Pre-and post-perihelion observations of C/2009 P1 (Garradd): Evidence for an oxygen-rich heritage?

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We conducted pre- and post-perihelion observations of Comet C/2009 P1 (Garradd) on UT 2011 October 13 and 2012 January 8, at heliocentric distances of 1.83 and 1.57 AU, respectively, using the high-resolution infrared spectrometer (NIRSPEC) at the Keck II 10-m telescope on Mauna Kea, HI. Pre-perihelion, we obtained production rates for nine primary volatiles (native ices): H2O, CO, CH3OH, CH4, C2H6, HCN, C2H2, H2CO, and NH3. Post-perihelion, we obtained production rates for three of these (H2O, CH4, and HCN) and sensitive upper limits for three others (C2H2, H2CO, and NH3). CO was enriched and C2H2 was depleted, yet C2H6 and CH3OH were close to their current mean values as measured in a dominant group of Oort cloud comets. This may indicate processing of its pre-cometary ices in a relatively oxygen-rich environment.

Our measurements indicate consistent pre- and post-perihelion abundance ratios relative to H2O, suggesting we were measuring compositional homogeneity among measured species to the depths in the nucleus sampled. However, the overall gas production was lower post-perihelion despite its smaller heliocentric distance on January 8. This is qualitatively consistent with other studies of C/2009 P1, perhaps due to seasonal differences in the heating of one or more active regions on the nucleus.

On October 13, the water profile showed a pronounced excess towards the Sun-facing hemisphere that was not seen in other molecules, including H2O on January 8, nor in the dust continuum. Inter-comparison of profiles from October 13 permitted us to quantify contributions due to release of H2O from the nucleus, and from its release in the coma. This resulted in the latter source contributing 25–30% of the total observed water within our slit, which covered roughly ±300 km by ±4500 km from the nucleus. We attribute this excess H2O, which peaked at a mean projected distance of 1300–1500 km from the nucleus, to release from water-rich, relatively pure icy grains.

1. Introduction

More than any other Solar System material, the ices contained in the nuclei of comets (i.e., their native ices) retain a relatively well-preserved record of conditions when and where these primitive small bodies formed. Comets reside for long periods of time in the outer Solar System, and clues to its formation and evolution are provided through their volatile compositions (e.g., see reviews by Mumma and Charnley, 2011; DiSanti and Mumma, 2008; Bockelée-Morvan et al., 2005).

Comets today belong to (at least) two distinct dynamical reservoirs, the Kuiper Belt (KB) and the Oort cloud (OC), thought to be the dominant source regions for ecliptic and nearly isotropic (long-period and dynamically-new) comets, respectively. Until relatively recently it was thought that short-period comets formed more or less in situ in the KB (at heliocentric distances $R_h > 30$ AU), while those from the OC formed in the $R_h \sim 5–30$ AU region and were subsequently ejected through gravitational interaction with the giant planets. If true, this suggested distinctly differing compositions might be expected for these two dynamical populations of comets (Mumma et al., 1993).

This reasoning has since evolved to new paradigms, stemming from the Nice model (Gomes et al., 2005; Morbidelli et al., 2008).
that predicts considerable disruption of the outer Solar System due to outward migration of young Saturn through the 1.2 orbital resonance with Jupiter. The more recent “Grand Tack” model (Walsh and Morbidelli, 2011) invokes inward migration of the giant planets within the first $5 \times 10^5$ years of the Solar System – as a means of explaining the relatively small mass of Mars and also the formation of small bodies (especially asteroids) in the inner Solar System ($R_0 \sim 1-3$ AU) – followed by their outward migration. These models predict compositional “blurring” of comets along dynamical lines, in the sense that diversity in cometary compositions should exist in both KB and OC reservoirs, and indeed this is observed. The models however do not account for the observed discovery fraction (up to 90%) of OC comets may have originated in the environs of neighboring stars in the Sun’s birth cluster (Levison et al., 2010), although more recent modeling suggests revising this fraction downward (Brasser et al., 2012).

Here we report abundances for nine primary volatiles in the dynamically new Comet C/2009 P1 (Garradd; hereafter C/2009 P1) based on observations obtained near perihelion (q = 0.56 AU, $\Delta$ = 1.836 AU, d/r = +19.2 km s$^{-1}$, $d_r$/dr = −12.2 km s$^{-1}$) on 2011 October 13 and shortly following perihelion (December 23, q = 1.55 AU) on 2012 January 8 (Table 1) using the NIRSPEC infrared high-resolution echelle combination (McLean et al., 1998, 2000) at the Keck II 10-m telescope on Mauna Kea, Hawaii. On October 13, C/2009 P1 reached the Keck II west elevation limit at 06:32 UT, which is the maximum elevation limit without vignetting. The high terrestrial water burden on October 13 (~5 precipitable mm) limited the number of accessible cometary water lines, particularly in order 27 of the KL1 setting (see Section 3.1). The water burden on January 8 was relatively modest (~1.5 mm), however the air mass of C/2009 P1 was higher compared with October 13. Spectral extracts, representing sums over nine spatial pixels (1.78 arcsec) centered on peak emission intensities, are shown for October 13 (Figs. 1 and 2) and January 8 (Fig. 3).

