High-Resolution Infrared Spectroscopic Measurements of Comet 2P/Encke: Unusual Organic Composition and Low Rotational Temperatures

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Abstract

We present high-resolution infrared spectroscopic measurements of the ecliptic comet 2P/Encke, observed on 4-6 Nov. 2003 during its close approach to the Earth, using the Near Infrared Echelle Spectrograph on the Keck II telescope. We present flux-calibrated spectra, production rates, and mixing ratios for H$_2$O, CH$_3$OH, HCN, H$_2$CO, C$_2$H$_2$, C$_2$H$_6$, CH$_4$ and CO. Comet 2P/Encke is a dynamical end-member among comets because of its short period of 3.3 years. Relative to "organics-normal" comets, we determined that 2P/Encke is depleted in HCN, H$_2$CO, C$_2$H$_2$, C$_2$H$_6$, CH$_4$ and CO, but it is enriched in CH$_3$OH. We compared mixing ratios of these organic species measured on separate dates, and we see no evidence of macroscopic chemical heterogeneity in the nucleus of 2P/Encke, however, this conclusion is limited by sparse temporal sampling. The depleted abundances of most measured species suggest that 2P/Encke may have formed closer to the young Sun, before its insertion to the Kuiper belt, compared with "organics-normal" comets – as was previously suggested for other depleted comets (e.g. C/1999 S4 (LINEAR)). We measured very low rotational temperatures of 20 - 30 K for H$_2$O, CH$_3$OH and HCN in the near nucleus region of 2P/Encke, which correlate with one of the lowest cometary gas production rates ($\sim 2.6 \times 10^{27}$ molecules s$^{-1}$) measured thus far in the infrared. This suggests that we are seeing the effects of more efficient radiative cooling, insufficient collisional excitation, and/or inefficient heating by fast H-atoms (and icy grains) in the observed region of the coma. Its extremely short orbital period, very low gas production rate, and classification as an ecliptic comet, make 2P/Encke an important addition to our growing database, and contribute significantly to the establishment of a chemical taxonomy of comets.
1. **INTRODUCTION**

The establishment of a taxonomic classification for comets based on their chemical composition is essential to understanding the formation and evolution of our Solar System (for a recent review, see Mumma & Charnley 2011). Comets are relatively unaltered remnants from the creation of the Solar System 4.6 billion years ago, and are currently found in two major dynamical reservoirs: the Kuiper belt and the Oort cloud (Gladman 2005).

The dynamical classification of a comet is based on its orbital Tisserand invariant with respect to Jupiter ($T_j$). For Jupiter-family comets: $2 < T_j < 3$; for Chiron-type comets: $T_j > 3$ & $a > a_j$; for Encke-type comets: $T_j > 3$ & $a < a_j$; and for nearly isotropic (i.e., Oort cloud) comets: $-2 < T_j < 2$, where “a” is the semi-major axis of a comet (Levison 1996). Identifying the long-term dynamical reservoir of a comet does not, however, identify its formative region. The “Nice” model predicts significant dynamical dispersion of icy bodies in the outer proto-planetary disk (Tsiganis et al. 2005), and while it suggests that comets currently found in the Kuiper belt formed beyond 5 AU from the Sun, the newer “Grand Tack” model (Walsh et al. 2011) points to the possible origin of many Kuiper belt and Oort cloud comets in the terrestrial planets region. Another new model (Levison 2010) questions whether all Oort cloud comets indeed formed in our proto-planetary disk, and suggests that many may have been captured after ejection from the proto-planetary disks of other stars in the Sun’s birth cluster. Clearly, a different metric is needed to clarify a comet’s formative region.

Current models for the protoplanetary disk suggest the presence of strong radial gradients in chemistry and temperature, and direct sampling of cometary material confirms the presence of pre-cometary grains that formed over extremely diverse conditions, ranging from the interstellar
medium to the near-Sun inner planetary region (Brownlee et al. 2006). These models also predict compositional and isotopic diversity amongst the ices formed in different regions, and thus in comet nuclei that accumulated from them. The recent discovery of ocean-like water in the ecliptic comet 103P/Hartley 2 (Hartogh et al. 2011) emphasizes this diversity, re-opens the question of the role of comets in delivering Earth’s water, and makes the need for a robust compositional taxonomy even more compelling.

Optical surveys of product species (such as OH, CN, NH, C₂, C₃, etc.) revealed that the fraction of comets depleted in C₂ and C₃ radicals (relative to CN) is greater among Jupiter family comets than among Oort cloud comets (A’Hearn et al. 1995, Fink 2009, Langland-Shula & Smith 2011, Cochran et al. 2012). However, it is often problematic to uniquely interpret the origin of product species. They can originate from the photo-dissociation of primary (a.k.a. parent) volatiles (i.e., species native to the cometary nucleus and released under the influence of solar radiation), from refractory grains, or even from chemical processes in the coma. Thus, there are multiple possible (and unknown) pathways and parents for each observed radical. Also, comets that are termed ‘typical’ in product species (C₂, C₃, CN) are sometimes not “organics-normal” in their primary volatile composition (8P/Tuttle, Bonev et al. 2008; 10P/Tempel 2, Paganini et al. 2012; 9P/Tempel 1, Mumma et al. 2005; 6P/d’Arrest, Dello Russo et al. 2009). In short, it is critically important to develop a chemical taxonomy based on primary volatile composition.

Infrared and radio spectroscopic observations of comets enable the measurement of gas production rates of primary volatile species. These surveys now permit quantitative sampling of eight or more primary species at infrared wavelengths, simultaneously with water, the (usually) dominant species. Several important primary volatiles (e.g., CH₄, C₂H₂, C₂H₆, etc.) are readily measured at infrared wavelengths, but (being symmetric) their pure rotational transitions are
forbidden and so they cannot be observed at mm and sub-mm wavelengths. Radio observations are, however, very useful in studying the rotational transitions of more complex molecules (provided that they have a permanent dipole moment), and are thus complementary to infrared studies.

