



REMOTE INFRARED OBSERVATIONS OF PARENT VOLATILES IN COMETS: A WINDOW ON THE EARLY SOLAR SYSTEM

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ABSTRACT

Organic volatiles and water in Oort Cloud comets were investigated at infrared wavelengths. The detected species include H₂O, CO, CH₃OH, CH₄, C₂H₂, C₂H₆, OCS, HCN, NH₃, and H₂CO. Several daughter fragments (CN, OH, NH₂, etc.) are also measured, and OH prompt emission provides a proxy for water. Long-slit spectra are taken at high spectral dispersion and high spatial resolution, eliminating several sources of systematic error. The resulting parent volatile production rates are highly robust, permitting a sensitive search for compositional diversity among comets. Here, seven OC comets are compared. Six (including Halley) exhibit similar compositions (excepting CO and CH₄). Their low formation temperatures (~30 K) suggest this group probably formed beyond 30 AU from the young sun. However, C/1999 S4 is severely depleted in hypervolatiles and also in methanol, and it likely formed near 5–10 AU. C/2001 A2 is discussed briefly to illustrate future prospects.

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INTRODUCTION

The structure and composition of cometary nuclei are key to understanding the formation and evolution of matter within the early Solar System (Mumma et al. 1993, Irvine et al. 2000). The ices are especially sensitive to temperature and to radiation processing, so their identities and abundances are seen as central to cometary science.

Comets likely formed at diverse distances from the young sun, ranging from just outside the nebular "frost line" ($R_h \sim 5$ AU) to distances beyond 100 AU. During the formation period, nebular temperatures ranged from about 200 K near Jupiter (~5 AU) to about 30 K near Neptune (~40 AU) (Boss 1998). Other conditions also varied strongly with location in the protoplanetary disk.

Some disk models predict vaporization of interstellar ices at the accretion shock, within 30 AU of the young sun (Chick and Cassen 1997). Other distance-dependent effects include radiation processing, neutral-neutral chemistry, ion-molecule chemistry (Aikawa and Herbst 1999), and condensation fractionation (Notesco et al. 1997). Transport of material into the giant-planets' region — inward from 100 AU and outward from 1 AU — also has been proposed (Aikawa and Herbst 1999, Drouart et al. 1999). Once formed, dynamical models predict that cometsimals may migrate radially by up to 1/3 of their formation distance from the sun. Thus, the composition of a final comet nucleus should depend on its distance of formation, and it might contain fractions with diverse chemistries.

Icy planetesimals (comet nuclei) today reside in two principal reservoirs: the Kuiper-Edgeworth belt and the Oort Cloud (OC). In the current paradigm, OC comets were ejected from the giant-planets' region of the solar nebula (5–40 AU). Each of the four giant planets scattered about the same number of comets into the OC (Dones et al. 2000). Dynamical models for its subsequent evolution suggest that roughly half of comets remaining in the OC after 4 Gyr (today) originated in the 5–30 AU region, the remainder formed beyond 30 AU (Dones et al. 2000). We might therefore expect to find chemical differences among even a small sample of OC comets.

The challenge in testing nebular models is twofold: first to identify the region of origin of a given comet and then to measure its composition. Comets from individual reservoirs are recognized by their orbital properties (Carusi and Valsecchi 1987). OC comets display values less than two for the dynamical Tisserand parameter (T_i) (Levison and Duncan 1994); they include short-period comets in Halley-type orbits, long-period comets, and dynamically-new comets. Comets with $2 < T_i < 3$ belong to Jupiter's dynamical family and can come from either reservoir (Kuiper belt or Oort cloud) (Levison and Duncan 1997). Studies of non-native products such as C_2 and CN have revealed differences among Jupiter-family comets (JFCs), but not as clearly among OC comets (A'Hearn *et al.* 1995). The detailed causal factors affecting this difference are not understood.

Chemical differences among OC comets are revealed when parent volatiles are studied directly. Before 1996 only a few parent species could be measured, and secure inferences regarding origins were limited by the lack of simultaneous abundance measurements for multiple species. Nevertheless, measurements of methanol (Mumma 1997, Bockelée-Morvan *et al.* 1995) and CO (Tozzi *et al.* 1998) suggested chemical diversity among OC comets. (However, CO can be native to the nucleus but it can also have a distributed source in the coma. It is necessary to separate the two contributions, see below.) This situation has improved dramatically in recent years.

Here, we report abundances for six OC comets, based primarily on infrared spectroscopy of seven parent volatile species. We compare them with results obtained for 1P/Halley on the Giotto space mission, and we show that this population is chemically diverse.

OBSERVATIONS

The first secure detections of cometary parent volatiles were achieved in comet Halley, by remote observations. H_2O was detected in high-dispersion infrared spectra acquired on NASA's Kuiper Airborne Observatory (Mumma *et al.* 1986) and HCN was detected at millimeter wavelengths from the ground (Schloerb *et al.* 1986). Spacecraft measurements provided a good overview of its chemistry (Combes *et al.* 1988, Eberhardt *et al.* 1999, see reviews in Altwegg *et al.* 1999).

Ground-based infrared spectra (2 - 5 μm) were limited to modest resolving power ($\lambda/\delta\lambda \sim 600$ -1200) until 1992. Nonetheless, methanol was identified in several comets (Hoban *et al.* 1991, Davies *et al.* 1993), a new spectral feature was identified near 3.42 μm (DiSanti *et al.* 1995) and sensitive searches for H_2CO were reported (Reuter *et al.* 1992). Early high-dispersion instruments provided a tentative detection of CO (DiSanti *et al.* 1992a) and sensitive upper limits for CH_4 (Brooke *et al.* 1991) and OCS (DiSanti *et al.* 1992b).

The first infrared spectrometer to combine high-dispersion with a large format 2-D detector array was CSHELL at the NASA Infrared Telescope Facility; it revolutionized this field. With it, cometary H_2O was detected for the first time from a ground-based observatory (in Shoemaker-Levy 1992 XXIV and in 1995 6P/d'Arrest, Mumma *et al.* 1995), demonstrating that the dominant parent volatile could be measured routinely along with trace constituents. CSHELL was upgraded with a 256x256 InSb array in 1995, providing the capability to exploit the 1-5.5 μm region. The apparition of a bright OC comet early in 1996 provided a suitable target.