### 2. Observations and data processing

We observed C/2009 P1 pre-perihelion on UT 2011 October 13, and also shortly following perihelion (December 23, q = 1.55 AU) on 2012 January 8 (Table 1) using the NIRSPEC infrared high-resolution echelle combination (McLean et al., 1998, 2000) at the Keck II 10-m telescope on Mauna Kea, Hawaii. On October 13, C/2009 P1 reached the Keck II west elevation limit at 06:32 UT, which translated to approximately 1 h and 40 min of clock time following focus and acquisition at the start of the night. In spite of this limited available time, the combination of broad spectral coverage and high-throughput optics afforded by NIRSPEC allowed us to sample a large suite of primary volatiles using three distinct cross-disperser/echelle combinations (Table 1). On January 8, C/2009 P1 became available in the east toward the end of the night, only allowing accommodation of a setting that encompasses the largest number of organic molecules simultaneously with H$_2$O.

For our observations, we oriented the slit along the Sun-comet line (PA = 76° on October 13, 330° on January 8), which was maintained throughout our observations of C/2009 P1 by using NIRSPEC in active rotator (i.e., ‘Position Angle’) mode. Comet and supporting flux standard star spectral frames (Table 1, note ‘a’) were acquired in our standard ABBA cadence, with both A- and B-beams present in the slit (e.g., see Villanueva et al., 2011a; Bonev, 2005; DiSanti et al., 2001b) and separated by 12 arcsec.

Cometary and stellar data were processed using our custom algorithms (e.g., Villanueva et al., 2011a; Bonev, 2005; DiSanti et al., 2001) that correct for anamorphic optics and provide highly accurate spatial and spectral registrations. We matched abundances of molecular absorbers in the terrestrial atmosphere to extracted spectral, using the Line-By-Line Radiative Transfer Model (LBLRTM; Clough et al., 2005) together with our custom updates (Villanueva et al., 2011b). The high terrestrial water burden on October 13 (~5 precipitable mm) limited the number of accessible cometary water lines, particularly in order 27 of the KL1 setting (see Section 3.1). The water burden on January 8 was relatively modest (~1.5 mm), however the air mass of C/2009 P1 was higher compared with October 13. Spectral extracts, representing sums over nine spatial pixels (1.78 arcsec) centered on peak emission intensities, are shown for October 13 (Figs. 1 and 2) and January 8 (Fig. 3).

### 3. Rotational temperatures, production rates, and spatial distributions

#### 3.1. Excitation analysis

Because vibrational bands are in general not sampled completely, obtaining accurate production rates for observed molecules requires knowledge of the relative populations of their rotational levels. These are characterized by a rotational temperature ($T_{rot}$), determined by comparing observed and modeled intensities (fluorescence efficiencies; i.e., g-factors) for emission lines

<table>
<thead>
<tr>
<th>NIRSPEC setting</th>
<th>UT start–end</th>
<th>Molecule (order)$^b$</th>
<th>$T_{rot}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pre-perihelion – UT 2011 October 13</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KL2</td>
<td>04:42–05:42</td>
<td>H$_2$O (26)</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HCN, $C_2$H$_2$, NH$_3$ (25)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH$_4$ (23)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H$_2$CO (21)</td>
<td></td>
</tr>
<tr>
<td>MWA</td>
<td>05:52–06:15</td>
<td>H$_2$O (15, 16)</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO (16)</td>
<td></td>
</tr>
<tr>
<td>KL1</td>
<td>06:26–06:35</td>
<td>H$_2$O (26, 27)</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH$_4$ (23)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH$_3$OH (22, 23)</td>
<td></td>
</tr>
<tr>
<td><strong>Post-perihelion – UT 2012 January 8</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KL2</td>
<td>15:21–15:43</td>
<td>H$_2$O (26)</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HCN, $C_2$H$_2$, NH$_3$ (25)</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>CH$_4$ (23)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H$_2$CO (21)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ On October 13 (January 8), flux calibration was established through spectra of the bright infrared standard star HR-8541 (HR-4357) acquired immediately following (prior to) the comet observations.

$^b$ Measured primary molecules and NIRSPEC echelle order in which their emissions occur.