Our group has identified "organics-enriched", "organics-normal", and "organics-depleted" comets on the basis of mixing ratios of organic volatiles, such as CH$_3$OH, HCN, H$_2$CO, C$_2$H$_2$, C$_2$H$_6$, CH$_4$, and CO (Mumma et al. 2003; Crovisier et al. 2007; DiSanti and Mumma 2008). The Oort cloud comets C/2001 A2 (LINEAR) (Magee-Sauer et al. 2008), and C/2007 W1 (Boattini) (Villanueva et al. 2011a) have been identified as enriched in most organic species, and the Oort cloud comet C/1999 S4 (LINEAR) (Mumma et al. 2001; 2003) has been identified as severely depleted in most organics. Among ecliptic comets, 17P/Holmes is enriched (Salyk et al. 2007, Dello Russo et al. 2008) and 73P/Schwassman-Wachmann-3 is severely depleted (Villanueva et al. 2006, Dello Russo et al. 2007). However, 17P/Holmes was observed while outbursting at ~2.4 AU (most comets are observed much closer to the Sun). It is likely that a fraction of the water in its inner coma was ejected in the form of ice (Yang et al. 2009), which (if depleted in organics) could cause enrichment in the organic gases measured at infrared wavelengths. Such polar and apolar ices were identified recently in comets 103P/Hartley 2, C/2006 W1 (Boattini), and 10P/Tempel 2 (Mumma et al. 2011, Villanueva et al. 2011a, Paganini et al. 2012). Chemical diversity is found in each dynamical reservoir, and a more expansive sample of comets from both the Kuiper belt and the Oort cloud is needed in order to identify the true origin of an individual comet and the fractional representation of taxonomic classes within each dynamical reservoir.

Here we present the organic composition of the ecliptic comet 2P/Encke, and discuss its organic depletion, its low rotational temperatures, and aspects of its possible origins. 2P/Encke (hereafter
Encke) is the prototypical “Encke-type” comet, with $T_J = 3.025$, period of 3.3 years, and aphelion distance of 4.09 AU. Encke’s aphelion distance is unusually small, and dynamical simulations suggest that the comet may have been in a dormant state for a long period of time, after it became dynamically decoupled from Jupiter (Levison et al. 2006). Encke was discovered in 1786 by Méchain, at the Paris Observatory, and up to the time of our observations, it had returned to perihelion 67 times since its discovery (Sekanina 1991).

2. OBSERVATIONS AND DATA REDUCTION

Comet Encke reached closest approach to Earth (with $\Delta = 0.261$ AU) on 17 Nov. 2003, and perihelion ($q = 0.338$ AU) on 30 Dec. 2003. We characterized the comet on 4-6 Nov. 2003 (Table 1), using the cross-dispersed Near Infrared Echelle Spectrograph (NIRSPEC) at Keck-II atop Mauna Kea, HI. NIRSPEC has a $1024 \times 1024$ InSb detector array; and provides resolving power $\lambda/\Delta \lambda \sim 25000$ when using the 0.432” entrance slit. A single spectral frame (covering $1024 \times 1024$ pixels) samples multiple echelle orders, e.g., orders 21-26 in the KL2 grating setting; and orders 22-27 in the KL1 grating setting (Table 1). This large spectral grasp is one of the main strengths of NIRSPEC since the simultaneous detection of multiple organic species and water minimizes numerous systematic uncertainties. The slit has a length of 24”, corresponding to 121 pixels of 0.198” each in the spatial direction.

We nodded the telescope by 12” (± 6” along the instrument slit) in a sequence A1, B1, B2, A2 (where A and B correspond to the two different positions of the comet in the slit). The difference in frames (A1–B1–B2+A2) and the further combination of the A and B beams cancels dark current and telescope thermal background, as well as sky emission lines (to second order in a Taylor series expansion about the mean air mass). We cropped individual echelle orders from the difference frame and (after flat field division) "masked" them in order to remove hot pixels and
cosmic ray hits. We re-sampled the data in the spatial and spectral directions, correcting for the initial tilt, to ensure that (in the re-sampled data) the pixels along each column correspond to a common frequency and that all pixels along a given row sample a common spatial position in the coma.

We generated terrestrial transmittance spectra using our adapted (Villanueva et al. 2011b) version of the LBLRTM (Layer-by-Layer Radiative Transfer Model, Clough et al. 2005) spectral synthesis program, and convolved the fully resolved synthetic spectra to the instrumental resolution in order to determine the telluric abundances of H$_2$O, CO$_2$, O$_3$, N$_2$O, CO, C$_2$H$_6$ and CH$_4$ (by matching the synthetic and measured spectrum, through an iterative fitting process). We performed frequency calibration of the data by aligning modeled sky emission lines with those observed in the data frames. We scaled the convolved (to $\lambda/\Delta\lambda \sim 25000$) telluric model to the cometary continuum level; subtracting this isolated the residual emission spectrum of the comet, still multiplied by the atmospheric transmittance function. The fully-resolved best-fit model provided a precise value for the transmittance at each Doppler-shifted line position. We used spectra of a flux standard star to convert the counts per second in the comet data to flux density in W m$^{-2}$ [cm$^{-1}$]$^{-1}$. Detailed descriptions of our standard data analysis procedures are given in the literature (e.g., Radeva 2010, Villanueva et al. 2009, Bonev 2005, DiSanti et al. 2001, and references therein).

3. RESULTS

We present quantitative results for H$_2$O, CH$_3$OH, HCN, H$_2$CO, C$_2$H$_2$, C$_2$H$_6$, CH$_4$, and CO (Table 2) in comet Encke. We present production rates for five species (H$_2$O, CH$_3$OH, HCN, C$_2$H$_6$, and CH$_4$), 3-σ upper limits for three others (CO, H$_2$CO, C$_2$H$_2$), and rotational temperatures for H$_2$O,
CH$_3$OH and HCN. We give mixing ratios for all trace species (production rates of organic species as percentages relative to water), for the three dates of observation. Results for Encke are compared with those for other comets in Table 3.

3.1. **Spectral Gallery**

Figure 1 presents a nucleus-centered, flux-calibrated spectral extract, which contains the spatially summed signal from nine spatial pixels centered on the nucleus, spanning a range of 1.78" (~ 387 km). The synthetic model of the terrestrial atmosphere is shown as a dashed line (superimposed on the cometary spectrum) in the upper panel of the figure. The corresponding residual spectrum of H$_2$O (after subtraction of the transmittance model from the measured cometary spectrum) is shown in the lower panel, with the ±1-σ noise envelope superimposed (dashed line). The noise envelope is largest at frequencies that correspond to sky emission lines (compare the upper and lower panels of Fig. 1). Figures 1-18 in the Electronic Supplementary Material present all remaining spectral orders for the three dates of observation.

3.2. **Measured Rotational Temperatures**

At infrared wavelengths, we sample the innermost coma over a range in nucleus-centered distance that depends on the comet’s geocentric distance (see Table 1). In this inner region, collisions thermalize the rotational populations ($P_m$) of the ground vibrational level of each molecule (Xie and Mumma 1992), and a rotational temperature ($T_{rot}$) is extracted to model these populations: $P_m = \frac{g_m \exp(-E_m/kT_{rot})}{Z(T_{rot})}$, where $g_m$ is the statistical weight of level 'm', $E_m$ is the energy of the level, and $Z$ is the partition function. For Encke at the time of observation, the 1.78" nucleus-centered extract spanned 387 km at the comet, corresponding to ± 194 km from the nucleus, as projected onto the sky plane. The number density of molecules at ~ 194 km from
the nucleus was approximately $8 \times 10^6$ cm$^{-3}$ (for $Q_{\text{gas}} \sim 3 \times 10^{27}$ s$^{-1}$, see Discussion, §4). For a more active comet, the same number density would be measured at a greater distance from the nucleus, e.g., at $\sim 346$ km, even for the modestly productive comet C/2007 W1 (Boattini) ($Q \sim 1.2 \times 10^{28}$ s$^{-1}$). Under these conditions, the rotational population of H$_2$O in C/2007 W1 (Boattini) was well thermalized (retrieved $T_{\text{rot}} \sim 80$ K) (Villanueva et al. 2011a), and in comet Encke the rotational population should be thermalized for all higher densities (i.e., within the sampled 1.78" nucleus-centered extract).