Comet Hyakutake was observed with CSHELL in March and April 1996 (Table 1). Saturated hydrocarbons (methane and ethane; Mumma *et al.* 1996) and acetylene (Brooke *et al.* 1996) were discovered and H_2O , CO, HCN, CH_3OH and other species were securely detected (Figure 1). The spectra shown in Figure 1 are nucleus-centered extracts. Owing to slit losses, uncorrected production rates based on them underestimate the true values for native ices, but the mixing ratios are less affected. Moreover, optical depth effects caused the retrieved production rate for CO to be too low, a more complete fluorescence model was needed for ethane, and the small geocentric distance caused distributed sources to be missed almost entirely. These difficulties are surmounted with long-slit analyses and improved fluorescence models. These were developed during analysis of Hale-Bopp data and were recently applied retrospectively to the Hyakutake database (Dello Russo *et al.* 2002a, Magee-Sauer *et al.* 2002a, DiSanti *et al.* 2003). The mixing ratios given in Table 2 reflect those improvements.

CSHELL observations of Hale-Bopp began in June 1996 and continued until Sept. 1997 (Table 1). Thousands of high-quality spectra were collected. Like Hyakutake (Figure 1), most spectral lines were extended along the slit direction. This provided an opportunity to extract rotational temperatures at various positions about the nucleus, and thereby to determine the column density for each species at each location. It became apparent that new analysis procedures were needed to fully exploit these high-quality data. They are discussed elsewhere (Dello Russo *et al.* 1998, Magee-Sauer *et al.* 1999, Dello Russo *et al.* 2000, Dello Russo *et al.* 2001, DiSanti *et al.* 2001a).

Table 1. OC comets observed in this work.

Comet	Selected dates UT	Q_h^a	R_h AU	Δ AU	Δ -dot km/sec	FoM ^b
C/1996 B2 Hyakutake	March 24.5, 1996	2.5	1.06	0.106	-14.5	22
C/1995 O1 Hale-Bopp	April 6.2, 1997	107	0.918	1.40	18.4	87
C/1999 H1 Lee	August 21.6, 1999	1.26	1.06	1.36	-28.7	0.85
C/1999 S4 LINEAR	July 13.6, 2000	0.45	0.81	0.55	-54.9	1.1
C/1999 T1 McN-Hartley	January 14.7, 2001	1.6	1.28	1.35	-11.0	0.82
C/2001 A2 LINEAR	July 9.5, 2001	0.3	1.16	0.275	11.5	0.87
C/2000 WM1 LINEAR	November 25.6, 2001	0.3	1.32	0.36	-18.5	0.54
C/2002 C1 Ikeya-Zhang	March 22.0, April 13.8, 2002	6.6 2.1	0.51 0.78	0.76 0.465	-31.2 -12.8	24 6.5

a. Q_h = Retrieved water production rate at R_h (10^{29} molecules s^{-1}). b. Figure of Merit (FoM) = $Q_h R_h^{-1.5} \Delta^{-1} \cdot 10^{-29}$.

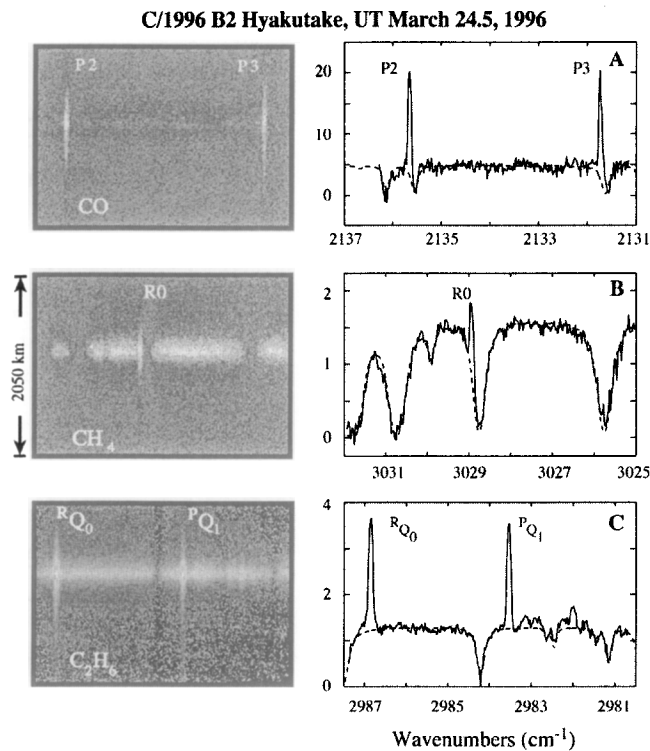


Fig. 1. Discovery of saturated hydrocarbons in comets. (Left Panels). CSHELL high-dispersion ($\lambda/\delta\lambda=20,000$), long-slit spectra of comet C/1996 B2 (Hyakutake) show emission from parent volatiles and dust. The slit (30 arc-sec long) subtends 2050 km and samples the comet at 0.2 arc-sec/pixel. Telluric absorption lines appear dark against the cometary continuum (bright horizontal emission), and their cometary counterparts are Doppler-shifted to higher frequencies by the comet's motion. Top: The P2 and P3 lines of carbon monoxide 1-0 band near 4.69 μm . Middle: The R0 line of methane v_3 near 3.30 μm . Bottom: The RQ_0 and PQ_1 branches of ethane v_7 near 3.35 μm . (Right Panels). Spectral extracts show the signal summed over 1.4 arc-sec (7 rows) centered on the peak continuum signal. The flux density scale is $10^{-16} \text{ W m}^{-2} (\text{cm}^{-1})^{-1}$. The synthetic transmittance model, convolved to the resolution of each comet spectrum, is also shown (dotted curves). After Mumma et al. (1996).

