-, H_2 CO-, and perhaps NHcontaining compounds in the dust grains, the problem remains of understanding how such a large amount of CO is released in a relatively short time after the dust left the nucleus. Therefore, as an alternative, anisotropic outgassing from the nucleus should be considered. Images from the VEGA and Giotto missions have shown that the emission of dust and (presumably) gas from the nuclear surface was highly anisotropic. Although it can be expected that an anisotropic localized outgassing will become isotropicized at larger distances, due to the lateral pressure gradients close to the nucleus, as well as due to the increasing gas temperature from chemical heating further out, numerical calculations by Kitamura (1986) and Kömle and Ip (1986) have shown recognizable anisotropies in the outflow to still persist at a distance of a few thousand kilometers.

However, no noticable structures seem to be present in the radial profile of H_2O along the Giotto trajectory which would be expected from bulk anisotropies. Another, perhaps more likely alternative is a locally enhanced CO/H₂O ratio in one or several of the active regions on the nucleus. Combi (1987) has proposed that such trace gas jets remain fairly well focused even at large cometocentric distances. Combi's alternative mechanism of a collimated flow of CHON grains being photosputtered is critically dependent on the grain sizes. Submicron-sized particles are quickly lost from the jet due to the solar radiation pressure. The localized injection of a trace gas, in Combi's model, does not disturb the expansion of the bulk and other trace gases. Also, temporal variations in the CO/H₂O ratio at the nucleus would result in radial changes of the coma gas composition without necessarily influencing the bulk gas properties. It is obvious that such variability in the composition of the volatiles has implications for the formation of Comet Halley as well as for its evolution during earlier passages through the inner solar system.

4. Isotopic Composition

Isotopic abundances from measurements in the volatile fraction of Comet Halley have been reported so far (Table 2) for the elements hydrogen, carbon, nitrogen, oxygen, and sulfur. The ${}^{34}S/{}^{32}S$ ratio as determined from ion mass spectra in the inner coma was 0.045 ± 0.010 (Krankowsky et al. 1986), in agreement with the terrestrial ratio of 0.044. The mass spectrometric measurement of the isotopic composition of light volatile elements in the coma is difficult, because the low-abundance isotopes are always heavier than the abundant isotopes and can thus be masked by hydrides. Only for the ion H_3O^+ is the interference with other masses, expected on the isotopic H_2DO^+ , limited to a few possible species, which can be corrected for with sufficient accuracy. From such spectra, Eberhardt et al. (1987b) deduced a value of 0.0023 ± 0.0006 for the ¹⁸O/¹⁶O ratio in the water of Halley. While this figure is identical with the terrestrial ratio, the errors in the preliminary evaluation are too large for a meaningful comparison with observed meteoritic ^{16}O abundance variations. For the hydrogen in Halley's water, Eberhardt et al. (1986b, 1987b) found an isotopic ratio of $0.6 \times 10^{-4} \le D/H \le 4.8 \times 10^{-4}$. The wide limits for the D/H isotope ratio come from the still uncertain abundance of NH_3 in Halley. The contribution of H_2 ¹⁸O⁺ to the measured signal on mass 20 amu/e depends on the relative abundance of the ions H_2O^+ and NH_4^+ in the coma. In comparison, Schleicher *et al.* (1986) obtained an upper limit of OD/OH $< 4 \times 10^{-4}$ for the Comet Halley from IUE observations. Emission lines of $^{13}C^{14}N$ resolved for the first time in ground-based spectra have been utilized to determine the ${}^{12}C/{}^{13}C$ isotope ratio of CN in Comet Halley (Wyckoff et al. 1989a). A ${}^{12}C/{}^{13}C$ ratio of 65 ± 9 has been found, which is 2.7σ lower than the bulk solar system value (89.9). For the nitrogen isotope ratio 14 N/ 15 N, a 2σ lower bound of 200 has been estimated, consistent with the bulk solar system ratio of 250. As discussed by Wyckoff et al., carbon isotope measurements in four comets have been obtained previously. In all cases, $C_2(1, 0)$ Swan band intensities of the isotopes were used. Within the large error bars, the isotope ratios retrieved are compatible with the solar system value.

Despite the relatively wide limits on the deuterium abundance found in Halley's water, some conclusions with respect to the origin of the cometary water are evident (Eberhardt et al. 1986b, 1987b). The deuterium abundance in Halley is comparable to the D/H ratio in the solar sytem objects poor in hydrogen, such as the Earth, the silicate fraction in meteorites, and Titan. But Halley's water is distinctly enriched in deuterium compared with the protosolar hydrogen and with hydrogen accreted in gaseous form from the solar nebula in bodies such as Jupiter and Saturn. In contrast, some molecules in interstellar molecular clouds (IMC) show a much larger enrichment due to deuteration by ion-molecule reactions. As noted by Geiss (1987, 1988), this does not preclude IMCs from having contributed to cometary water, because condensation could have interrupted deuteration of water.