Accurate rotational temperatures are vital for calculating production rates of detected species, especially given that most measurements sample only a sub-set of ro-vibrational levels. To extract a rotational temperature for a given molecule, we compare the ratios of measured intensity and modeled fluorescence efficiency factor (g-factor) for the sampled spectral lines. The g-factors (in photons molecule$^{-1}$ s$^{-1}$) predict the intensity of each line at a given $T_{\text{rot}}$. Therefore, the temperature that most accurately describes the rotational level populations should provide the best agreement, within error, for the ratios of flux/g-factor for the measured lines.

For the present analyses, we used the improved solar model and improved fluorescence models developed by our group (see Villanueva et al. 2011a (Boattini - solar & fluorescence models); 2012a (H$_2$O); 2012b (CH$_3$OH), and original sources cited therein).

The excitation analyses for three molecular species are shown in Fig. 2. They demonstrate our approach and the agreement (within error) among production rates obtained from individual lines at the retrieved (optimized) $T_{\text{rot}}$ that corresponds to the solution with zero slope. The rotational temperatures derived for water, methanol, and hydrogen cyanide in Encke agree within experimental error (Table 2): $T_{\text{rot}}$(H$_2$O) = $29^{+7/-10}$ K (4 Nov., KL1 setting), $T_{\text{rot}}$(H$_2$O) = $30^{+2/-2}$ K (5 Nov., KL1 setting), $T_{\text{rot}}$(CH$_3$OH) = $24^{+5/-6}$ K (5 Nov., KL1 setting), and $T_{\text{rot}}$(HCN) = $20^{+\ldots}$
These temperatures are much lower than those we normally obtain for the inner coma of comets (see Discussion, §4). Fig. 3 illustrates the fit of the synthetic fluorescence models (convolved with modeled terrestrial transmittance) to the cometary spectra at each $T_{rot}$. The rotational temperatures retrieved from H$_2$O on the respective dates of observation were adopted for other species, for which $T_{rot}$ could not be extracted due to an insufficient spread of excitation energies amongst the measured lines.

Our approach assumes that the observed medium is optically thin at infrared wavelengths. Optical depth effects must be considered for very active comets such as Ikeya-Zhang or Hale-Bopp (Dello Russo et al. 2004, DiSanti et al. 2001). In Encke, optical depth effects are negligible because the comet has very low gas production rates – Q(H$_2$O) is about 100 times smaller in Encke than in Ikeya-Zhang, and about 1000 times less than in Hale-Bopp.

### 3.3 Production Rates

We extracted a production rate $Q_i$ from each measured spectral line, assuming spherical outflow with uniform velocity. Then, $Q_i = \frac{4\pi\Delta^2 F_i}{g \tau (hcv) t_i f(x)}$, where $F_i$ is the flux of the $i^{th}$ line collected from a box on the sky centered on the nucleus and measuring 0.432” (slit-width) x 1.782” (extract length). Other parameters include the geocentric distance $\Delta$ [meters], the terrestrial transmittance ($t_i$) at the frequency of the $i^{th}$ line; the fraction ($f(x)$) of the total coma content of the targeted species sampled by the beam; the energy ($hcv$) of a photon with wavenumber $\nu$ (cm$^{-1}$) the line g-factor ($g_i$) at $T_{rot}$; the molecular lifetime ($\tau$); and the assumed expansion velocity (0.8 $\times$ $R_h^{0.5}$ km s$^{-1}$) (cf., Mumma et al. 2003). The weighted-mean production rate for each species is calculated from the individual production rates obtained from the sampled lines (using the
retrieved rotational temperature), where the weight is the inverse of the respective squared stochastic error for a given line (cf. Fig. 2).

We first derive production rates from nucleus-centered extracts (which provide the highest signal-to-noise ratio), but the 'nucleus-centered' Q underestimates the 'global', or 'terminal', production rate owing to loss of flux in the instrumental slit (as a result of seeing effects or comet drift in the slit, etc.). Therefore, we determine the mean values of production rates (symmetric Qs) from extracts equidistant on both sides of the measured spatial intensity profile (Figure 4) – these reach a terminal value at ~ 1'' from the nucleus. We calculate a growth factor for each species, as the ratio between the terminal and nucleus-centered production rate. Some molecules do not have sufficient signal-to-noise ratio away from the nucleus, which requires adopting a growth factor (usually from H$_2$O, measured simultaneously, in the same setting), for the calculation of their terminal production rates. This procedure (averaging of production rates) also corrects for 1-dimensional asymmetries in the gas outflow (Xie and Mumma 1996a, 1996b).

We retrieved production rates for H$_2$O in the KL1, KL2, and MW_A setting, and for the following organic species: CH$_3$OH, HCN, H$_2$CO, C$_2$H$_2$, C$_2$H$_6$ (v$_5$ and v$_7$ bands), CH$_4$ and CO. We present 3-σ upper limits for those species for which we cannot claim a firm detection: H$_2$CO on 4 & 6 Nov.; C$_2$H$_2$ on 4 & 6 Nov.; C$_2$H$_6$ (v$_5$ band) on 6 Nov., and CO on 5 & 6 Nov. CO measurements were combined from 5 & 6 Nov. to improve the signal-to-noise ratio, given the limited time on source in the MW_A setting. The instrumental setting, time on source, global production rate and mixing ratio for each molecule is presented in Table 2. The production rates of the dominant volatile - water, agree within 2-σ on all three dates, and for all three settings used.
4. DISCUSSION

Our high-resolution infrared spectra of comet Encke on three consecutive dates reveal its unusual composition, and very low rotational temperatures consistent with its low water production rate. 6P/d’Arrest is another example of a comet with a very low production rate (comparable to that of Encke), which is also characterized by low rotational temperatures (30-50 K) (Dello Russo et al. 2009). The local collisional excitation rate (c) is directly proportional to the production rate of a comet, according to: \( c = n \sigma V_t \), where \( n \) is the number density \( \left( n \sim \frac{Q}{4 \pi V_o^2} \right) \), \( \sigma \) is the collisional cross-section for excitation, \( V_t \) is the thermal velocity, and \( V_o \) is the gas outflow velocity (Weaver and Mumma 1984). Is it possible that the low rotational temperatures observed in comet Encke are the signature of relaxation by radiative decay dominating collisions in controlling its rotational level population?