Several observational aspects are illustrated in Figure 2. An image of the thermal continuum at $3.5 \mu\text{m}$ ($\lambda/\delta\lambda \sim 70$) reveals enhancements in dust to the NE and NW (sunward) of the nucleus on UT 1997 April 30.2 (Figure 2A). High-dispersion spectra were measured with the slit positioned as shown (Figure 2A). The intensity profiles measured along slit show that CO is extended to the east while H₂O is symmetric about the nucleus and dust is extended to the west (Figure 2B). Rotational temperatures at each step along the slit are obtained from individual line intensities using a standard Boltzmann analysis (Figure 2C). They reveal an increase in temperature with increasing distance from the nucleus, as expected if photolytic heating and electron collisions are at work (Chin and Weaver 1984, Bockelée-Morvan and Crovisier 1987, Xie and Mumma 1992).

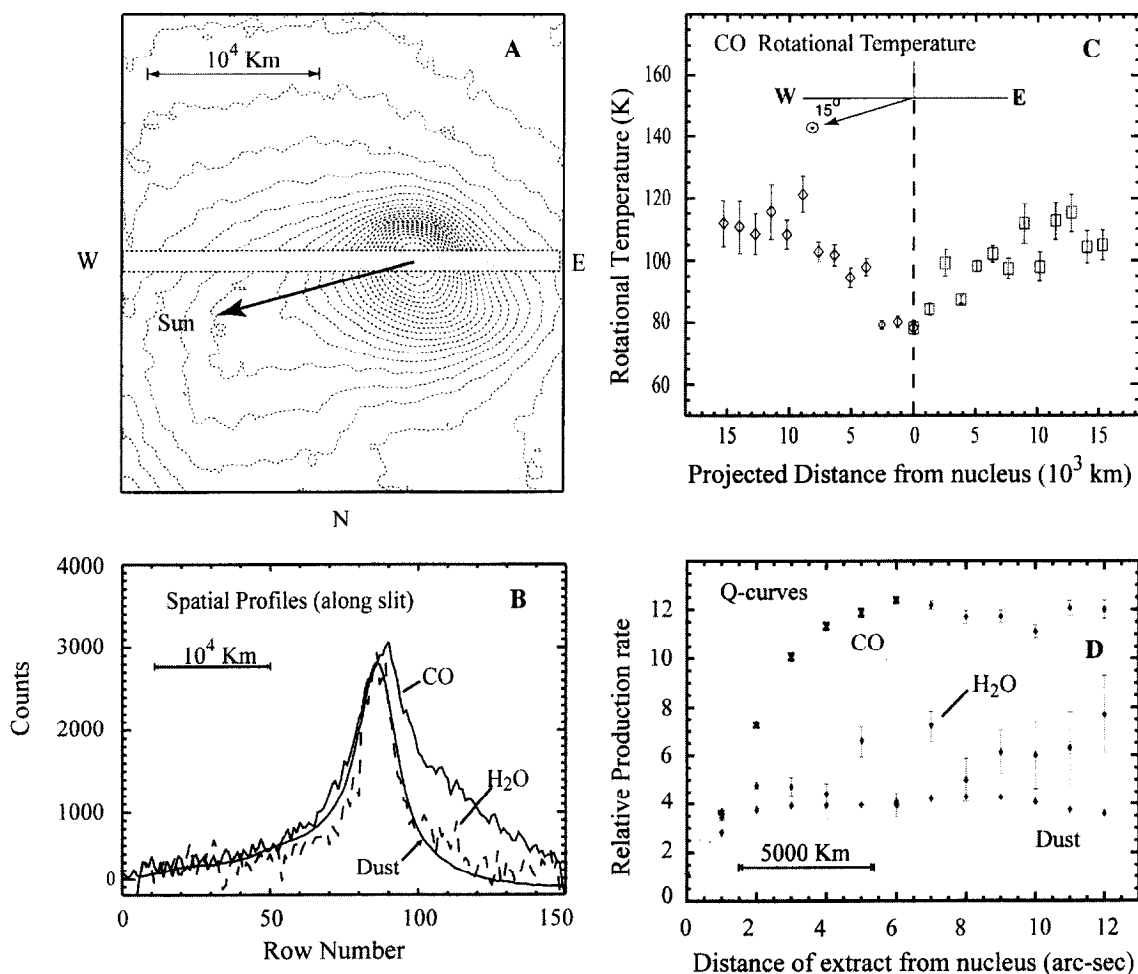


Fig. 2. Hale-Bopp as seen with CSHELL on UT 1997 April 30.2. A. Image of thermal continuum at $3.5 \mu\text{m}$ ($\lambda/\delta\lambda \sim 70$). The East-West slit position is indicated (grey bar), as is the direction towards the Sun projected onto the sky plane. Dust jets are apparent towards the NE and NW. B. Spatial profiles along the slit as extracted from high dispersion spectra (normalized to CO). C. Rotational temperatures for CO measured at various positions along the slit. D. Symmetric Q-curves showing the slower rise to terminal values for CO, compared with H₂O and dust.

Production rates (in molecules s^{-1}) are calculated by assuming the idealized case of spherically symmetric outflow. The intensities measured at symmetric east-west positions are averaged to minimize the effects of outflow asymmetry (Xie and Mumma 1996). A symmetric Q curve is calculated from these mean emission intensities measured at 1-arcsec intervals along the spatial direction of the slit, using the following relation:

$$Q = \frac{4\pi\Delta^2 F_i}{g_i \tau (hc \nu) f(x)} \quad (1)$$

The parameter Δ is the geocentric distance in meters, $h\nu$ is the energy (J) of a photon with wavenumber ν (cm^{-1}), $f(x)$ is the fraction of molecules expected in the sampled region, and F_i is the flux (W m^{-2}) from line i incident on the terrestrial atmosphere. The photodissociation lifetime (τ) and the line fluorescence efficiency (g_i photons s^{-1} molecule $^{-1}$) are evaluated for a heliocentric distance of 1 AU. We take the outflow velocity (v_{gas}) to be $0.8R_h^{-0.5}$ km s^{-1} for all comets except Hale-Bopp. Radio observations of Hale-Bopp indicated $v_{\text{gas}} = 1.1R_h^{-0.5}$ km s^{-1} , a consequence of the unusually high gas production rate from that comet (Biver et al. 1999a).