$^c$ Total on-source integration times.
spanning a sufficiently large range of rotational energies. Our line g-factors are based on ro-vibrational band fluorescence models we developed for each molecule: H2O multiple bands (Figs. 1a, 2c and 3c; Villanueva et al., 2012a), OH, v1 and v2 - v1 (Figs. 1b, 2c and 3a-3c; Bonev, 2005, Bonev et al., 2006), C2H6 v7 (Fig. 2a; Villanueva et al., 2011b), CH4 v3 (Figs. 1b and 3b; Gibb et al., 2003), C2H2 v3 and v2 + v4 + v5 (Figs. 1c and 3a; Villanueva et al., 2013; Kawakita and Mumma, 2011), HCN v1 (Figs. 1c and 3a; Lippi et al., 2013; Villanueva et al., 2013), H2CO v1 and v5 (Reuter et al., 1989; DiSanti et al., 2006), and CH3OH v2 (Fig. 2a; DiSanti et al., 2012b). These models make use of a realistic solar flux that includes Fraunhofer lines and incorporates the cometary heliocentric velocity (dR/dt in Table 1) in calculating fluorescent pumping rates (see Villanueva et al., 2011a for additional details).

The high terrestrial water burden on October 13 resulted in poor transmittance for many of the cometary H2O lines, and so introduced correspondingly large uncertainties in line-by-line production rates retrieved from transmittance-corrected line fluxes (see Eq. (1) below). The H2O line near 3514.4 cm⁻¹ (rest frequency) is normally the strongest observed in the L-band, but it suffered from high opacity (transmittance less than 1%), and was not detected (Fig. 2c). Using observed lines in the three orders shown in Fig. 2c yielded a poorly constrained rotational temperature for water (T_rot = 42 ± 24 K).

We retrieved more precise rotational temperatures independently for HCN, CH4, CO, C2H6, and CH3OH on October 13 (Table 2). Their weighted mean value (T_rot = 48 ± 4 K; 1σ uncertainty) is consistent with T_rot measured for C/2009 P1 near R = 2.1 AU (40 ± 7 K; Villanueva et al., 2012c) and 2.0 AU (50 K; Paganini et al., 2012). We take our weighted mean T_rot (48 K) to be the most probable temperature, and adopt this for all molecules on October 13. From our January 8 observations, we measured T_rot = 55 ± 10 K based on water lines in order 26 (Fig. 3c). We were unable to determine T_rot for HCN nor CH4, and therefore adopt 55 K for all molecules measured on January 8.

We note that individual values of T_rot measured on October 13 agree within their 1σ uncertainties (Table 2), as is generally found among molecules from studies of previous comets. This is consistent with electrons and fast H-atoms, released primarily
through photo-dissociation of H$_2$O, controlling $T_{\text{rot}}$ in the coma (see Xie and Mumma, 1996; DiSanti et al., 2001 and references therein). It may also explain the similar $T_{\text{rot}}$ (also within 1σ) measured post-perihelion for H$_2$O, for example if the smaller $R_n$ on January 8 was compensated by the lower water production rate $Q(H_2O)$. Our lower post-perihelion $Q(H_2O)$ is consistent with pre-/post-perihelion asymmetries found by other observers of C/2009 P1 (Section 4.3), and holds regardless of the exact values we adopt for $T_{\text{rot}}$, both on October 13 and January 8 (see Section 3.2.1).

### 3.2. Production rates

Our formalism for determining production rates is based on the spatial distribution of emissions along the slit (i.e., the spatial profiles; Fig. 4) and is well documented in the literature (e.g., Villanueva et al., 2011a; Bonev, 2005). A brief summary is provided here.

We calculate a nucleus-centered molecular production rate ($Q_{\text{nc}}$) from signal contained in the central nine spatial pixels centered on the peak emission intensity. For a given emission line (or, in the case of blends, for each group of lines):

$$Q_{\text{nc, line}} = \frac{4\pi A^2}{\tau f(x)} \frac{F_{\text{line}}}{g_{\text{line}}}$$  \hspace{0.5cm} (1)

In Eq. (1), $\tau$ (s) and $g_{\text{x}}$ (W molecule$^{-1}$) represent the photo-dissociation lifetime and fluorescence g-factor (both evaluated at $R_n = 1$ AU), $F_{\text{line}}$ (W m$^{-2}$) is the line flux at the top of the terrestrial atmosphere, and geocentric distance ($A$) is expressed in meters. For each molecular species, the quantity $f(x)$ represents the fraction of all molecules in the coma contained in the beam assuming release solely from the nucleus (i.e., purely native release). It is a geometrical parameter that decreases with increasing distance from the nucleus and depends on $R_n$, $A$, and gas outflow speed $v_{\text{gas}}$, assumed to be spherically-symmetric and equal to 800 $R_n^{0.5}$ m s$^{-1}$ (Biver et al., 2006, 2002). Because $f(x)$ varies approximately as $t_{\text{sen}}^{-1}$ for our field of view, our production rates are relatively insensitive to assumed photo-dissociation lifetime (e.g., see DiSanti et al., 2001). In practice $Q_{\text{nc}}$ for a molecule is the mean of its line-by-line nucleus-centered production rates weighted by their individual stochastic errors.