Xie and Mumma (1992) examined this question in a detailed study of water in comet 1P/Halley that included collisions of electrons with water, water with water, infrared fluorescent pumping of \( \text{H}_2\text{O} \) with rotational cascade, and radiative decay of \( \text{H}_2\text{O} \) rotational levels. They applied their model for conditions measured during the Giotto coma flythrough (14 March 1986; 0.9 AU). For a water production rate of \( 5 \times 10^{29} \text{ s}^{-1} \) and kinetic temperature of 60 K, they evaluated the excitation & de-excitation rates over the nucleocentric distance range of 1000 km to 3 x 10^5 km. In their model, the water density was \( \sim 6 \times 10^6 \text{ cm}^{-3} \) at 3000 km, well within the coma region where \( \text{H}_2\text{O} \) rotational emission lines are optically-thick and radiative trapping reduces the escape-to-space probability significantly. Xie and Mumma (1992) showed that electron and neutral-neutral collisions dominate rotational excitation and de-excitation of water under such conditions. Since cross-sections and radiative decay times are similar for other polar gases
(CH$_3$OH, H$_2$CO, HCN, CO), we expect they too will be controlled by collisions. Radiative decay rates are zero for apolar gases (CH$_4$, C$_2$H$_6$, etc.), so collisions will control their rotational temperatures so long as fluorescent pumping rates remain small. This is true within the volume sampled in our investigation, since the pumping rates for all molecules are less than one event per 1000 seconds. For conditions in 2P/Encke ($Q = 2.6 \times 10^{27}$ s$^{-1}$, $v_0 \sim 0.8$ km/s), the density of $6 \times 10^6$ cm$^{-3}$ is reached at $\sim 200$ km nucleocentric distance. Most of the molecules sampled in our beam fall within this distance range. We therefore conclude that rotational populations in all molecules sampled in this study (Table 2) are controlled by collisions.

In an attempt to explain the high rotational temperatures found in the near nucleus region of 73P/Schwassmann-Wachmann 3, Fougere et al. 2012 suggest that sublimation of water from warm grains introduced excess heat to the near-nucleus coma, thus preventing adiabatic cooling of the expanding gas and maintaining rotational temperatures far above the adiabatic limit. A similar effect is consistent with the release of water-rich icy grains in C/2006 W1 (Boattini), as inferred from the distinct spatial distributions of polar and apolar volatiles in the coma (Villanueva et al. 2011a). Moreover, our observed (unusual) depletions of primary volatiles in Encke, and its unusual thermal history, suggest that release of ice-mantled grains (and the concomitant excess heat injected by sublimation) is not likely. Thus, we may be seeing the expected adiabatic cooling of expanding gas.

We must also consider the effects of low thermalization efficiency of fast H-atoms, which are by-products of H$_2$O and OH photodissociation, and whose thermalization increases the temperature of the coma (for comets with high gas production rates) after the initial temperature decrease introduced by expansive adiabatic cooling (Combi et al. 2004). However, re-heating
normally operates at greater nucleocentric distances than we sampled in Encke. A detailed
evaluation of these competing effects is deferred to a future publication.

Historically, Encke’s spectral continuum at optical wavelengths has long been noted as unusual.
Optical observations demonstrate a very weak continuum consistent with a deficiency of sub-
micrometer sized dust in Encke. This behavior and observations of a strong thermal IR
continuum (Ney 1974, Campins et al. 1982) were argued to imply a lower than typical fraction of
small dust particles in Encke’s coma (i.e., most dust particles had radii between 5 and 10 μm, or
even > 20 μm) (Gehrz & Ney 1989, Jewitt et al. 2004, Lisse et al. 2004). We observed a strong
infrared continuum, consistent with a substantial contribution from micron-sized grains.

The gaseous activity of Encke reported here agrees with contemporaneous measurements
obtained from the Odin space observatory. Our water production rate in Encke of (2.6 ± 0.1) \times
10^{27} \text{s}^{-1} (weighted mean from all settings, 4-6 Nov.) at a mean heliocentric distance of 1.2 AU, is,
as expected, lower than that measured closer to the Sun: \(Q(\text{H}_2\text{O}) = (4.9 ± 0.7) \times 10^{27} \text{s}^{-1}\), at \(R_h\) of
1.01 AU (16 Nov. 2003), from Odin observations of the 557 GHz line of \(\text{H}_2\text{O}\) (Biver et al. 2007)
(although there is agreement at the 3-σ level). Scaling our production rate, to account for
differences in heliocentric distance, by \(R_h^{-2}\) (\(R_h = 1.2\) AU), provides agreement at the 1-σ level
with Odin measurements.

Encke is an important addition to the growing database of ecliptic comets that have been
characterized at infrared wavelengths. Its composition is unusual in being depleted in most
organic species (HCN, \(\text{H}_2\text{CO}, \text{C}_2\text{H}_2, \text{C}_2\text{H}_6, \text{CH}_4, \text{and CO}) but enriched in \(\text{CH}_3\text{OH}\). The weighted-
mean mixing ratios for measured species are presented in Table 3, along with those of other
Jupiter-family comets (21P/Giacobini-Zinner, 73P/Schwassman-Wachmann-3, 9P/Tempel 1,
6P/d’Arrest, 10P/Tempel 2 and 17P/Holmes) and three Oort cloud (current) ‘end-member’ comets (the severely depleted C/1999 S4 (LINEAR), and the significantly enriched comets C/2001 A2 (LINEAR) and C/2007 W1 (Boattini)). The only organics-enriched member of the presented Jupiter-family group is 17P/Holmes, whose enrichment is most likely overestimated, given its heliocentric distance of observation (2.4 AU) – where water in the inner coma is more likely in the form of ice (as previously discussed (§1)). Table 3 indicates that: (1) the number of ecliptic comets observed at infrared wavelengths is insufficient for statistical analysis, and no clear trends are seen in the current sample; (2) Encke is the ecliptic comet with highest methanol mixing ratio, studied in the infrared.

Encke’s composition is also presented in Fig. 5, in comparison to that of the severely depleted JFC 73P/Schwassman-Wachmann-3C (hereafter 73P/S-W 3-C), the severely depleted C/1999 S4 (LINEAR) (hereafter C/1999 S4), and the enriched C/2001 A2 (LINEAR) (hereafter C/2001 A2) and C/2007 W1 (Boattini). Fig. 5 clearly illustrates the significant depletion of Encke in HCN, H₂CO, C₂H₂ & CO; its moderate depletion in C₂H₆ and CH₄; and its enrichment in CH₃OH.