The resulting Q-curve rises from the nucleocentric value to a terminal value that is taken to represent the "global" production rate for the species. The retrieved nucleus-centered value is always too small, owing to slit losses induced by seeing, drift, guiding error, and other observing factors, but the terminal value is reached quickly for species released directly from the nucleus (H_2O , C_2H_6 , CH_4 , dust, etc.). We measure their ratio (growth factor) directly; if not measured directly, another scaling method must be used for correcting the retrieved nucleus-centered value. Species having a distributed source rise more slowly to the terminal value (e.g. CO, OCS) (compare Q-curves for CO, H_2O , and dust, Figure 2D).

Production and release of OCS (Dello Russo et al. 1998), HCN (Magee-Sauer et al. 1999), H_2O (Dello Russo et al. 2000), C_2H_6 (Dello Russo et al. 2001), and CO (DiSanti et al. 1999, DiSanti et al. 2001a) were characterized in this way, throughout the apparition of Hale-Bopp. Their heliocentric evolution is compared with that of dust in Figure 3. We first convert the production rates to units of mass loss (kg/sec) to ease comparison of gas and dust. We also scale the measured rates by the insolation to reveal "specific" production from the comet. A constant specific production will then appear as a horizontal line in Figure 3. We compare our results for H_2O , CO, and C_2H_6 with total dust production as measured at millimeter wavelengths (Jewitt and Matthews 1999), and with millimeter production rates for CH_3OH and HCN (Biver et al. 1999a, Bockelée-Morvan et al. 2000). The specific production rate for dust is constant (within errors, not shown). Specific rates for HCN, CO, and CH_3OH (pre-perihelion), are constant for $2 < R_h < 4$, but show some increase for $R_h < 1.5$ AU. Their mixing ratios are summarized in Table 2.

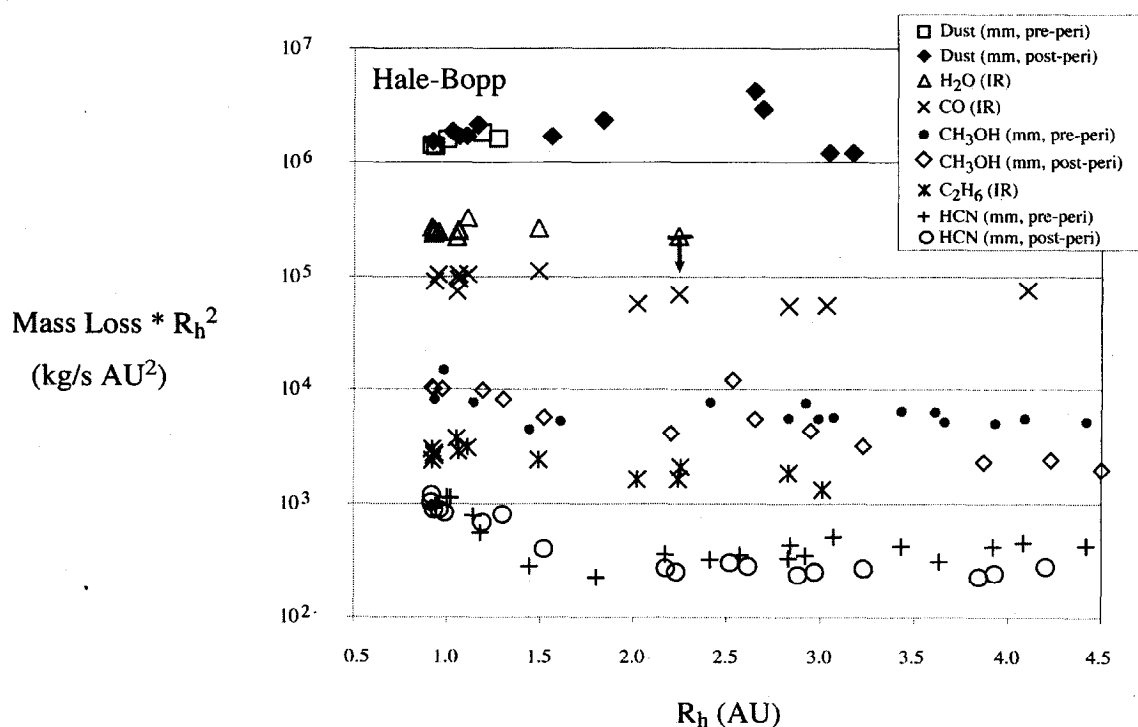


Fig. 3. Production rates for selected parent volatiles and dust in Hale-Bopp. Production rates are given in kg/sec and are normalized by R_h^2 . Thus, a species whose production is limited solely by insolation would fall along a horizontal line. The mixing ratios are essentially constant, excepting HCN within $R_h < 1.5$ AU. Dust production is taken from Jewitt and Matthews (1999), CH_3OH and HCN from Biver et al. (1999a).

A major advance occurred in 1999 with the advent of NIRSPEC (Near Infrared Spectrometer) at the W. M. Keck Observatory. NIRSPEC is cross-dispersed and it features a 1024x1024 InSb detector array. Multiple orders are collected simultaneously, and the on-chip spectral grasp within each order is four times that of CSHELL. In the key organics region (2.9-3.6 μm), six orders fall on the chip (three echelle settings are needed to cover the free spectral range). Near 4.7 μm , three orders are sampled simultaneously. C/1999 H1 Lee was the first comet observed with NIRSPEC (Mumma *et al.* 2001a); seven parent volatiles were measured in a space of two hours: H₂O, CO, CH₃OH, CH₄, C₂H₂, C₂H₆, and HCN. Since then, four more OC comets were observed with NIRSPEC (McN-H, S4, A2, and WM1; Table 1).

Examples of the extracted spectra are shown in Figure 4. Panel A shows the spatial-spectral image of order 23.1, after processing (compare Figure 1C). Panels 4B, 4C, and 4D show extracts for orders 23.1, 23.2, and 25.1 (.1 and .2 designate different echelle settings). Spectral lines for five parent volatile species are noted, along with prompt emission from OH. OH prompt emission (two lines near 3.04 μm) was first detected in comet Hyakutake (Brooke *et al.* 1996); our spectra of comet Lee show that OH prompt emission occurs throughout the L-band. This emission tracks the water column density directly, and it provides a proxy for water itself (Mumma *et al.* 2001a). Many other lines are present in these spectra, and their analysis is ongoing.