For each molecule having emission with sufficient signal-to-noise, we then calculate the production rate at regular intervals (steps) along the slit (i.e., along the spatial profile) using Eq. (1), based on the encompassed $F_{\text{line}}$ and incorporating the value of $f(x)$ at each step. Outside the seeing-dominated inner coma, the production rates so determined increase to a constant value (within noise) that we take to be the terminal (or total) production rate ($Q_{\text{tot}}$). This establishes a “growth factor” (GF) as the ratio $Q_{\text{tot}}/Q_{\text{nc}}$ (e.g., see Appendix B2 in Bonev et al., 2006, and Dello Russo et al., 1998 for details regarding the “Q-curve” formalism), or:

$$Q_{\text{tot}} = Q_{\text{nc}} \times \text{GF}.$$  \hspace{0.5cm} (2)

We generally find growth factors among simultaneously-measured primary volatiles to agree within uncertainties. For this reason we adopt a common value, given by the weighted mean of measured growth factors for all (native) species within each given setting (see Section 3.2.1). However, release of molecules in the coma can result in larger growth factors. In Section 3.3 we discuss the influence of an additional, extended source of H$_2$O on October 13.

#### 3.2.1. Dependence of production rates on $T_{\text{rot}}$ and GF

We obtained consistent production rates whether we used a common rotational temperature or each individually measured $T_{\text{rot}}$ (see note ‘b’ of Table 2). Including $\sigma T_{\text{rot}}$ increases uncertainties in $Q_{\text{nc}}$ (listed in parentheses), and using individually measured $\sigma T_{\text{rot}}$ likely overestimated $\sigma Q_{\text{nc}}$ since their $T_{\text{rot}}$ were less well constrained. For this reason, and because $T_{\text{rot}}$ was not measured for all species, we take $\sigma Q_{\text{nc}}$ (and $\sigma Q_{\text{tot}}$) based on the “combined” $\sigma T_{\text{rot}}$ (+4 K on October 13) to provide the most consistent measure of molecular production rates.

The influence of growth factor is also summarized in Table 2. We found no evidence that any molecules other than H$_2$O on October 13 were subject to effects other than atmospheric seeing. Since seeing-related flux loss is a common systematic effect within a given setting, we used the same GF for all co-measured species except H$_2$O on October 13. For KL1 we applied the weighted mean GF from CH$_4$ and CH$_3$OH, emphasizing that their growth factors agree well within error. Similarly, for KL2 we used the weighted mean GF from HCN and CH$_4$ on October 13, and that from HCN, CH$_4$, and H$_2$O on January 8. On the other hand, in addition to seeing the spatial distribution for H$_2$O on October 13 was seemingly influenced by release from a source in the coma, as evidenced by its larger growth factors. In summary, for all molecules, both their production rates and abundances relative to H$_2$O were insensitive to individually measured rotational temperatures or (excepting H$_2$O on October 13) growth factors.

#### 3.3. Significance of spatial profiles in assessing volatile release

Comparing spatial profiles permits testing the nature of release of individual volatile species and dust. Fig. 4 shows emission profiles from October 13 and January 8 for each molecular species...
The spatial profiles for H$_2$O on October 13 were clearly broader outside the seeing-dominated region, relative to $Q_{\text{rot}}$. Production rates for individually measured $T_{\text{rot}}$ are listed. On January 08, the value measured for H$_2$O was adopted for all molecules. Here and in subsequent tables, all uncertainties represent 1σ and upper limits represent 3σ. Values in parentheses indicate that temperatures were adopted from measurements of other molecules.