Our weighted mean mixing ratios (from different dates) for CH₃OH (3.48 ± 0.27%), H₂CO (< 0.13% at 3-σ), and HCN (0.09 ± 0.01%) in Encke are consistent with those measured at radio wavelengths: CH₃OH (4.1%), H₂CO (< 1.4 %, 3-σ), and HCN (0.09%) (Crovisier et al. 2007). Infrared and radio measurements both indicate enrichment of Encke in CH₃OH and depletion in HCN, and our infrared measurements alone indicate depletion in CH₄, C₂H₂, C₂H₆, H₂CO and CO. By contrast, optical observations of a sample of 85 comets found Encke to be ‘typical’ in carbon-chain molecules (A’Hearn et al. 1995; see also Fink et al. 2009), but Cochran et al. (2012) find Encke to be CH/CN-enriched. However, the product species sampled at optical wavelengths can have multiple origins (including release from grains), which greatly complicates
drawing cosmogonic implications from their measured abundance ratios. One possible explanation for the discrepancy between infrared (confirmed by radio) and optical measurements is that some carbon-chain parent molecules not sampled in the infrared may be more abundant in Encke, resulting in typical values for \( \text{C}_2 \) and \( \text{C}_3 \) but depletion in \( \text{C}_2\text{H}_6 \) and \( \text{C}_2\text{H}_2 \) (acetylene is a possible parent of \( \text{C}_2 \), but \( \text{C}_2\text{H}_6 \) is not (Weiler 2012)). Several other comets also show discordant comparisons in product and primary volatile (i.e., potential parent) species (§1).

It is very difficult to determine whether the depletion of 2P/Encke is evolutionary or primordial. Successive depletion during its numerous orbits around the Sun could have induced preferential loss of the most volatile ices (\( \text{CO} \) and \( \text{CH}_4 \), having sublimation temperatures of 25 K and 31 K, respectively) over those having higher sublimation temperatures (e.g., \( \text{CH}_3\text{OH} \), 99 K) (Yamamoto 1985). For example, ecliptic comet 73P/S-W 3-C, has a short period (5.4 years) and is a severely depleted end-member. However, the ecliptic comet 103P/Hartley 2 (\( P = 6.5 \) years) is normal in its organic primary composition (although depleted in \( \text{C}_2\text{H}_2 \), and highly enriched in \( \text{CO}_2 \) (A'Hearn et al. 2011)), and ‘typical’ in its product species. Taken together, these 3 examples suggest that something other than evolutionary processing (e.g., formative conditions) influenced current volatile compositions, although Encke with its very short orbital period and small perihelion distance may represent a special case.

It is possible that if an ecliptic comet formed later in the Solar System’s evolutionary timeline than did Encke, more ionizing x-ray flux from the Sun would reach greater distances thanks to nebular clearing, and the resulting higher H-atom densities – combined with lower temperatures enhancing H-retention on the surfaces of grains – would increase the efficiency of H-atom addition reactions (e.g., more \( \text{C}_2\text{H}_6 \) would form from \( \text{C}_2\text{H}_2 \), and \( \text{CH}_3\text{OH} \) from \( \text{CO}_2 \); see below). The conversion efficiency for \( \text{C}_2\text{H}_2 \) into \( \text{C}_2\text{H}_6 \) can be calculated as \( \text{C}_2\text{H}_6/(\text{C}_2\text{H}_2 + \text{C}_2\text{H}_6) \), and is >
0.8 in Encke. This relatively high value could result from formation in a region with higher H-atom densities, and/or lower temperatures, than were experienced by comets with a lower C$_2$H$_2$ hydrogenation efficiency. High hydrogenation efficiency is also consistent with the low upper limits for CO & H$_2$CO, but significant enrichment of CH$_3$OH in Encke: (H$_2$CO + CH$_3$OH)/(CO + H$_2$CO + CH$_3$OH) > 0.7. Alternatively, a high initial endowment of CO with low conversion to H$_2$CO and CH$_3$OH could indicate that the 'missing' CO (the most volatile species) was lost during Encke's numerous orbits around the Sun. The relatively efficient conversion implied for C$_2$H$_2$ (to ethane) may also suggest that most CO that condensed onto its pre-cometary grains later converted to CH$_3$OH. If true, the severe depletion of CH$_3$OH in C/1999 S4 together with its enrichment in Encke is consistent with this view.

It is important to note that comet Encke is not as severely depleted as C/1999 S4, which comes from the Oort cloud and is considered to be dynamically new. It was previously suggested that C/1999 S4 is depleted because it likely formed closer to the young Sun than 'organics-normal' comets (Mumma et al. 2001). That is a possible explanation for comet Encke's depletion as well, but if so it probably formed farther from the Sun than did C/1999 S4, given Encke's less severe depletion.

In addition to heliocentric distance, other factors must be considered to explain the depletion (or enrichment) of a cometary nucleus, such as localized heating, or formation of the nucleus from fractions originating in regions with diverse chemical composition. Our quantitative production rates on three consecutive dates can test for potential heterogeneity of Encke's nucleus. If the nucleus were heterogeneous, we would expect to see variability in the measured mixing ratios as it rotates and different vents are sequentially activated under the influence of solar radiation (depending on the size of the fractions, locations of vents, etc.). The rotation period of Encke was
measured to be $11.056 \pm 0.024 \text{ h}$ (sidereal, Jockers et al. 2011), $11.083 \pm 0.003 \text{ h}$ (synodic, Lowry and Weissman 2007), and $11.079 \pm 0.009 \text{ h}$ (synodic, Fernández et al. 2005). Our KL2 observations were separated by $\sim 47 \text{ h} 30 \text{ m}$ (4.3 rotation periods) and we likely observed release from different regions of Encke's nucleus, but our KL1 observations were separated by $\sim 22 \text{ h}$ (2.0 periods), and may sample the same region. We present a comparison of the mixing ratios in comet Encke on different dates in Figure 6, and see agreement in the abundances measured for each species within $1-\sigma$ ($2-\sigma$ for HCN). This lack of temporal variability in the measured organic abundances is consistent with compositional homogeneity in the mean volatile release (averaged over all active vents, regardless of possible chemical diversity), similar to comet 103P/Hartley-2 (Mumma et al. 2011, Dello Russo et al. 2011), C/2000 WM1 (Radeva et al. 2010), and C/2004 Q2 (Bonev et al. 2009). However, our sparse temporal sampling and limited spatial information prevent us from drawing a definitive conclusion on this question.

