MOLECULAR ABUNDANCES IN COMETS

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Abstract. The molecular composition of cometary volatiles is a basic information on the nature of comets and a clue to their formation mechanisms. It is only recently that direct identifications of cometary volatiles were obtained through in situ exploration as well as from remote sensing at UV, IR and radio wavelengths. An inventory of known cometary volatiles is presented, with a critical review of the evaluations of their abundances.

1. Introduction

The molecular composition of cometary volatiles is a basic information on the nature of comets and an important clue to their formation mechanisms. For a long time, the only information on this composition was coming from the signatures of dissociation products in the visible spectrum. It is only recently that we obtained direct identifications of cometary volatiles by in situ exploration as well as by remote sensing at UV, IR and radio wavelengths. An inventory of known cometary volatiles will be presented, with a critical review of the evaluation of their abundances. Previous reviews on this topic were made recently by Krankowsky (1991) and Mumma *et al.* (1993b) and as part of the comprehensive review of Festou *et al.* (1993). The implications for the nucleus composition, structure, and evolution, as well as the possible link to the interstellar medium, are only briefly mentioned here, as they are treated elsewhere in this volume (Rickman 1993; Greenberg & Shalabiea 1993). Cometary isotopic ratios, which also contain a strong cosmogonic message, will not be discussed due to lack of space. A recent review is given by Krankowsky (1991) : in summary, the [D]/[H] ratio is enriched; the other known ratios (such as $[^{18}O]/[^{16}O]$ and $[^{13}C]/[^{12}C]$) are close to terrestrial.

2. The methods and their reliability

There are now several ways to measure cometary volatile abundances, each of them having its own advantages and drawbacks. A synopsis is given in Table I.

A decade ago, if one excepts the CO molecule detected in the UV, no cometary parent molecule was directly observed. One had to *guess* the nature of the parent volatiles from the presence of the radicals, atoms and ions observed in the visible spectrum of comets. With the opening of new spectral domains, several parent molecules are now reliably identified. The existence of others, however, has still to be inferred from educated guesses.

Most of the electronic and fundamental vibrational bands of interest for cometary parent molecules are emitted through resonant fluorescence excited by the Sun (Yamamoto 1982; Crovisier & Encrenaz 1983; Weaver & Mumma 1984). Their excitation rates (the so-called *g-factors*) depend only upon the solar radiation and the molecular constants. It is thus straightforward to derive column densities from

TABLE I
Methods for the evaluation of molecular abundances in comets.

Method	Example	Problems and reliability
Rotational lines (individual)	HCN (radio)	modelling of rotational distribution required
Rovibrational lines (individual)	CH_4 (IR)	idem
Vibrational bands (total)	CH_3OH (IR)	blending and identification
Electronic bands	CO (UV)	generally not available for parent molecules
Mass spectroscopy	N_2	mass ambiguity, chemical modelling required
Observation of dissociation products	NH_3 (from NH)	chemical modelling and space distribution required

band intensities, at least for optically thin lines. Problems, however, may arise for the identification of these bands from low-resolution spectra.

Individual rotational lines and rovibrational lines observed at high resolution lead to unambiguous identifications. It is more tricky to retrieve production rates, however, because one then needs to know the rotational population distribution. In some cases when it is possible to observe simultaneously several lines and to measure this distribution (e.g. CH_3OH at radio wavelengths), reliable results may be obtained. In other cases, one has to rely on models. Molecules are expected to evolve to *fluorescence equilibrium*, governed by the balance between spontaneous decay and fluorescence excitation of the vibrational or electronic bands (Crovisier 1984, 1987; Weaver & Mumma 1984). However, radio and IR telescopes generally sample the inner coma where this equilibrium is not yet reached. More sophisticated models must be used, in which the coma kinetic temperature and collision rates are important (but unfortunately ill-known) parameters.