### Table 2: Volatile composition of C/2009 P1

<table>
<thead>
<tr>
<th>Molec.</th>
<th>$T_{\text{rot}}$ (K)</th>
<th>$Q_{\text{obs}}$ ($10^{25}$ s$^{-1}$)</th>
<th>GF</th>
<th>$Q_{\text{wc}}$ ($10^{25}$ s$^{-1}$)</th>
<th>X/H$_2$O (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pre-perihelion – UT 2011 October 13</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>48 ± 4</td>
<td>4640 ± 312 (352)</td>
<td>1.94 ± 0.069</td>
<td>8980 ± 752</td>
<td>100</td>
</tr>
<tr>
<td>HCN</td>
<td>48 ± 4</td>
<td>14.4 ± 0.84 (0.95)</td>
<td>1.498 ± 0.071</td>
<td>21.5 ± 1.76</td>
<td>0.236 ± 0.018</td>
</tr>
<tr>
<td>CH$_3$N$_2$</td>
<td>55$^{56}/57$</td>
<td>13.3 ± 0.99 (1.45)</td>
<td>1.497 ± 0.086</td>
<td>20.0 ± 2.37</td>
<td>0.219 ± 0.0307</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>48 ± 4</td>
<td>52.9 ± 2.40 (6.07)</td>
<td>1.498 ± 0.071</td>
<td>79.2 ± 9.84</td>
<td>0.882 ± 0.0089</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>50 ± 10</td>
<td>55.7 ± 2.53 (14.3)</td>
<td>1.498 ± 0.071</td>
<td>83.4 ± 21.8</td>
<td>0.913 ± 0.249</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>50 ± 10</td>
<td>55.7 ± 2.53 (14.3)</td>
<td>1.501 ± 0.148</td>
<td>83.6 ± 23.0</td>
<td>0.914 ± 0.261</td>
</tr>
<tr>
<td><strong>Post-perihelion – UT 2012 January 8</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>48 ± 4</td>
<td>5200 ± 1680 (1690)</td>
<td>1.83 ± 0.126</td>
<td>9540 ± 3150</td>
<td>100</td>
</tr>
<tr>
<td>CO</td>
<td>48 ± 4</td>
<td>565 ± 26 (35.9)</td>
<td>1.52 ± 0.056</td>
<td>860 ± 63.0</td>
<td>9.12 ± 0.80$^b$</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>48(10)$^b$</td>
<td>565 ± 26 (63.2)</td>
<td></td>
<td>860 ± 101</td>
<td>9.12 ± 1.22$^b$</td>
</tr>
<tr>
<td><strong>KL1 setting</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>48 ± 4</td>
<td>6250 ± 566 (579)</td>
<td>1.680 ± 0.085</td>
<td>10,600 ± 1100</td>
<td>100</td>
</tr>
<tr>
<td>CH$_3$N$_2$</td>
<td>44$^{55}/56$</td>
<td>45.9 ± 2.43 (3.79)</td>
<td>1.482 ± 0.085</td>
<td>68.1 ± 5.61</td>
<td>0.644 ± 0.098</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>44$^{55}/56$</td>
<td>44.7 ± 2.32 (2.49)</td>
<td>1.480 ± 0.090</td>
<td>66.2 ± 6.36</td>
<td>0.621 ± 0.100</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>48 ± 4</td>
<td>153 ± 15 (15.7)</td>
<td>1.482 ± 0.085</td>
<td>226 ± 26$^d$</td>
<td>2.14 ± 0.38</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>45$^{55}/56$</td>
<td>151 ± 15 (15.7)</td>
<td>1.501 ± 0.266</td>
<td>232 ± 51.1</td>
<td>2.15 ± 0.52</td>
</tr>
</tbody>
</table>

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$^a$ Relatively precise rotational temperatures were measured for five primary volatiles on October 13 (HCN, CH$_3$N$_2$, CH$_3$H, and CH$_2$OH). Their weighted mean (48 ± 4 K, adopted for all molecules) and (in a second row) individually measured $T_{\text{rot}}$ are listed. On January 08, the value measured for H$_2$O was adopted for all molecules. Here and in subsequent tables, all uncertainties represent 1σ and upper limits represent 3σ. Values in parentheses indicate that temperatures were adopted from measurements of other molecules.

$^b$ Nucleus centered production rate. For each entry, the first uncertainty corresponds to the larger of the stochastic or standard error among lines sampled, and the second uncertainty incorporates uncertainty in $T_{\text{rot}}$. Production rates for individually measured $T_{\text{rot}}$ are also listed (second row).

$^c$ Scaling factor (growth factor, GF) for Q outside the seeing-dominated region, relative to $Q_{\text{wc}}$. Values in parentheses indicate that GF was adopted from measurements of other molecules.

$^d$ Total production rate (Eq. (2)). For each molecule, the uncertainty includes both those in mean GF and $Q_{\text{wc}}$. All molecules are assumed to have the same $T_{\text{rot}}$, hence both pre- and post-perihelion, and $\sigma_{\text{tot}}$ is not included in determining our “most probable” abundances (shown in bold). On October 13, uncertainties in GF are included since emissions span multiple settings.

$^e$ CO abundance, compared to the weighted mean global production rate for H$_2$O for the three settings on October 13 ($\sim$9430 ± 606 × 10$^{25}$ molecules s$^{-1}$), at $T_{\text{rot}}$ = 48 ± 4 K (first row) and at the $T_{\text{rot}}$ measured for CO.

$^f$ The production rate listed for CH$_3$OH is the weighted mean of those from orders 22 (232 ± 32 × 10$^{25}$ molecules s$^{-1}$) and 23 (216 ± 39 × 10$^{25}$ molecules s$^{-1}$).
The value of $Q_{\text{tot}}$ for H$_2$O in MWA is consistent with those in KL1 and KL2, albeit with larger uncertainty.

C/2009 P1 is the third recent comet to show evidence for (at least) two distinct phases of ice within the nucleus, one dominated by polar ice and the other by a-polar ice. In C/2007 W1 (Boattini), the polar molecules H$_2$O and CH$_3$OH showed asymmetric profiles in the anti-sunward hemisphere, and a source of small particles composed of relatively pure polar (water-rich) ice was proposed (Villanueva et al., 2011a). Comet 103P/Hartley-2 showed symmetric H$_2$O and CH$_3$OH profiles, while C$_2$H$_6$ was strongly asymmetric and HCN was intermediate (Mumma et al., 2011). Although a polar molecule the distribution of HCN was closer to that of C$_2$H$_6$ in both C/2007 W1 and 103P, suggesting a source associated primarily with the a-polar ice contained in the nucleus. This also appears to be the case with C/2009 P1.