5. SUMMARY

The ecliptic comet Encke is an important addition to our growing database of comets studied at infrared wavelengths, first, because fewer ecliptic comets have been studied in comparison to Oort cloud comets, and second, because it is a dynamical end-member owing to its very short orbital period of 3.3 years. Our investigation of Encke resulted in the following conclusions:

1. Encke exhibits one of the lowest gas production rates for water among comets in our sample, with $Q(\text{H}_2\text{O})$ being $(2.6 \pm 0.1) \times 10^{27} \text{ s}^{-1}$ (weighted mean from all settings, 4-6 Nov.) at a mean heliocentric distance of 1.2 AU. The scatter among individual measurements is somewhat larger than the error in the mean (Table 2).
2. Encke exhibits very low rotational temperatures in the near-nucleus coma ($T_{\text{rot}} \sim 20 - 30$ K, for H$_2$O, CH$_3$OH and HCN). Collisions are sufficient to maintain the rotational level populations. The absence of excess heating by water released from icy-mantled grains likely permits the predicted adiabatic cooling of outflowing gas in the near nucleus coma to control the rotational temperature.

3. Encke is depleted in HCN, H$_2$CO, C$_2$H$_2$, C$_3$H$_6$, CH$_4$ and CO, but is enriched in CH$_3$OH (it being the least volatile primary species other than H$_2$O). Our measurements of CH$_3$OH, H$_2$CO and HCN agree with those from radio observations. The comet may have lost most of its volatiles during its numerous orbits around the Sun, or it may have formed closer to the young Sun than did organics-normal and organics-enriched comets.

4. Mixing ratios in Encke are consistent on different dates, but the temporal sampling of our data is insufficient for a firm conclusion as to whether its nucleus is homogeneous in the bulk. More observations of Encke are necessary to confirm its homogeneity.

In our growing database of Oort cloud and ecliptic comets, we see no correlation of chemical composition with originating dynamical reservoir or orbital period. For example, the dynamically new comet C/1999 S4 is more severely depleted than Encke, and so is the 5.4 year period (split) ecliptic comet 73P/SW 3-B and -C; while the 6.5 year period ecliptic comet 103P/Hartley 2 is normal in its composition (except for its depletion in acetylene). More comets need to be observed at infrared wavelengths, which sample primary volatiles native to the cometary nucleus, and uniquely sample the symmetric hydrocarbons. The ‘organics-depleted’, ‘organics-normal’ and ‘organics-enriched’ (along with ‘atypical’) compositional classes should be regarded as a (plausible) working hypothesis. A statistically significant sample of comets will permit us to test this classification. At present we do not know if comets currently categorized as
"depleted" or "enriched" are in fact compositional end members. Future observations would elucidate whether the current classes are well separated or if there is a more continuous distribution of abundances amongst the comet population. Measurements of cosmogonic parameters, such as spin temperature of water (indicating its formation temperature) and D/H ratios in comets, are needed in order to evaluate cometary composition as one of the keys in understanding the formation and evolution of our Solar System.

Special Acknowledgment:

This NIRSPEC investigation of comet 2P/Encke was initiated as part of our group's long-term study of cometary volatile composition, and in support of the planned 12 November 2003 encounter of Encke by the CONTOUR spacecraft (J. Veverka, Principal Investigator). The spacecraft was launched successfully on 3 July 2002, but it failed to achieve the trajectory needed to intercept the comet owing to its breakup during the orbit insertion maneuver (http://solarsystem.nasa.gov/missions/profile.cfm?MCode=CONTOUR&Display=ReadMore). But by inspiring this and other related investigations that returned new fundamental knowledge regarding this iconic comet, CONTOUR also succeeded! Thanks, Joe!

M. J. Mumma, for the Team.

General Acknowledgments:

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(RTOP 344-53-51 to MJM). GLV and MAD acknowledge support from NASA’s Planetary Astronomy (08-PAST08-0034 to GLV, 09-PAST09-0034 to MAD) and Planetary Atmospheres (08-PATM08-0031 to GLV, 09-PATM09-0080 to MAD) Programs. BPB acknowledges support by NSF’s Astronomy and Astrophysics Research Grants program NSF (1211362; 0807939) and by Cooperative Agreement NASA#NNX08AW44A. We thank Hideyo Kawakita and Reiko Furusho for their helpful feedback in preparing the observations. The data presented herein were obtained at the W. M. Keck Observatory, operated as a scientific partnership among CalTech, UCLA, and NASA. This Observatory was made possible by the generous financial support of the W. M. Keck Foundation.
References


A’Hearn, M. F. and 33 co-authors, 2011. EPOXI at comet Hartley 2. Science, 332, 1396-1400


Bonev, B. P., 2005. Towards a chemical taxonomy of comets: infrared spectroscopic methods for quantitative measurements of cometary water, University of Toledo, dissertation


Radeva, Y. L., 2010. Infrared spectroscopy of parent volatiles in comets: Chemical diversity and a new fluorescence model for the ethane ν3 band, University of Maryland, dissertation


Villanueva, G. L., Mumma, M. J., and Magee-Sauer, K., 2011. Ethane in planetary and cometary atmospheres: Transmittance and fluorescence models of the ν7 band at 3.3 μm. JGRE 116, E08012


Table 1: Log of Observations of comet Encke.

<table>
<thead>
<tr>
<th>UT Time (2003)</th>
<th>Integration time [min]</th>
<th>Setting$^1$</th>
<th>Frequency range of setting [cm$^{-1}$]</th>
<th>$R_h$$^|$ [AU]</th>
<th>$\Delta$$^|$ [AU]</th>
<th>$\Delta_{dot}$$^|$ [km s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 Nov., 5:09-7:17</td>
<td>84</td>
<td>KL2</td>
<td>3464 – 2759</td>
<td>1.210</td>
<td>0.313</td>
<td>-13.59</td>
</tr>
<tr>
<td>9:29-9:52</td>
<td>20</td>
<td>KL1</td>
<td>3521 – 2833</td>
<td>1.208</td>
<td>0.312</td>
<td>-13.19</td>
</tr>
<tr>
<td>5 Nov., 7:23-8:30</td>
<td>48</td>
<td>KL1</td>
<td>3521 – 2833</td>
<td>1.194</td>
<td>0.305</td>
<td>-12.45</td>
</tr>
<tr>
<td>9:31-10:05</td>
<td>12</td>
<td>MW_A</td>
<td>2162 - 1996</td>
<td>1.193</td>
<td>0.304</td>
<td>-12.25</td>
</tr>
<tr>
<td>6 Nov., 4:40-6:21</td>
<td>80</td>
<td>KL2</td>
<td>3464 – 2759</td>
<td>1.180</td>
<td>0.299</td>
<td>-11.78</td>
</tr>
<tr>
<td>9:18-9:50</td>
<td>14</td>
<td>MW_A</td>
<td>2162 - 1996</td>
<td>1.178</td>
<td>0.297</td>
<td>-11.31</td>
</tr>
</tbody>
</table>

$^1$The KL1 setting simultaneously samples CH$_3$OH, C$_2$H$_6$ & H$_2$O. The KL2 setting simultaneously samples HCN, CH$_4$, C$_2$H$_2$, C$_2$H$_6$, H$_2$CO & H$_2$O; and the MW_A setting simultaneously samples CO & H$_2$O.