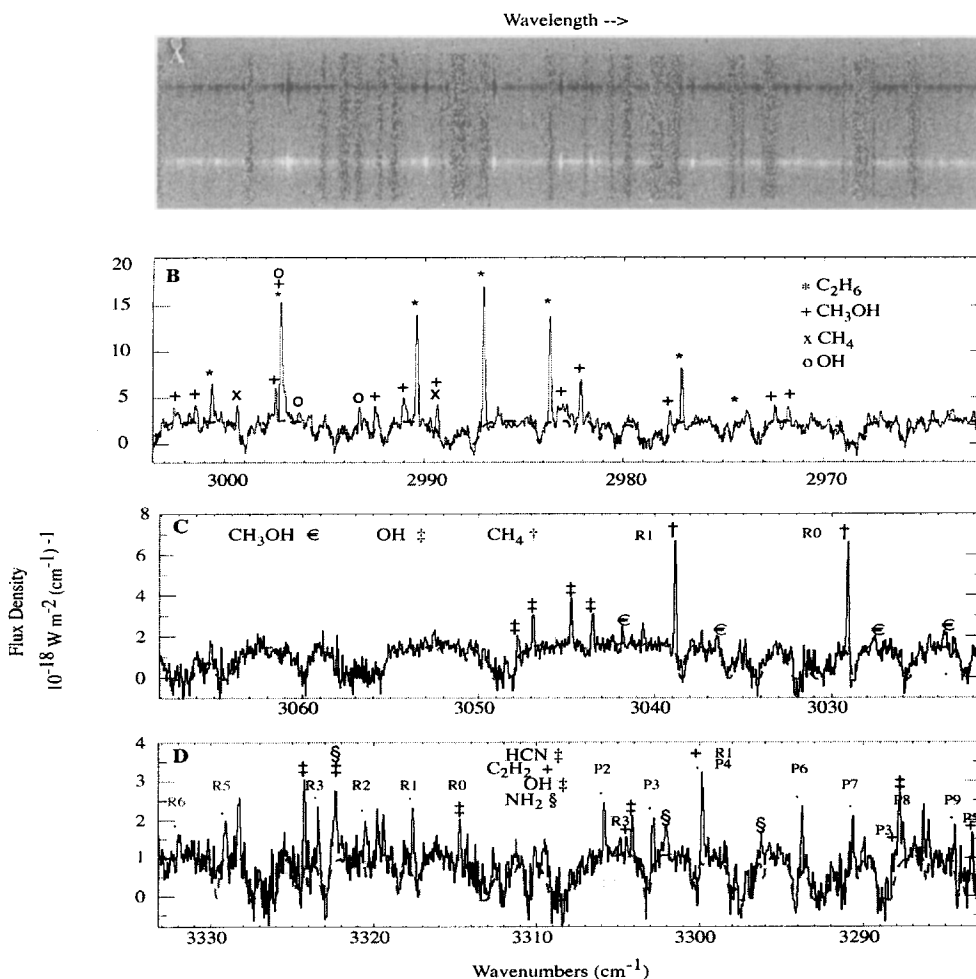


Fig. 4. Detection of parent volatiles in comet C/1999 H1 (Lee) with NIRSPEC (Mumma *et al.* 2001a). A. The appearance of one spectral order in the A-B difference frame after registration and straightening. Detections of cometary continuum and molecular emissions are evident in both beams. B. Spectrum extracted from 5 rows centered on each beam in panel A; C₂H₆, CH₃OH, CH₄, and OH prompt emission are seen. C. Detection of CH₄, OH prompt emission, and lines of CH₃OH ν_2 and ν_3 . D. Detection of HCN, C₂H₂, NH₂, and OH prompt emission. See Mumma *et al.* (2001a) for additional details.

In Figure 5, the NIRSPEC spectrum of CO in comet Lee is compared with a single CSHELL grating setting for CO in Hyakutake. Inspection of spectral lines of H₂O and CO shows that their relative intensities are reversed in the two comets, graphic evidence that CO is far more abundant in Hyakutake.

For many vibrational bands, the increased spectral grasp of NIRSPEC samples enough spectral lines to extract a rotational temperature with a single grating setting. Boltzmann analyses for HCN and CO are shown in Figure 6, based on line intensities taken from Figures 4D and 5A, respectively (Mumma et al. 2001a).

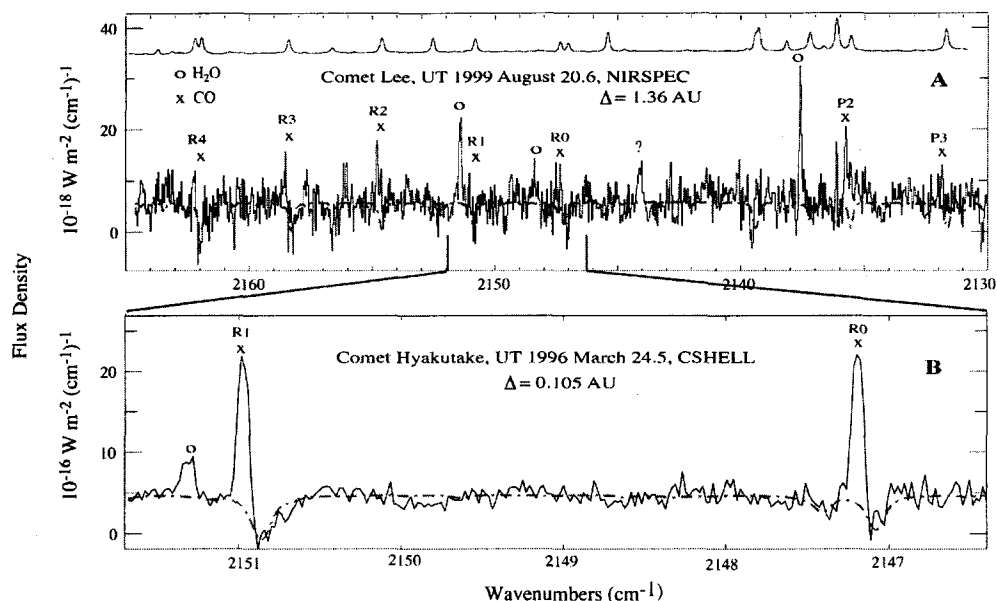


Fig. 5. Detection of CO and H₂O in comets Lee (A) and Hyakutake (B). In Hyakutake ($R_h = 1.06$), the CO R1 line is much brighter than the neighboring H₂O line, but in comet Lee ($R_h = 1.08$) their relative intensities are reversed. The rotational temperatures were comparable in the two comets when observed. This reversal visually confirms the much lower mixing ratio of CO in comet Lee. After Mumma et al. 2001a.