In contrast, on January 8 the water profile showed no such evidence of a bimodal distribution, and its growth factor was consistent with those measured for CH$_4$ and HCN (Fig. 4h–j) and with release solely from the nucleus. For this reason we adopted the weighted mean GF for H$_2$O, CH$_4$, and HCN (1.48 ± 0.13; Table 2) for all co-measured volatiles on January 8. Both H$_2$O and CH$_4$ peaked slightly anti-sunward of the continuum, however their noise levels make it difficult to determine if any displacement is significant. We present additional pre-/post-perihelion comparisons in Section 4.3.

4. Comparisons among C/2009 P1 observations

4.1. Compositional comparison with other infrared observations

Fig. 5 shows a comparison of our abundance ratios with those obtained near 2.1 and 2.0 AU (Villanueva et al., 2012c; Paganini et al., 2012, respectively), relative to H$_2$O (Fig. 5a; Table 2) and HCN (Fig. 5b; Table 3). Those studies found growth factors of 1.8 for H$_2$O and 1.4 for other species, similar to those we found here. Our abundances on October 13 (at $R_0 = 1.83$ AU pre-perihelion) are consistent with those reported approximately 1 month earlier (near $R_0 = 2.1$ AU; Villanueva et al., 2012c) for HCN, CH$_4$, NH$_3$, and C$_2$H$_6$ (using NIRSPEC) and for CO (using CSHELL), whether expressed relative to H$_2$O or HCN. Our retrieved abundances relative to H$_2$O are systematically lower than those reported for CO, CH$_3$OH, CH$_4$, C$_2$H$_6$, and HCN from CRIRES observations near 2.0 AU, however it was pointed out (Paganini et al., 2012) that adopting the value for $Q$(H$_2$O) from optical observations of OH (Section 4.2) brings the CRIRES results into the “normal” range (see Section 5). Perhaps the outgassing pattern (particularly of H$_2$O) was changing with time, as suggested by comparisons among spatial profiles from infrared observations (e.g., compare Fig. 4a and e, and see Section 4.4). This could lead to abundance ratios relative to H$_2$O that are sensitive to rotational phase and slit geometry. Our measured abundances relative to HCN (Fig. 5b; Table 3) show much better agreement with the CRIRES results.
CH₄ (relative to H₂O) were unchanged (within 1σ uncertainties), and upper limits (3σ) for H₂C₂O, NH₃, and C₂H₂ on January 8 were also consistent with their measured values on October 13. Cometary nuclei are thought to be processed to depths of tens of centimeters during their residence time in the Oort cloud, primarily through irradiation by interstellar cosmic rays (Stern, 2003; also see Mumma et al., 1993). A typical comet loses approximately 1 m from its surface per perihelion passage—so dynamically new comets this could lead to pre-/post-perihelion compositional differences resulting from surface erosion of irradiated layers. Regardless of the dynamical status of C/2009 P1 (dynamically new or long-period returning), the agreement between pre- and post-perihelion abundance ratios suggests, for the active region(s) and to the depths sampled, compositional homogeneity among measured ices that may reflect its primordial endowment.

A notable result is that the overall gas production in C/2009 P1 was lower on January 8 despite being closer to perihelion: Qtot for H₂O was lower by ~23% relative to its mean value among settings on October 13 (Table 2, see note 'T'). Subsequent observations of C/2009 P1 by EPoxy/MRI on UT 2012 February 23 (Rₕ = 1.7 AU) and April 06 (Rₕ = 2.1 AU) yielded values for Q(OH) (2.3 and 1.4 × 10^28 molecules s⁻¹, respectively; Bodewits et al., 2012) that indicated a pronounced post-perihelion decrease in activity, at least in water production. SOHO/SWAN observations showed a steep (Rₕ ~ 2.1 to 1.6 AU (Combi et al., 2012) that was approximately three times our measured water production on October 13, consistent with additional release of H₂O in the much larger SOHO field-of-view and again suggesting aperture-dependent pre-perihelion water production. The lack of a “water excess” in our January 8 observations (compare Fig. 4h with Figs. 4a and 4e, and see Section 4.4) suggests loss of one or more active regions, perhaps due to seasonal changes in pole orientation affecting insolation received locally on the nucleus. The agreement among our pre- and post-perihelion abundance ratios (Table 2) is also consistent with loss of one or more sources releasing volatiles directly from the nucleus along with extended release of H₂O, such that the production rates of H₂O and measured trace species decreased by similar amounts.

### 4.4. Comparison of spatial profiles – establishing pre-perihelion “excess” H₂O emission

On October 13, the weighted mean intensities for both H₂O and CH₃OH were in the sunward-facing hemisphere (Fig. 4), yet only H₂O revealed a pronounced excess intensity that peaked between 1300 and 1500 km sunward as projected on the sky plane. A weaker secondary peak near +3000 to +3500 km was also seen in the KL2 water profile. This approximate “distance doubling” of peaks in the water profile could be associated with the same grain source, for example if material released previously and tied to nucleus rotation was also responsible for the weaker peak. Alternatively this secondary peak could indicate an additional source of...
water-rich grains having a larger characteristic scale for release of H2O in the sunward-facing hemisphere.