$^\|$ $R_h$ is the heliocentric distance, $\Delta$ is the geocentric distance, and $\Delta_{dot}$ is the line-of-sight velocity.
Table 2. Production rates and mixing ratios of volatiles in 2P/Encke.¹

<table>
<thead>
<tr>
<th>Setting / Time on Source</th>
<th>Molecule (T&lt;sub&gt;rot&lt;/sub&gt;)</th>
<th>Global Q [10&lt;sup&gt;-25&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;]</th>
<th>Mixing Ratio %</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 Nov. 2003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KL1 / 20 min</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O (29&lt;sup&gt;-7&lt;/sup&gt;/±10 K)</td>
<td>215.7 ± 25.3</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; ν&lt;sub&gt;7&lt;/sub&gt; (29 K)</td>
<td>0.7 ± 0.1</td>
<td>0.32 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>CH₃OH (29 K)</td>
<td>8.5 ± 1.5</td>
<td>3.93 ± 0.69</td>
</tr>
<tr>
<td>KL2 / 84 min</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O (29 K)</td>
<td>272.2 ± 86.7</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>H&lt;sub&gt;2&lt;/sub&gt;CO           (29 K)</td>
<td>&lt;0.4 at 3σ</td>
<td>&lt;0.13 at 3σ</td>
</tr>
<tr>
<td></td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; ν&lt;sub&gt;5&lt;/sub&gt; (29 K)</td>
<td>1.0 ± 0.4</td>
<td>0.36 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>CH₄ (29 K)</td>
<td>0.9 ± 0.4</td>
<td>0.31 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>HCN (29 K)</td>
<td>0.4 ± 0.1</td>
<td>0.13 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt; (29 K)</td>
<td>&lt;0.3 at 3σ</td>
<td>&lt;0.10 at 3σ</td>
</tr>
<tr>
<td>5 Nov. 2003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KL1 / 48 min</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O (30&lt;sup&gt;-2&lt;/sup&gt;/±2 K)</td>
<td>298.0 ± 23.9</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; ν&lt;sub&gt;7&lt;/sub&gt; (29 K)</td>
<td>0.9 ± 0.1</td>
<td>0.31 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>CH₃OH (24&lt;sup&gt;-5&lt;/sup&gt;/±6 K)</td>
<td>9.1 ± 1.0</td>
<td>3.01 ± 0.28</td>
</tr>
<tr>
<td></td>
<td>CH₃OH (30 K)</td>
<td>10.2 ± 1.0</td>
<td>3.40 ± 0.29</td>
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</tbody>
</table>
### MWA Combined

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</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>321.8 ± 82.0</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>(30 K)²</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>CO</td>
<td>&lt; 5.7 at 3σ</td>
<td>&lt; 1.77 at 3σ</td>
</tr>
<tr>
<td></td>
<td>(30 K)²</td>
<td></td>
<td></td>
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</tbody>
</table>

### 6 Nov. 2003

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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KL2 / 80 min</td>
<td>H₂O</td>
<td>256.4 ± 20.4</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>(30 K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂CO</td>
<td>&lt; 0.3 at 3σ</td>
<td>&lt; 0.13 at 3σ</td>
<td></td>
</tr>
<tr>
<td>(30 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₆ v₅</td>
<td>&lt; 0.6 at 3σ</td>
<td>&lt; 0.23 at 3σ</td>
<td></td>
</tr>
<tr>
<td>(30 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>1.3 ± 0.7</td>
<td>0.52 ± 0.28</td>
<td></td>
</tr>
<tr>
<td>(30 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCN</td>
<td>0.18 ± 0.03</td>
<td>0.07 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>(20²/₁₈ K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCN</td>
<td>0.21 ± 0.04</td>
<td>0.08 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>(30 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₂</td>
<td>&lt; 0.2 at 3σ</td>
<td>&lt; 0.08 at 3σ</td>
<td></td>
</tr>
<tr>
<td>(30 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹Production rates for H₂O assume an equilibrium Ortho-to-Para ratio of 3.0. Detailed analysis of the OPR in comet Encke is reserved for a further publication.

²The production rates of H₂O and CO for MW A are based on data from 5 Nov. (12 min on source) and 6 Nov. (14 min on source), which were combined to provide a higher signal to noise ratio.
Table 3. Mixing ratios in 2P/Encke, in other Jupiter-family comets; and in ‘organics-depleted’ and ‘organics-enriched’ end-member Oort Cloud comets.