Unique information was obtained, during the *Giotto* fly-by of P/Halley, by the Neutral Mass Spectrometer (*NMS*; Krankowsky *et al.* 1986), the Ion Mass Spectrometer (*IMS*; Balsiger *et al.* 1986) and the *PICCA* instrument (Mitchell *et al.* 1992). These data are not easy to interpret. The main reason is that these instruments measured mass per charge (m/q) ratios with a low resolution and could not distinguish between species with the same atomic mass (i.e. CO, N_2 and C_2H_4) without further information. In several cases, a useful guideline for the interpretation of mass spectra was provided by complementary information from remote-sensing spectroscopy. Retrieving the abundance of parent molecules from ion densities requires a careful chemical modelling, which is hampered by our incomplete knowledge of ion-molecule reaction rates and of the actual coma chemical composition. Some of the preliminary interpretations were erroneous and the detailed analyses are still going on.

These observations lead to determinations of column densities (of densities for mass spectroscopy), which in turn have to be converted into production rates to get finally abundances. This requires the knowledge of the spatial distribution, modelling of which involves the molecular lifetimes and expansion velocities. In the best cases, information on the scale lengths can be obtained from brightness profiles, on the expansion velocities, from the radio line shapes. In the worst cases, one does not even know whether the species under study is coming from the nucleus, or from a distributed source, which results in a large uncertainty upon the production rate (see the discussions on CO and H_2CO in the next Section). The derivation of relative abundances is difficult because observations are rarely simultaneous and cometary activity may be variable. In addition to these problems, most observations of cometary parent molecules are made with state-of-the-art techniques which may be subject to calibration difficulties.

3. Molecular identifications and abundances

Our present knowledge of the cometary volatile abundances is summarized in Table II. In the following, all abundances will be given relative to water.

3. 1. WATER

Water is well studied through its dissociation products : through the OH radical which can be observed in the near UV from the *IUE* satellite or even from the ground, and in the radio at 18 cm wavelength; through space observations of the Lyman α line of hydrogen; through observation of the prompt emission of the forbidden lines of oxygen. The problems in deriving water production rates from these indirect observations were discussed in a special session of a preceding *Asteroids Comets Meteors* conference (Lagerqvist *et al.* 1990). Up to now, water was directly observed in only two comets, through its IR vibrational bands : in P/Halley from the *KAO* (Mumma *et al.* 1986) and from the *VEGA IKS* and *TKS* IR spectrometers (Combes *et al.* 1988; Krasnopolsky *et al.* 1986), in comet Wilson 1987 VII from the KAO (Larson *et al.* 1988). It is expected that future space observations in the submillimetre and far-infrared ranges (e.g. with *ISO*, *SWAS* and *FIRST*) will easily detect the fundamental rotational lines of water. Water was, of course, observed by the *Giotto NMS* (Krankowsky *et al.* 1986). It was found to constitute 80 % (by number) of the whole cometary gas, thus confirming its status of dominant cometary volatile.

3. 2. CARBON MONOXIDE AND CARBON DIOXIDE

Carbon monoxide was first detected in comet West 1976 VI by rocket UV observations (Feldman & Brune 1976), then observed in several comets with the *IUE*, sounding rockets or the Space Shuttle (Feldman 1991; Feldman *et al.* 1991). Its fundamental vibrational band at 4.7 μm was marginally detected by the *VEGA-1* infrared spectrometer in P/Halley (Combes *et al.* 1988) and one of its rovibrational lines was tentatively detected in Austin 1990 V (DiSanti *et al.* 1992b). CO was also studied by the *NMS* in P/Halley (Eberhardt *et al.* 1987). Highly different CO abundances were observed : from 2 % in Bradfield 1979 X to 15–20 % in comets West 1976 VI and P/Halley. Analyses of UV observations made with different fields of view as well as the CO density evolution observed in situ by *NMS* show that the

TABLE II
A review of the volatile composition of comets.