In contrast, CH4, CO, C2H6, and HCN exhibited similar distributions, albeit with subtle differences: CH4 and CO peaked (slightly) toward the anti-sunward-facing hemisphere and showed slight degrees of asymmetry in that direction, perhaps indicating 'night-side' release. C2H6 and HCN peaked coincident with the continuum and overall were more symmetric, however a statistically-significant excess in HCN emission was seen near +3000 km (Fig. 4b), close in position to the simultaneously-measured secondary water peak in the KL2 setting (Fig. 4a). Our data do not permit discerning if these two features are related. Addressing this and related questions requires detailed knowledge of the nature and actual three dimensional distributions of sources, outflow, and release.

We estimated the fractional abundance of H2O attributable to the "excess" emission through comparison with the combined profiles of C2H6 and HCN. We postulate its origin in H2O-rich particles in the coma that contributed 25–30% of the total water within our slit (see Appendix A for details).

Evidence for excess H2O was also observed in C/2009 P1 using NIRSPEC on UT 2011 September 9 (\( \beta = 26^\circ, R_0 = 2.1\) AU; Villanueva et al., 2012c). For those observations, the slit was oriented approximately 45° from the Sun-comet direction. The excess was most pronounced in the sunward-facing hemisphere (see Fig. 2) with a peak near projected distance +1500 km. A relatively smaller excess was seen on the opposite hemisphere, qualitatively consistent with our observations given the difference in slit orientations. A pronounced sun-side asymmetry was also seen in spectra of C/2009 P1 near \( R_0 = 2.0\) AU, using CRIRES with the slit along the projected Sun-comet direction (Paganini et al., 2012). Taken together, this suggests that the source region(s) on the nucleus giving rise to this excess H2O may have persisted and was/were illuminated similarly for at least the

**Table 4**

<table>
<thead>
<tr>
<th>No.</th>
<th>Cometa</th>
<th>Originb</th>
<th>CO/H2Oc</th>
<th>C2H2/H2Oc</th>
<th>CH3OH/H2Oc,d</th>
<th>C2H6/H2Oe</th>
<th>C3H8/H2Oe,f</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C/2001 A2 (LINEAR)</td>
<td>NIC/OC</td>
<td>3.9 ± 1.1 ( ^g )</td>
<td>0.5 ± 0.1 ( ^g )</td>
<td>3.0 ± 0.1 ( ^g )</td>
<td>1.7 ± 0.2 ( ^g )</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>C/1996 B2 (Hyakutake)</td>
<td>NIC/OC</td>
<td>14.9 ± 1.9 ( ^h )</td>
<td>0.16 ± 0.08 ( ^i )</td>
<td>1.7 ± 0.4 ( ^i )</td>
<td>0.62 ± 0.07 ( ^i )</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>C/1995 O1 (Hale–Bopp)</td>
<td>NIC/OC</td>
<td>12.0 ± 0.4 ( ^j )</td>
<td>0.31 ± 0.10 ( ^j )</td>
<td>1.7 ± 0.4 ( ^j )</td>
<td>0.56 ± 0.04 ( ^j )</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>C/1999 H1 (Lee)</td>
<td>NIC/OC</td>
<td>1.8 ± 0.2 ( ^k )</td>
<td>0.27 ± 0.03 ( ^k )</td>
<td>2.02 ± 0.48 ( ^k )</td>
<td>0.67 ± 0.07 ( ^k )</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>153P/Keya–Zhang</td>
<td>HTC/OC</td>
<td>4.7 ± 0.8 ( ^l )</td>
<td>0.18 ± 0.05 ( ^l )</td>
<td>1.75 ± 0.33 ( ^l )</td>
<td>0.62 ± 0.18 ( ^l )</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1P/Halley</td>
<td>HTC/OC</td>
<td>3.5 ( ^m )</td>
<td>0.3 ( ^m )</td>
<td>1.7 ± 0.4 ( ^m )</td>
<td>0.4 ( ^m )</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>C/2004 Q2 (Machholz)</td>
<td>NIC/OC</td>
<td>5.1 ± 0.51 ( ^n )</td>
<td>0.09 ± 0.01 ( ^n )</td>
<td>1.58 ± 0.06 ( ^n )</td>
<td>0.56 ± 0.03 ( ^n )</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>8P/Tuttle</td>
<td>HTC/OC</td>
<td>0.45 ± 0.09 ( ^o )</td>
<td>&lt;0.04 ( ^o )</td>
<td>1.94 ± 0.10 ( ^o )</td>
<td>0.25 ± 0.03 ( ^o )</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>C/2001 WM, (LINEAR)</td>
<td>NIC/OC</td>
<td>0.52 ± 0.12 ( ^p )</td>
<td>&lt;0.05 ( ^p )</td>
<td>1.12 ± 0.07 ( ^p )</td>
<td>0.47 ± 0.03 ( ^p )</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>C/1999 S4 (LINEAR)</td>
<td>NIC/OC</td>
<td>0.3 ± 0.3 ( ^q )</td>
<td>&lt;0.12 ( ^q )</td>
<td>&lt;0.18 ( ^q )</td>
<td>0.11 ± 0.02 ( ^q )</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>73P/S-W1 ( ^a )</td>
<td>JFC/KB</td>
<td>0.5 ± 0.13 ( ^r )</td>
<td>0.23 ± 0.06 ( ^r )</td>
<td>0.033 ( ^r )</td>
<td>0.14 ± 0.02 ( ^r )</td>
<td>0.18 ± 0.03 ( ^r )</td>
</tr>
<tr>
<td>12</td>
<td>103P/Hartley 2 ( ^s )</td>
<td>JFC/KB</td>
<td>0.15–0.45 ( ^t )</td>
<td>0.110 ± 0.011 ( ^t )</td>
<td>1.78 ± 0.08 ( ^t )</td>
<td>0.73 ± 0.03 ( ^t )</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>C/2007 N1 (Lulin)</td>
<td>NIC/OC</td>
<td>2.19 ± 0.10 ( ^u )</td>
<td>0.076 ± 0.008 ( ^u )</td>
<td>3.6 ± 0.18 ( ^u )</td>
<td>0.65 ± 0.08 ( ^u )</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>C/1999 T1 (McInt-Hartley)</td>
<td>NIC/OC</td>
<td>17 ± 4 ( ^v )</td>
<td>0.13 ± 0.03 ( ^v )</td>
<td>3.0 ± 0.3 ( ^v )</td>
<td>0.67 ± 0.03 ( ^v )</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>C/2007 W3 (Boattini)</td>
<td>NIC/OC</td>
<td>4.5 ± 0.51 ( ^w )</td>
<td>0.29 ± 0.02 ( ^w )</td>
<td>3.67 ± 0.11 ( ^w )</td>
<td>1.96 ± 0.04 ( ^w )</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>C/2009 P1 (Garradd)</td>
<td>NIC/OC</td>
<td>9.12 ± 0.80 ( ^x )</td>
<td>0.056 ± 0.023 ( ^x )</td>
<td>2.1 ± 0.4 ( ^x )</td>
<td>0.64 ± 0.09 ( ^x )</td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \) ID numbers for comets refer to points in Fig. 6. Abundances are relative to H2O = 100.