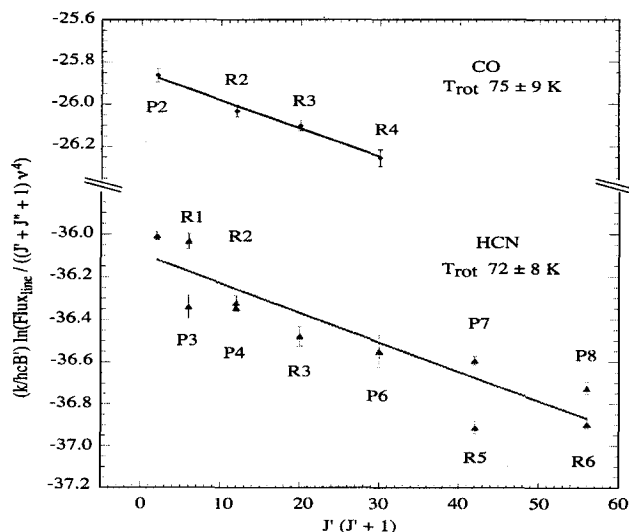


Fig. 6. Rotation diagrams for comet Lee, at $R_h = 1.07$ AU. The rotational temperatures retrieved for CO and HCN agree within their confidence limits. Temperatures derived for H₂O and C₂H₆ are consistent with those shown here for CO and HCN. After Mumma et al. (2001a).

The final species to be discussed here is methanol. An emission feature was discovered near 3.52 μm in low-resolution ground-based spectra of comet Halley; methanol and formaldehyde were suggested as possible progenitors but a firm identification was not possible (Knacke *et al.* 1986). In comet Austin, this feature was identified as the ν_3 band of CH_3OH , and production rates were derived from the integrated band intensity (Hoban *et al.* 1991). The band envelopes in comets Austin and Swift-Tuttle (Davies *et al.* 1993) were consistent with a low rotational temperature ($\sim 50\text{-}70$ K). In later comets, intensities of individual lines could not be extracted from high-resolution spectra owing to insufficient instrumental sensitivity, so production rates were derived from the integrated Q-branch intensity near 2844 cm^{-1} . Infrared and millimeter production rates for CH_3OH agree when measured in the same comet and on the same dates.

NIRSPEC has improved this situation. Comet Lee showed strong Q-branch emission (triply-peaked) along with several lines in the P- and R-branches (Figure 7A). Spectral lines in C/2001 A2 were intrinsically brighter by almost a factor of two compared with those in comet Lee (see FoM, Table 1), and many rotational lines were identified (Figure 7B). Improved line-by-line fluorescence models for $\text{CH}_3\text{OH } \nu_3$ are under development; once available, they will permit extraction of robust rotational temperatures for methanol.

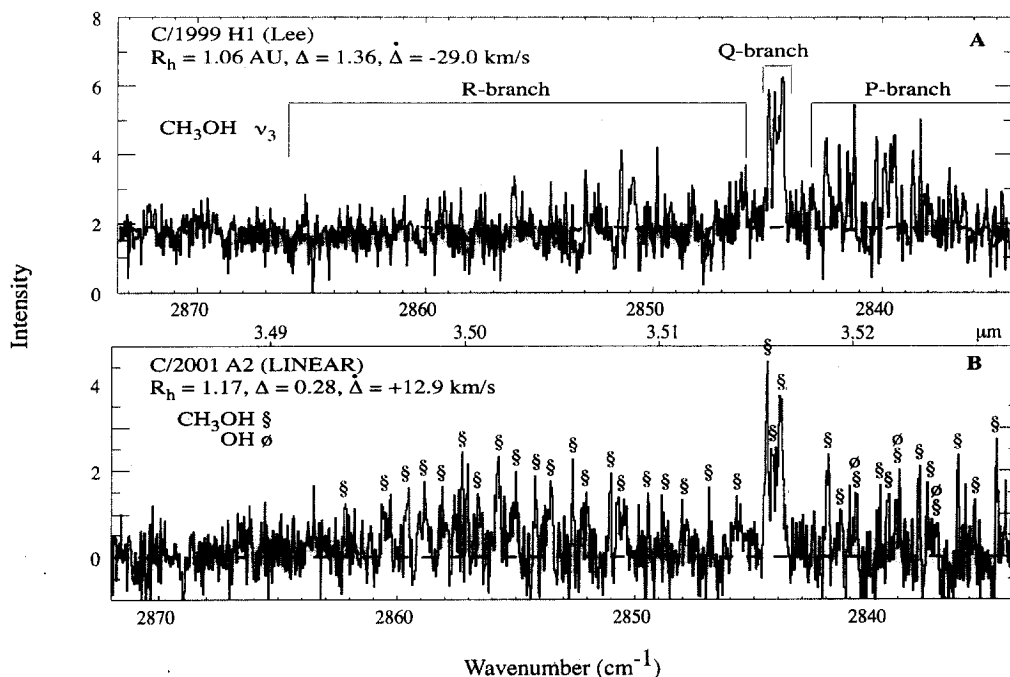


Fig. 7. Detection of methanol and OH prompt emission in two comets, with NIRSPEC. Nucleus-centered extracts are shown. A. Comet Lee shows strong Q-branch emission (triply-peaked) along with several lines in the P- and R-branches (Mumma *et al.* 2001a). B. Comet C/A2 (LINEAR) was somewhat brighter, and many more P- and R-branch lines were detected. Rotational temperatures may be extracted from them via Boltzmann analyses, in future. Several lines of OH appear in prompt emission, and several other OH multiplets appear in other orders. These OH emissions track H_2O itself, and they can provide a direct measure of the water production rate.