<table>
<thead>
<tr>
<th>Comet</th>
<th>CH₃OH</th>
<th>HCN</th>
<th>H₂CO</th>
<th>C₂H₂</th>
<th>C₂H₆</th>
<th>CH₄</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>73P/S-W 3-C①</td>
<td>0.149</td>
<td>0.242</td>
<td>0.147</td>
<td>0.049</td>
<td>0.107</td>
<td>&lt;0.25</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>± 0.029</td>
<td>± 0.014</td>
<td>± 0.033</td>
<td>± 0.020</td>
<td>± 0.011</td>
<td></td>
<td>± 0.13</td>
</tr>
<tr>
<td>21P/Giacobini-Zinner②</td>
<td>1.22</td>
<td>&lt;0.27</td>
<td>&lt;0.8</td>
<td>&lt;0.42</td>
<td>0.136</td>
<td>-</td>
<td>10.25</td>
</tr>
<tr>
<td></td>
<td>± 0.11</td>
<td>± 0.029</td>
<td>± 0.014</td>
<td>± 0.020</td>
<td>± 0.011</td>
<td>± 0.13</td>
<td></td>
</tr>
<tr>
<td>9P/Temple 1③ (pre-impact)</td>
<td>1.3</td>
<td>0.18</td>
<td>-</td>
<td>-</td>
<td>0.23</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>± 0.2</td>
<td>± 0.06</td>
<td>± 0.02</td>
<td>± 0.01</td>
<td>± 0.02</td>
<td>± 0.02</td>
<td></td>
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<tr>
<td>9P/Temple 1③ (post-impact, including ejecta)</td>
<td>0.99</td>
<td>0.22</td>
<td>-</td>
<td>0.13</td>
<td>0.40</td>
<td>0.54</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>± 0.17</td>
<td>± 0.03</td>
<td>± 0.01</td>
<td>± 0.02</td>
<td>± 0.02</td>
<td>± 0.02</td>
<td></td>
</tr>
<tr>
<td>6P/δ'Arrest④</td>
<td>1.42</td>
<td>0.034</td>
<td>0.36</td>
<td>&lt;0.052</td>
<td>0.256</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>± 0.30</td>
<td>± 0.008</td>
<td>± 0.09</td>
<td>± 0.052</td>
<td>± 0.061</td>
<td>± 0.06</td>
<td></td>
</tr>
<tr>
<td>10P/Temple 2⑤</td>
<td>1.58</td>
<td>0.13</td>
<td>&lt;0.11</td>
<td>&lt;0.07</td>
<td>0.39</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>± 0.23</td>
<td>± 0.02</td>
<td>± 0.01</td>
<td>± 0.02</td>
<td>± 0.02</td>
<td>± 0.02</td>
<td></td>
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<tr>
<td>103P/Hartley 2⑥</td>
<td>2.28</td>
<td>0.26</td>
<td>0.23</td>
<td>0.08</td>
<td>0.75</td>
<td>&lt;1.2</td>
<td>-</td>
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<tr>
<td></td>
<td>± 0.38</td>
<td>± 0.02</td>
<td>± 0.01</td>
<td>± 0.02</td>
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<tr>
<td>17P/Holmes⑦</td>
<td>3.0</td>
<td>0.538</td>
<td>-</td>
<td>0.344</td>
<td>1.90</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>± 1.0</td>
<td>± 0.075</td>
<td>± 0.053</td>
<td>± 0.053</td>
<td>± 0.54</td>
<td>± 0.54</td>
<td></td>
</tr>
<tr>
<td>2P/Encke⑧</td>
<td>3.48</td>
<td>0.09</td>
<td>&lt;0.13</td>
<td>&lt;0.08</td>
<td>0.32</td>
<td>0.34</td>
<td>&lt;1.77</td>
</tr>
<tr>
<td></td>
<td>± 0.27</td>
<td>± 0.01</td>
<td>± 0.03</td>
<td>± 0.03</td>
<td>± 0.10</td>
<td>± 0.10</td>
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<tr>
<th>Mixing Ratios in End-Member Oort Cloud Comets</th>
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<tr>
<td>C/1999 S4⑨ (Organics-Depleted)</td>
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<tr>
<td>(Organics-Depleted)</td>
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<tr>
<td>C/2001 A2⑩ (Organics-Enriched)</td>
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<tr>
<td>(Organics-Enriched)</td>
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<tr>
<td>C/2007 W1 (Boattini)\textsuperscript{XI}</td>
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<td>----------------------------------------</td>
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<tr>
<td>(Organics-Enriched)</td>
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\textsuperscript{I}Dello Russo et al. 2007 (C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{2}, HCN, H\textsubscript{2}CO & CH\textsubscript{3}OH, 14.5 May 2006), Villanueva et al. 2006 (CH\textsubscript{4}, 7 Apr. 2006), DiSanti et al. 2007a (CO, 27 & 30 May 2006).

\textsuperscript{II}Weaver et al. 1999 (C\textsubscript{2}H\textsubscript{2}, HCN, H\textsubscript{2}CO, Oct. 25-29 1998), Mumma et al. 2000 (CO, Oct. 2-10 1998) & DiSanti et al. 2012 (C\textsubscript{2}H\textsubscript{6} & CH\textsubscript{3}OH, Jun. 3 2005).


\textsuperscript{IV}Dello Russo et al. 2009 (11 Aug. 2008).

\textsuperscript{V}Paganini et al. 2012 (26 Jul. 2010).

\textsuperscript{VI}Mumma et al. 2011 (22 Oct. 2010, mixing ratios in agreement with those presented for other dates; CH\textsubscript{4} is for 16 Nov.).

\textsuperscript{VII}Dello Russo et al. 2008 (27 & 31 Oct. 2007).

\textsuperscript{VIII}This work. Values are weighted means from different dates; 3-\sigma upper limits are provided where indicated.

\textsuperscript{IX}Mumma et al. 2003 (13 Jul. 2000).


\textsuperscript{XI}Villanueva et al. 2011a (9 & 10 Jul. (weighted means), mixing ratios relative to symmetric water).
Figure 1: 2P/Encke cometary spectrum and superimposed terrestrial transmittance model (dashed line) for KL1, Order 27, on 5 Nov. 2003 (upper panel), and residual spectrum (lower panel). Spectral lines of H$_2$O, OH, and blends are seen. The flux density scale is shown at left, and the (±1-σ) noise envelope is shown as dashed lines centered on zero flux density, in each panel.
Figure 2: Excitation analysis for H$_2$O on 4 Nov. (Panel A), CH$_3$OH on 5 Nov. (Panel B), H$_2$O on 5 Nov. (Panel C), and HCN on 6 Nov. (Panel D). At the retrieved $T_{\text{rot}}$, the agreement among production rates derived from individual measured lines is satisfactory, for each species. Rotational temperatures for H$_2$O in the KL1 setting (Panels A & C) are retrieved from the combination of spectral lines in echelle orders 26 and 27.
Figure 3: Residual features for H₂O on 4 Nov. (Panel A1 for Order 26 & Panel A2 for Order 27); CH₃OH on 5 Nov. (Panel B), H₂O on 5 Nov. (Panel C1 for Order 26 & Panel C2 for Order 27), and HCN on 6 Nov. (Panel D), with the fluorescence model for each molecule superimposed in red. The combination of spectral lines sampled in orders 26 and 27 for H₂O on 5 Nov. resulted in the best-constrained $T_{rot}$ of $30 \pm 2/_{+2}$ K.
Figure 4: Emission spatial profiles for H$_2$O and C$_2$H$_6$ (KL1 setting, Nov. 5) in black, and dust continuum in red. Asymmetry in the spatial profile is compensated by extracting production rates on both sides of the profile, and reporting an averaged global production rate. The continuum profile is clearly displaced from the gas profile, suggesting preferential outgassing towards the sun. The orientation of the instrument slit (89°) is shown on the sky plane, as well as the aspect in the Sun-Nucleus-Observer plane.
**Figure 5:** Comparison among mixing ratios of organic species in the severely depleted ecliptic comet 73P/S-W 3-C, the severely depleted Oort cloud comet C/1999 S4, the ecliptic comet Encke, and the enriched Oort cloud comets C/2001 A2 and C/2007 W1 (Boattini). Organic species are presented on the figure in terms of decreasing sublimation temperature (from left to right). Comet Encke is enriched in CH$_3$OH; and depleted in HCN, H$_2$CO, C$_2$H$_2$, C$_2$H$_6$, CH$_4$ & CO.
Volatile Abundances Relative to $\text{H}_2\text{O}$

Figure 6: Agreement among mixing ratios of organic species in 2P/Encke on 4-6 Nov. 2003, within $1\sigma$ ($2\sigma$ for HCN). The lack of variability would suggest homogeneity of Encke’s nucleus, however, we lack sufficient temporal sampling to make a firm conclusion.