species	abundance	comets	methods	references
H_2O	100.	many	photodiss. prod.	
		P/H, Wilson	IR	1, 2, 3, 4, 5
		P/H	NMS	6
CO	2.–20.	several	UV	7, 8, 9
		P/H, Austin	IR	2, 10
		P/H	NMS	11
CO_2	2.7	P/H	IR	2
	3.5	P/H	NMS	6
	6.	P/Hartley 2	CO prompt em.	12
H_2CO	0.03–1.5	several	radio	13, 14, 15, 16
	$< 1.$	several	IR	17
	4.	P/H	IR	2
	> 3.8	P/H	NMS, IMS	18, 19, 20
CH_3OH	1.–7.	Austin, Levy, P/S-T	radio	16, 21, 22, 23, 24
		several	IR	25, 26
		P/H	NMS, IMS	19, 27
C_2H_5OH	< 0.5	Levy	radio	28
HCOOH	< 0.2	Austin, Levy	radio	28
CH_4	< 0.5–2.	P/H, Wilson, Levy	IR	5, 29, 30, 31
	2.	P/H	IMS	32
NH_3	0.1–0.3	several	NH, NH_2 (vis.)	33
	0.4–1.0	P/H	NH (UV)	34
	0.5–2.	P/H	IMS, NMS	32, 35
HCN	0.05–0.2	several	radio	15, 23, 24, 36, 37
		P/H	NMS, IMS	35
HC_3N	< 0.02	P/H, Levy	radio	28, 36
N_2	0.2–0.02	P/H, Bradfield	N_2^+ (vis.)	38, 39
	< 1.5	P/H	NMS, IMS	11, 19
H_2S	0.1–0.3	Austin, Levy, P/S-T	radio	21, 22, 24, 40
		P/H	IMS, NMS	19, 41
CS_2	0.1	several	CS (UV)	9
S_2	0.05	IRAS-A-A	UV	42, 43
OCS	< 0.3	Levy	radio	40
	< 0.5	P/H, Austin	IR	2, 44
H_2CS	< 0.1	Levy	radio	28
SO_2	< 0.001	P/H, Bradfied	UV	45
He	$< 3.$	Austin	UV	46
Ar	$< 17.$	Austin, Levy	UV	8, 46

origin of CO is twofold : one part is coming from the nucleus region, another one from a distributed source with a scale length of the order of 10^4 km.

Carbon dioxide, which cannot be observed from the ground due to the absence of allowed rotational lines and to strong telluric absorption of its IR bands, was strongly suspected from the existence of ${CO_2}^+$. CO_2 was observed only in P/Halley

Notes to Table II :

Comets : IRAS-Araki-Alcock 1983 VII, P/Halley 1986 III, Wilson 1987 VII, Bradfield 1987 XXIX, Austin 1990 V, Levy 1990 XX, P/Hartley 2 1991 XV, P/Swift-Tuttle 1992t.
References : **1** Mumma et al. 1986; **2** Combes et al. 1988; **3** Krasnopolsky et al. 1986; **4** Weaver et al. 1986; **5** Larson et al. 1988; **6** Krankowsky et al. 1986; **7** Feldman & Brune 1976; **8** Feldman et al. 1991; **9** Feldman 1991 and references therein; **10** DiSanti et al. 1992b; **11** Eberhardt et al. 1987; **12** Weaver et al. 1994; **13** Snyder et al. 1989; **14** Colom et al. 1992; **15** Schloerb & Ge 1992; **16** Bockelée-Morvan et al. 1993c; **17** Reuter et al. 1992; **18** Krankowsky 1991; **19** Geiss et al. 1991; **20** Meier et al. 1993; **21** Bockelée-Morvan et al. 1990; **22** Bockelée-Morvan et al. 1991; **23** Bockelée-Morvan et al. 1993b; **24** Despois et al. 1993; **25** Hoban et al. 1991; **26** Hoban et al. 1993; **27** Eberhardt et al. 1991; **28** Crovisier et al. 1993; **29** Drapatz et al. 1986; **30** Kawara et al. 1988; **31** Brooke et al. 1991; **32** Allen et al. 1987; **33** Wyckoff et al. 1991b; **34** Feldman et al. 1993; **35** Ip et al. 1990; **36** Crovisier & Schloerb 1991 and references therein; **37** Wootten et al. 1993; **38** Wickoff et al. 1991a; **39** Lutz et al. 1993; **40** Crovisier et al. 1991; **41** Marconi et al. 1990; **42** A'Hearn et al. 1983; **43** Budzien & Feldman 1992; **44** DiSanti et al. 1992a; **45** Kim & A'Hearn 1991; **46** Stern et al. 1992.

through its strong ν_3 band at 4.3 μm by *VEGA-1* (Combes *et al.* 1988) and through mass spectroscopy by *NMS* (Krankowsky *et al.* 1986). In the UV spectrum of comet P/Hartley 2 1991 XV observed with the *HST*, Weaver *et al.* (1994) identified bands of the CO Cameron system around 200 nm that they attributed to CO prompt emission following photodissociation of CO_2. They estimated a carbon dioxide abundance of 6 % in this comet, and a CO abundance < 2 %.