We have presented selected spectra from our cometary database in sufficient detail to convey some impression of their richness and also of the highly robust nature of the results. The ability to quantify many parent volatiles quickly with a single instrument-telescope combination eliminates many sources of systematic error. It reduces the sensitivity to changes introduced by nucleus rotation and to atmospheric variability. Of the remaining systematic errors, some (such as in outflow velocity) affect extractions for all parent species in a given comet in the same way (e. g., Eqn. 1), while others (such as in g-factors) are common to all comets. The long-slit analysis methodology permits compensation for non-systematic errors such as slit losses, guiding and tracking inaccuracies, and so forth. The net result is a set of mixing ratios that permit meaningful comparison among the sampled population.

In the remaining space, we will discuss observations of C/1999 S4 (LINEAR) (hereafter C/S4), an OC comet whose composition differs dramatically from all other members in our sample.

C/1999 S4 — A TRULY UNUSUAL COMET

The organic chemistry of C/S4 was investigated with both CSHELL and NIRSPEC (Mumma et al. 2001b). Selected spectra of C/S4 are compared with those of comet Lee in Figure 8. The relative abundances of most trace species in C/S4 are smaller by factors of five to ten compared with other OC comets in our sample (Table 2). The abundance of native CO in C/S4 is the smallest in our entire sample of OC comets, CH₄ and C₂H₆ are less abundant by about a factor of six, and C₂H₂ is smaller by at least 2.5 compared with the other OC comets. Among the less volatile ices, H₂S and H₂CO are present in normal abundance relative to HCN (Bockelée-Morvan et al. 2001). Our simultaneous measurements of H₂O and HCN suggest that HCN is depleted by about a factor of two. CH₃OH and HCN have similar volatility, so they should be depleted by similar ratios if temperature was the controlling factor. But CH₃OH is much more strongly depleted than HCN. The upper limit for CH₃OH (< 0.17% of H₂O) is lower than even the smallest abundance measured for any other OC comet to date; a larger sample exhibits a somewhat wider range in CH₃OH abundance than seen in Table 2, ~ 0.5 - 5% relative to water (Mumma 1997, Biver et al. 2002).

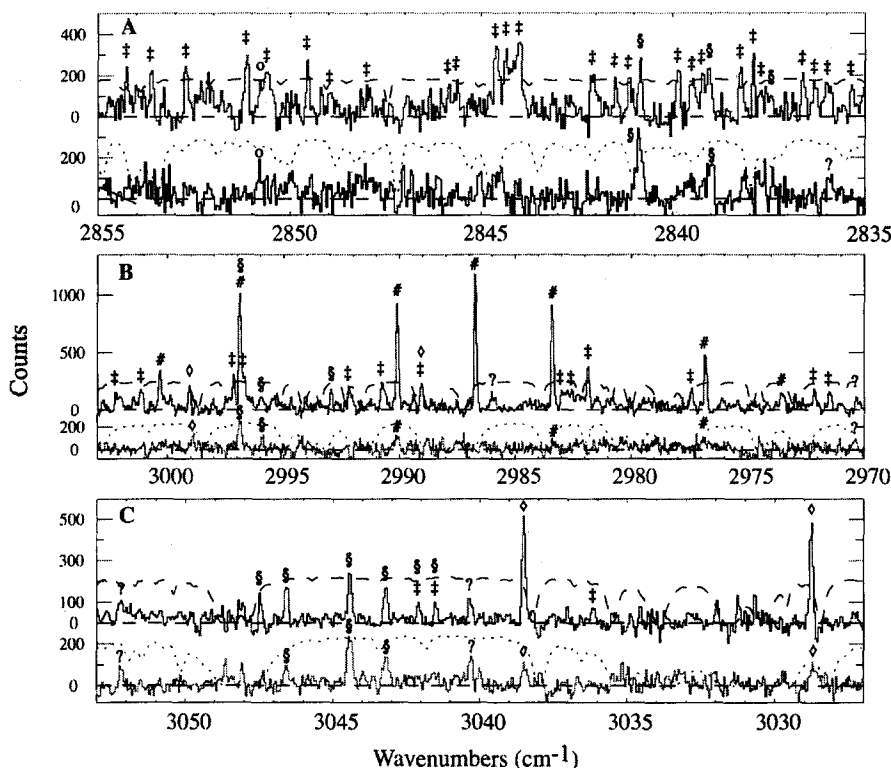


Fig. 8. Comparison of organic species in comets Lee and C/S4 (LINEAR) (after Mumma et al. 2001b). The spectrum of comet Lee is displaced above that of C/S4, in each panel. Spectral line identifications are given in Figures 4 and 7. OH prompt emission lines appear in each order, and the spectra are normalized so their intensities match in the two comets. This visually reveals the strong depletion in CH₃OH, C₂H₆, and CH₄ in C/S4 compared with comet Lee. A. The methanol ν_3 region. Note that the Q-branch near 2844 cm^{-1} is strong in comet Lee but is nearly missing in C/S4. B. The ethane ν_7 region. Note that Q-branches of ethane are strong in Lee but are greatly reduced in C/S4. C. The CH₄ ν_3 region. Note that R0 and R1 are strong in Lee but are weak in C/S4. The spectra are shown in the cometary rest frame; hence atmospheric absorption lines are not aligned.

The severe depletion of methanol in C/1999 S4, in the presence of a mild depletion of HCN but normal H₂S/HCN and H₂CO/HCN is difficult to explain on the basis of preferential sublimation or condensation fractionation. Chemical processing in advance of accumulation may provide the simplest explanation (see Mumma et al. 2001b). Interestingly, Marcos and Marcos (2002) argued that cometesimals could easily form in the Jupiter-

Saturn region by means of collisional accumulation followed by two-body accretion or by gravitational instability of a layer of macroscopic bodies.