Wyckoff *et al.* (1989a) have argued that the approximately 35% enrichment in ¹³C observed in CN relative to the bulk solar system value is not compatible with the formation of cometary nuclei in the vicinity of Uranus and Neptune. Measurements of the ${}^{12}C/{}^{13}C$ ratio in the outer solar system currently agree with the solar value (de Bergh 1988). However, CN in Halley is only a minor species, comprising less than 1% of the volatile carbon inventory of the comet (cf. Table 1). Meteorites were most probably formed within the orbit of Jupiter. Nevertheless, they contain minor phases showing isotopic anomalies including ¹³C enrichment due to incomplete mixing within the solar system of components from different nucleosynthesis sites. The highest observed ¹³C enrichment of about 3,000%

Element	Isotope Ratio	Chemical Form Measured					
D/H ¹² C/ ¹³ C ¹⁴ N/ ¹⁵ N ¹⁸ O/ ¹⁶ O ³⁴ S/ ³² S	$\begin{array}{c} 0.6 \times 10^{-4} - 4.8 \times 10^{-4} \\ 65 \pm 9 \\ \geq 200 \\ 0.0023 \pm 0.0006 \\ 0.045 \pm 0.010 \end{array}$	Water, protonated ions ¹ Cyanide radical ² Cyanide radical ² Water, protonated ions ¹ Sulfur ion ³					
¹ Eberhardt et e ² Wyckoff et al. ³ Krankowsky e	al. (1987b). (1989). t al. (1986).						

Table 2	. Isotope	Ratios	Measured	in	the	Volatile	Fraction	in	the	Coma o	f (Comet 1	Hall	ley
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corresponds to ${}^{12}C/{}^{13}C = 3.0$ (Wopenka *et al.* 1989). There is strong evidence that a sizeable fraction (50% to 90%) of the cometary CN stems from CHON particles (A'Hearn et al. 1986a,b; A'Hearn 1988). If only 2% by number of the CN originated from CHON particles with ${}^{12}C/{}^{13}C \approx 4$, corresponding to the equilibrium value for CNO burning in stars (Iben 1975), then the ${}^{12}C/{}^{13}C$ ratio of CN is lowered from 89.9 to 66³. Some information on the carbon isotope ratio in grains was gained from the particle impact analyzer (PUMA) on VEGA 1. The ${}^{12}C/{}^{13}C$ ratios observed range from 1 to 5,000 (Jessberger and Kissel 1990). But as was noted, the values smaller than 89.9 suffer from interference with the hydride 12 CH, which is not resolved from 13 C in the mass spectrometer. No simple instrumental explanation for the values greater than 89.9 exists. A carbon isotope ratio as high as ${}^{12}C/{}^{13}C = 159$ was discovered in a silicon carbide aggregate from the Murchison carbonaceous chondrite (Ming et al. 1989, Zinner et al. 1989). The authors infer much higher ratios in single grains that so far have not been analyzed. In graphite grains from the Murchison meteorite, anomalous carbon with ${}^{12}C/{}^{13}C \sim 4500$ has been found (Zinner and Wopenka 1990). Special nucleosynthesis sites and/or ion-molecule reactions were proposed to explain ${}^{12}C/{}^{13}C$ ratios higher than 89.9. As the isotopic composition of the bulk carbon in Halley (volatile and solid phase) is at present unknown, any conclusions based on the available carbon isotopic composition seem premature.

5. Elemental Abundance and Origin of Comets

In inferring the bulk chemical composition of Halley from the measurements performed in the coma, limitations must be kept in mind. What has been observed is the material from an outer layer that probably has been modified from its original state by previous passes through the inner solar system. This is particularly true for the volatiles. Prialnik and Bar-Nun (1987) have studied the thermal evolution of an initially very cold object in a Halley-like orbit. The phase transition from amorphous to crystalline ice is a major internal heat source. The transition occurs episodically, and the energy release during the amorphous to cubic transition at 137 K is sufficient to raise the temperature above the

³Based on an erroneous calculation Wyckoff *et al.* (1989) discussed and discarded the possibility that ¹³C-rich CHON particles could substantially lower the ¹²C/¹³C ratio in CN. The assumptions of Wyckoff *et al.* (that 10% of the CHON particles have ¹²C/¹³C \approx 4 and 50% of the CN stems from CHON particles) would give ¹²C/¹³C=48, considerably lower than the measured value of 65.

cubic to hexagonal transition temperature of 160 K. Each transformation episode converts a layer several tens to several hundreds of meters thick. A large fraction of gases such as CO, CH₄, and N₂ trapped at very low temperatures are released during the warming and phase transition. Prialnik and Bar-Nun (1987) argue that a fraction of the released gas may be trapped in gas pockets. In later apparitions, such gas pockets may be vented explosively. Thus, deeper layers of still amorphous, gas-rich ice can be exposed. The implications of this model for the present discussion are twofold. If most of the H₂O in the coma stems from the transformed surface shell of hexagonal ice, then the observed volatiles CO, N₂, CH₄ etc. are probably highly depleted compared with their initial abundance in the pristine ice. The depletion factors can be different for the different molecules. Conclusions about the origin of the cometary volatiles based on the observed abundance of CO, N₂, CH₄, NH₃, etc. in the coma must thus be viewed with caution.