3. 3. FORMALDEHYDE

The detection of formaldehyde was first claimed in P/Halley through its IR bands at 3.56 μm (Combes *et al.* 1988; subsequently reanalyzed by Mumma & Reuter 1989) and at 6 cm radio wavelength (Snyder *et al.* 1989). The derived abundance was 4 %. Formaldehyde was then detected at 226 and 352 GHz in P/Brorsen-Metcalf, Austin 1990 V, Levy 1990 XX and P/Swift-Tuttle (Colom *et al.* 1992; Schloerb & Ge 1992; Bockelée-Morvan *et al.* 1993c), with much smaller abundances (0.03 to 1 %) assuming direct release from the nucleus. Reuter *et al.* (1992) failed to detect H_2CO from the ground in the IR of several comets, with limits typically smaller than one percent (for direct release from the nucleus). On the basis of these results, Bockelée-Morvan & Crovisier (1992) questioned the detections and abundance determinations of formaldehyde in P/Halley.

H_2CO was also observed in situ in P/Halley by the *NMS* and *IMS* instruments (Krankowsky 1991; Geiss *et al.* 1991; Meier *et al.* 1993). Both observations show that formaldehyde is released from a distributed source. The abundance retrieved by *NMS* is 3.8 % at least (with 3 % produced inside the r $<$ 4700 km region) and the distribution is consistent with *no* formaldehyde directly released from the nucleus. The determinations given above from radio and IR observations, based upon a nucleus release, are thus underestimates of the true H_2CO abundances. A reliable determination will await the knowledge of the space distribution and of the origin of H_2CO. The difference, however, between the high abundance of

H_2CO in P/Halley and those in the other comets cannot be reconciled by the space distribution. H_2CO may not be a primary cometary volatile and therefore may be irrelevant for cosmogonic considerations. Meier *et al.* (1993) suggested that formaldehyde polymers on grains would sublimate as H_2CO monomers. In turn, photodissociation of H_2CO could contribute to part of the distributed source required for CO.

3. 4. METHANOL

Methanol was unambiguously identified in comets Austin 1990 V, Levy 1990 X and P/Swift-Tuttle through its rotational lines at millimetre and submillimetre wavelengths (Bockelée-Morvan *et al.* 1990, 1991, 1993b). Several rotational lines can be observed simultaneously with the same spectrometer : this allows one to derive the rotational distribution and to estimate the methanol abundance almost independently of any assumption on the excitation. The methanol ν_3 band was tentatively identified to a 3.52 μm emission feature in comet Austin by Hoban *et al.* (1991). This band was then retrieved in archive IR spectra and in spectra of subsequent comets (Bockelée-Morvan *et al.* 1993a; Hoban *et al.* 1993; Davies *et al.* 1993). Methanol is also detected from its protonated form $CH_3OH_2^+$ in the *Giotto* mass spectra (Geiss *et al.* 1991; Eberhardt *et al.* 1991). Methanol abundances from both radio and IR observations are reliable and in good agreement. They range from 1 to 7 %, depending upon the comet, and the variation from comet to comet seems to be real. This makes methanol one of the most abundant parent molecules. It must be noted that the photodissociation of CH_3OH cannot explain the distributed source of formaldehyde, because the dissociation product is presumably CH_3O rather than H_2CO, and because the lifetime of methanol is too large (10^5 s) to be reconciled with the H_2CO observations.

3. 5. METHANE

Methane was searched for through individual lines of its ν_3 band at 3.3 μm with the *KAO* or from the ground (Drapatz *et al.* 1986; Kawara *et al.* 1988; Larson *et al.* 1988; Brooke *et al.* 1991). The retrieved upper limits depend upon the assumptions made on the rotational temperature. They range from 0.2 to 2 % in comets P/Halley and Levy 1990 XX. Larson *et al.* (1988) reported a possible detection that exceeds the 3–σ level (corresponding to an abundance 1.4–4.5 %) in comet Wilson 1987 VII, but too marginal to constitute a definite detection of cometary methane. Allen *et al.* (1987) attributed a peak in the *IMS* mass spectra to $CH_3{}^+$ coming from methane and deduced an abundance of 2 % of CH_4 for P/Halley. This value is subject to caution since they neglected the contribution of methanol and other methyl compounds in their chemical model. Haider *et al.* (1993), from another model, revised the abundance to 0.5 %.