Table 2. Organic volatile composition of Oort Cloud comets

H ₂ O = 100	CO (native <i>only</i>)	CH ₄	C ₂ H ₂	C ₂ H ₆	HCN	CH ₃ OH	T _{form}
Lee	1.8 ± 0.2 ^a	1.45 ± 0.18 ^b	0.27 ± 0.03 ^a	0.67 ± 0.07 ^a	0.29 ± 0.02 ^a	2.1 ± 0.5 ^a	
Hale-Bopp	12.4 ± 0.4 ^{c,d}	1.45 ± 0.16 ^{b,e}	0.31 ± 0.1 ^f	0.56 ± 0.04 ^g	0.27 ± 0.04 ^{h,*}	2.1 ⁱ	~25-30 K ^j
Hyakutake	14.9 ± 1.9 ^{k,l}	0.79 ± 0.08 ^{b,k}	0.16 ± 0.08 ^{m,**}	0.62 ± 0.07 ^{k,o}	0.18 ± 0.04 ^p	1.7 - 2 ^q	~30 K
Ikeya-Zhang	4.7 ± 0.8 ^r	0.51 ± 0.06 ^b	0.18 ± 0.05 ^s	0.62 ± 0.13 ^t	0.18 ± 0.05 ^s	2.5 ± 0.5 ^u	
McNaught-Hartley ^{v,w}	~17	1.4 ± 0.8 ^b	TBD	0.65	(0.37)	1.7	
Above 5 comets:	1.8 - 17	0.5 - 1.5	0.2 - 0.3	0.6	0.2 - 0.3	2	
Halley (Giotto NMS ^x)	3.5 ^x	< 1 ^x	~ 0.3 ^x	~ 0.4 ^x	~ 0.2 ^x	1.7 ± 0.4 ^y	~30 K ^z
C/1999 S4 ^{aa}	0.9 ± 0.3	0.18 ± 0.06 ^{b,aa}	< 0.12	0.11 ± 0.02	0.10 ± 0.03	< 0.15	

a. Mumma *et al.* 2001a

b. Gibb *et al.* 2003.

c. DiSanti *et al.* 1999.

d. DiSanti *et al.* 2001a.

e. Weaver *et al.* 1999a.

f. Magee-Sauer *et al.* 2001.

g. Dello Russo *et al.* 2001.

h. Magee-Sauer *et al.* 1999.

i. Biver *et al.* 1999a.

j. Bockelée-Morvan *et al.* 2000.

k. Mumma *et al.* 1996.

l. DiSanti *et al.* 2003.

m. Magee-Sauer *et al.* 2001.

n. Brooke *et al.* 1996.

o. Dello Russo *et al.* 2002a.

p. Magee-Sauer *et al.* 2002a.

q. Biver *et al.* 1999b.

r. DiSanti *et al.* 2002.

s. Magee-Sauer *et al.* 2002b.

t. Dello Russo *et al.* 2002b.

u. DiSanti *et al.* 2002.

v. Mumma *et al.* 2001c

w. DiSanti *et al.* 2001b.

x. Eberhardt 1999.

y. Eberhardt *et al.* 1994.

z. Mumma *et al.* 1993.

aa. Mumma *et al.* 2001b.

* Variable; on another date the mixing ratio was (0.53 ± 0.07)^h. ** Brooke *et al.* (1996) measured (0.3 - 0.9)ⁿ.

DISCUSSION

Six of the seven OC comets in this study show similar organic chemistry (Table 2). The ices in comets Halley, Hyakutake, and Hale-Bopp revealed compositions similar to those in dense interstellar cloud cores (Mumma 1996, Mumma 1997, Crovisier 1999, Bockelée-Morvan and Crovisier 2000). The observed deuterium enrichment (Meier and Owen 1999), the low ortho-para ratios displayed by water (Mumma *et al.* 1993, Crovisier *et al.* 1997, Mumma 1989, Mumma *et al.* 1987), and the depletion of neon (Krasnopolsky *et al.* 1997, Krasnopolsky and Mumma 2001) with possible enhancement of argon (Stern *et al.* 2000) all support processing at temperatures near 30 K. This suggests accumulation of their pre-cometary ices in the Uranus-Neptune region, where the great distance from the sun and the large amount of intervening nebular material may have offered protection against extensive thermal and radiation processing.

Two symmetric hydrocarbons (acetylene, ethane) and methanol were comparably abundant in these six comets, consistent with a common origin. Native CO varied by a factor of ten among them, perhaps a signature of slightly different formation temperatures. Although comparably volatile to CO, methane shows a somewhat smaller range in abundance and the mixing ratios for these two species are not correlated (Gibb *et al.* 2003). A seventh comet (C/S4) differs greatly, possibly because it formed closer to the young sun (5-10 AU) (Mumma *et al.* 2001b). Data for two other comets (A2, WM1; Table 1) are now being reduced.

An emerging view is that most comets now in the Oort cloud were formed beyond 30 AU from the young sun. However, a small fraction may have formed closer to the sun, perhaps in the 5-10 AU range. Although under-represented in the Oort cloud for dynamical reasons, the latter group dominated the population of icy planetesimals in the 5-40 AU protoplanetary disk and they likely delivered water and pre-biotic organics to early Earth. The six comets exhibiting common chemistry (including Halley, Hyakutake, and Hale-Bopp) are likely not representative of this group. Measurements of HDO/H₂O in future comets are planned, to test this hypothesis (Gibb *et al.* 2002).

If JFCs formed at distances greater than 40 AU, i.e. in the Kuiper belt, then establishing their chemical taxonomy could provide an important tie point between remnant interstellar ices from the natal interstellar cloud core, and the more processed ices expected in OC comets ejected from the giant-planets' nebular region. A'Hearn *et*

al (1995) showed that the carbon chemistry of JFCs differs significantly from that of OC comets, with a much greater fraction of JFCs being depleted in the ratios C_2/CN and C_3/CN . The quintessential C_2 -depleted comet (21P/Giacobini-Zinner) is also deficient in ethane (Weaver et al. 1999b, Mumma et al. 2000). However, C_2 can be produced directly from C_2H_2 by photolysis but not from C_2H_6 , and the depletion of ethane does not directly test a depletion of acetylene. A direct measurement of acetylene in JFCs is of great interest, and a comparison of acetylene and ethane would also test the production of C_2H_6 by hydrogenation of C_2H_2 . The CO mixing ratio was either nearly normal (Mumma et al. 2000) or strongly depleted (Weaver et al. 1999b) in this comet. The reason for this difference is not known; the measurements were separated in time by several weeks so internal heterogeneity could be at work if different active vents were observed. Additional observations of this and other JFCs during especially favorable apparitions are of high priority.

Clearly, establishing a chemical taxonomy for comets promises to provide important new insights into processes in the early solar system.

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