The mass spectra from the NMS experiment on Giotto have shown that 80% of the volatiles making up the ice are water. The remaining 20% are accounted for by the parent molecules listed in Table 1, if the uncertainties in their relative abundances are taken into account. The molecular composition of the dust is more uncertain, however. The particle impact analyzers essentially determined the elemental composition, although from the relative abundances of key elements, by comparison with meteorites and interplanetary dust particles (IDP), extrapolations towards the mineralogical and structural aspects of the dust in Halley have been made (for a review, see Jessberger and Kissel 1990). The existence of a silicate-like and a refractory organic fraction has been discovered. The infrared observations attested to the presence of hydrocarbons in the dust, but left open the molecular forms and the abundances. That dust is also a carrier of volatile species has evolved from the detection of the CN and C_2 jets and from the detection of extended sources of CO and possibly H_2CO .

Various attempts—sometimes very detailed and speculative—to deduce the elemental inventory of comets (dust and gas) have been made recently (Geiss 1987, 1988; Delsemme 1988; Encrenaz *et al.* 1988; Jessberger and Kissel 1990). A factor of uncertainty common to these elemental balance sheets is the dust/gas mass ratio. The abundances of rockforming elements as measured in the dust are within a factor of two relative to the solar system abundances (Jessberger and Kissel 1990). Hydrogen is strongly depleted relative to the solar system. The puzzle of the missing carbon in comets seems to be solved. The refractory organics probably account for the deficit. While oxygen is represented in nearly solar proportion in the inventory, the authors, with the exception of Delsemme, agree on a nitrogen depletion in Halley.

A clue to the origin of comets lies in the distribution of carbon and nitrogen among their volatile molecular forms CO and CH₄, and N₂ and NH₃. In interstellar clouds, ionmolecule reactions at low temperatures favor the formation of CO and N₂ (Prasad and Huntress 1980, Mitchell *et al.* 1981). Condensation in a gas of solar composition at low pressure (10^{-4} atm) under equilibrium conditions (e.g., Lewis 1972; Anders 1986) does not resemble the abundances of the volatiles and the molecular forms of carbon and nitrogen in the coma of Halley, as noted by Geiss (1988). Homogeneous gas-phase chemistry in the solar nebula under equilibrium conditions and low pressure (e.g., Prinn and Fegley 1989) leads to a conversion of CO into CH₄ (and CO₂) and of N₂ into NH₃. But kinetic effects (Lewis and Prinn 1980) inhibit the conversion as the solar nebula cools and the molecular reaction time constants become comparable to the mixing times in the nebula, leaving CO and N₂ as the dominant molecular forms of carbon and nitrogen (CO/CH₄ \gg 1 and N₂/NH₃ \gg 1). In the postulated higher pressure environments in subnebulae around the giant protoplanets, however, kinetic quenching of the CO \Rightarrow CH₄, N₂ \Rightarrow NH₃, and CO \Rightarrow CO₂ conversions is shifted to lower temperatures (Fegley and Prinn 1989) favoring the reduced forms of carbon and nitrogen (CO/CH₄ \ll 1 and N₂/NH₃ \ll 1). In Halley, CO/CH₄ and N₂/NH₃ are intermediate between the molecular ratios expected for the interstellar material and the solar nebula, which points to some processing of Halley's volatiles in the subnebulae of the giant protoplanets, according to Fegley and Prinn (1989). The apparent nitrogen deficit in Halley, compared with the solar abundance, suggests that a sizeable fraction did not condense or was lost later. The reason could be that nitrogen was mainly present in the form of N₂ when Halley formed. In contrast, as Geiss (1988) noted, the similarly volatile CO bonds weakly to metals and other substances, which could have been responsible for its better retention. In addition, to a large part CO resides in Halley's dust in the form of H₂CO, POM, or other refractory organics, as implied by the observation of the distributed CO source (Eberhardt *et al.* 1987a).

The isotopic data observed in Halley (section 4) neither rule out nor confirm an interstellar origin of Halley's water. The ¹³C enrichment discovered in CN indicates the presence of unaltered interstellar material likely preserved in the dust grains. If the isotope ratios ${}^{12}C/{}^{13}C \gg 89.9$ found in a few dust particles (Jessberger and Kissel 1990) are real, then carbon from different nucleosynthesis sites has been incorporated into Halley.

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