3. 6. NITROGEN SPECIES

Ammonia was never directly observed if one excepts an unconfirmed detection at centimetre wavelengths (Altenhoff *et al.* 1984). From the bands of NH and NH_2 in the visible, Wyckoff *et al.* (1991b) estimated abundances of 0.1–0.3 %

in several comets, including P/Halley. Using a different approach, Feldman *et al.* (1993) estimated a higher abundance (0.4–1.0 %) in P/Halley and seven other comets from the NH bands observed by the *IUE* and *ASTRON* satellites. Still higher abundances (1–2 %) were retrieved by Allen *et al.* (1987) through chemical modelling of the *Giotto IMS* data (since NH_4^+ is blended with water-group ions, the determination is quite indirect). However, Ip *et al.* (1990) retrieved only 0.5 % from the same data, and Geiss *et al.* (1991) argued that these abundances might be overestimated, due to flaws in the chemical modelling (see also Haider *et al.* 1993). It may be anticipated that direct detection of the fundamental submillimetre rotational lines of NH_3 will be possible by observing from space and will permit a more reliable assessment of its abundance.

First claimed to be detected in comet Kohoutek 1973 XII (Huebner *et al.* 1974), hydrogen cyanide was definitely identified at millimetre wavelengths in P/Halley (Crovisier & Schloerb 1991 and references therein) and several subsequent comets (Bockelée-Morvan *et al.* 1990, 1993c; Schloerb & Ge 1992). Several rotational transitions (J 1–0, 3–2 and 4–3) have now been observed. Although the observations are not always simultaneous, or are made with different beams or telescopes, it may be expected that a careful modelling of these data will constrain the excitation conditions of the molecule and lead to a reliable determination of its abundance. Abundances presently observed range from 0.05 to 0.2 %. Ip *et al.* (1990) derived an abundance upper limit of 0.02 % for HCN in P/Halley from the *IMS* data; this might be due to flaws in their chemical model. Whether or not the observed HCN abundance can explain all the CN radicals observed in the visible is still a debated question. From first evaluations this is not the case (Crovisier & Schloerb 1991). Other potential CN-parents (HC_3N, CH_3CN...) were unsuccessfully searched for at radio wavelengths (Bockelée-Morvan *et al.* 1987; Crovisier & Schloerb 1991; Crovisier *et al.* 1993), and an early radio detection of CH_3CN (Ulich & Conklin 1974) could never be confirmed. The possibility that CN could be released from organic grains has been invoked (see the discussion in Greenberg & Shalabiea 1993).

Molecular nitrogen N_2 has no favourable spectral transition to be searched for. Wyckoff *et al.* (1991a) estimated its abundance to 0.02 % in P/Halley from the spectral signal of the ${N_2}^+$ ion in the visible. Observations of comet Bradfield 1987 XXIX by Lutz *et al.* (1993) suggest an abundance an order of magnitude higher. No stringent upper limit could be obtained from the *Giotto* mass spectrometers due to mass ambiguity with CO (Balsiger *et al.* 1986; Eberhardt *et al.* 1987). The $[N_2]/[NH_3]$ ratio appears to be much smaller in comets than in star-forming regions (where N_2 is traced by ${N_2}^+$; Womack *et al.* 1992). This may be interpreted either by a complete conversion of N_2 into NH_3 in the presolar nebula, or by the incapacity of comet nuclei to retain the highly volatile N_2.

Like molecular nitrogen, other very volatile species such as molecular hydrogen [which was searched for in the IR by Smyth *et al.* (1989) and in the UV as reported by Feldman (1991)] and noble gases [searched for in the UV by Feldman *et al.* (1991) and Stern *et al.* (1992)] are depleted in comets.

3. 7. SULPHUR SPECIES

H_2S was detected at millimetre wavelengths in comets Austin 1990 V, Levy 1990

XX (Crovisier *et al.* 1991) and P/Swift-Tuttle (Despois *et al.* 1993). Assuming a rotational excitation temperature similar to that of CH_3OH leads to abundances 0.1 to 0.3 %, depending on the comet. H_2S is also suspected in P/Halley from a peak at 35 amu/e in the data of the *PICCA* and *IMS* instruments on *Giotto* (Marconi *et al.* 1990; Geiss *et al.* 1991). S_2 was identified in *IUE* UV spectra uniquely in comet IRAS-Araki-Alcock 1983 VII during an outburst (A'Hearn *et al.* 1983; Budzien & Feldman 1992). The abundance is 5×10^{-4}, but this species may come from processing of the nucleus surface rather than being primordial.

No other sulphur parent molecule has yet been identified, but it seems very likely that the CS radical, currently observed in *IUE* UV spectra, comes from the CS_2 molecule, with abundances of the order of 0.1 % (Feldman 1991). Significant upper limits were obtained for OCS, H_2CS, SO and SO_2 (Table II). Whether or not sulphur is depleted with respect to oxygen in cometary volatiles is still a debated question (Azoulay & Festou 1986; Crovisier *et al.* 1991; Mumma *et al.* 1993b). The abundance of the sulphur molecules may not be enough to explain the production rate of the S atoms observed in the UV and other sulphur compounds may exist in comets.

3. 8. AROMATICS

The presence of aromatics is suggested by their characteristic emission feature at 3.28 μm. This feature was especially conspicuous in the spectrum of comet Levy 1990 XX (Davies *et al.* 1991), but it is apparently variable from comet to comet (Bockelée-Morvan *et al.* 1993a). Its intensity may be explained by a relatively small abundance of aromatics, if it is emitted after electronic excitation in the UV followed by internal conversion to vibrational excitation, as is invoked for the emission of similar bands of PAHs in the interstellar medium, rather than by resonant fluorescence : Bockelée-Morvan *et al.* (1993a) retrieved abundances of the order of 10^{-5}. Moreels *et al.* (1993) identified phenanthrene, a three-cycle PAH, in the visible spectrum of P/Halley recorded by the *VEGA-TKS* instrument, for which they estimated a production rate of 0.15% relative to water. Infrared and visible aromatics production rates are therefore controversial.

4. Pending problems

4. 1. WHAT SPECIES REMAIN TO BE IDENTIFIED ?

Water represents only 80 % (by number) of the cometary gases coming from the nucleus. It is suggested from Table II that the observed species cannot fully account for the remaining 20 %, and that a significant fraction (possibly 5 to 10 %) consists of species still to be identified. There are evidences of mass spectroscopy peaks at medium and high m/q which are still to be identified.

The problem of the origin of the cometary radicals observed in the visible is not fully solved : C_2 and C_3 are orphan radicals for which parents are still to be found. The CN radical production rate is not completely explained by HCN. It must be also noted that numerous features in visible cometary spectra are still unidentified (Arpigny *et al.* 1993); most of them are presumably due to radicals and ions.

The origin of the 3.4 μm cometary emission has been a puzzle since its discovery (Encrenaz *et al.* . 1988; Encrenaz & Knacke 1991). Thermal emission of small grains with an organic mantle and/or fluorescence of large molecules excited by solar UV were invoked because they could be caused by a small amount of matter and we were not expecting a large fraction of cometary volatiles besides water. This situation has to be reconsidered since we know now that methanol is present in comets with a large abundance (more than 5 % in some objects). However, methanol alone can only explain about half of the 3.4 μm emission (Reuter 1992; Bockelée-Morvan *et al.* 1993a). The remaining emission, which peaks at 3.43 μm, could be explained by a few percent of *CHO* species, but no definite identification could yet be proposed. Some species like HCOOH or C_2H_5OH are ruled out by radio observations (Table II).

A related problem may be that of the 2.8 μm excess emission (Tokunaga *et al.* 1987). In addition to hot vibrational bands of water (as was formerly proposed by Bockelée-Morvan & Crovisier 1989), the OH stretching-mode of other *CHO* species may be contributing to this emission.

4. 2. OUTGASSING FROM GRAINS

One of the new ideas on cometary processes that emerged from the exploration of Halley's comet was that a significant fraction of cometary volatiles could directly come from dust grains. Evidences for such a process are coming from the discovery of an important fraction of dust particles composed of *CHON* elements, thus presumably of organic molecules, and the fact already mentioned above that species such as CO and H_2CO are coming, at least partly, from a distributed source. From the space distribution of CN and possibly of other radicals, it was also suspected that part of these radicals may not come from gas-phase parent molecules, although the relation of such a source to dust is not yet clear.

The release of molecules and radicals from grains is an ill-known mechanism. That water and other volatiles could come from icy grains is not so new an idea. Such grains, however, would have a very short lifetime (at least at r = 1 AU). Their expected scale length is such that molecules outgassing from such grains should be indistinguishable from molecules directly coming from the nucleus by ground-based observations. It thus seems unreasonable to explain, for instance, the CO distribution (which needs a source with a scale length of the order of 10^4 km) by CO-coated grains. Photosputtering is presumably inefficient to explain large production rates. A more realistic process could be the progressive sublimation of *semi refractories* such as some polymers (like polyoxymethylene) or small PAHs, or the pyrolysis of organic refractories (Greenberg & Shalabiea 1993).

4. 3. VARIATIONS FROM COMET TO COMET

It is very important to study whether all comets show similar molecular abundances. Variations could betray different origins or different histories. The data for parent molecules are still very sparse, but a high comet-to-comet variability is suggested for methanol or formaldehyde. Schleicher (1993) reports a systematic study of the relative production rates of radicals : a rather homogeneous [CN]/[OH] ratio is found, but the existence of two populations is suspected from the [C_2]/[OH] ratio. Extreme cases are comet Yanaka 1988 XXIV, dramatically depleted in C_2 and CN, but with conspicuous NH_2 bands (Fink 1992; see Greenberg *et al.* 1993 for a discussion) and P/Wolf-Harrington, depleted in C_2 and C_3 compared to CN and OH (Schleicher *et al.* 1993).

4.4. VARIATION WITH HELIOCENTRIC DISTANCE; ACTIVITY OF DISTANT COMETS

The activity of comets at large heliocentric distances has been known for a long time (see Table 1 in Meech 1991). This topic dramatically came back with the observation of an outburst of P/Halley at 14 AU from the Sun (West *et al.* 1991) and was recently the subject of a workshop (Huebner *et al.* 1993). Since water can not likely sublimate at more than 4–5 AU from the Sun, more volatile species must be responsible for outgassing at these large distances. Very little could be learned from the cometary spectra, because of the very low fluorescence rates at large geocentric distances. The P/Halley spectrum during its outburst was featureless. The CN band was detected in the spectrum of Chiron at r = 10 AU (Bus *et al.* 1991). CN and CO^+ were detected in P/Schwassmann-Wachmann 1 at r = 6 AU (Cochran & Cochran 1991). These detections are puzzling, since HCN, the plausible parent for CN, is not expected to sublimate at Chiron's distance, and the ionization rate of CO at the heliocentric distance of P/Schwassmann-Wachmann 1 should be excessively small. Carbon monoxide is the most plausible volatile to explain cometary activity at large distance, but its direct identification will not be easy.

All the present determinations of cometary volatile abundances rely on the gas phase coma observed at heliocentric distances of the order of 1 AU. One cannot infer the nucleus volatile composition without taking into account the important sublimation fractionation effects (Espinasse *et al.* 1991; Prialnik 1993; Rickman 1993). The coma composition of distant comets may be surprisingly different.

5. Conclusion

We cannot yet propose a "standard" cometary composition, because we are still lacking data on several key molecules which can difficultly be observed from the ground, and also because this composition may highly vary from comet to comet. Table II summarizes our present knowledge of the subject. The composition is strikingly similar to that observed in interstellar matter (Yamamoto 1991; Greenberg & Shalabeia 1993), but it is still premature to draw a firm conclusion on the origin of comets. Awaiting accurate analyses from future space missions such as *Rosetta*, we can expect important progresses on our knowledge of cometary composition from the development of the microwave and infrared spectroscopic techniques in the near future.

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