\( ^b \) Present dynamical classification (NIC = Nearly Isotropic Comet, HTC = Halley Type Comet, JFC = Jupiter Family Ecliptic Comet) and likely storage reservoir (OC = Oort cloud, KB = Kuiper Belt).

\( ^c \) Previously published values for \( Q(\text{CH}_3\text{OH}) \) from IR observations using the \( v_3 \) Q-branch intensity have been inter-normalized to \( g(Q-\text{br}) = 1.5 \times 10^{-5} \text{ ph s}^{-1} \text{ molecule}^{-1} \) (Villanueva et al., 2012b).

\( ^d \) Magee-Sauer et al. (2008b).

\( ^e \) DiSanti et al. (2003).

\( ^f \) Magee-Sauer et al. (2002a).

\( ^g \) Biver et al. (1999a).

\( ^h \) Dello Russo et al. (2002a).

\( ^i \) DiSanti et al. (2001).

\( ^j \) Magee-Sauer et al. (1999).

\( ^k \) Biver et al. (1999b).

\( ^l \) Mumma et al. (2001b).

\( ^m \) DiSanti et al. (2002).

\( ^n \) Magee-Sauer et al. (2002b).

\( ^o \) Dello Russo et al. (2002b).

\( ^p \) Eberhardt (1999).

\( ^q \) Eberhardt et al. (1994).

\( ^r \) Bonev et al. (2009).

\( ^s \) Böhnhardt et al. (2008).

\( ^t \) Bonev et al. (2008).

\( ^u \) Radeva et al. (2010).

\( ^v \) Mumma et al. (2001a).

\( ^w \) DiSanti et al. (2007).

\( ^x \) Villanueva et al. (2006).

\( ^y \) Dello Russo et al. (2007).

\( ^z \) Weaver et al. (2011).

\( ^A \) Dello Russo et al. (2011).

\( ^B \) Mumma et al. (2011).

\( ^C \) Mumma et al. (2001c) and DiSanti et al. (in preparation);

\( ^D \) Villanueva et al. (2011a).

\( ^E \) This work.

\( ^f \) For 8P, 73P, and 103P, entries having multiple references represent weighted mean values among cited papers.
5-week period encompassing those observations and the ones on October 13 reported here.

5. Taxonomy of primary volatile abundances: placing C/2009 P1 in context

As a working hypothesis, comets can be classified “organics normal,” “organics depleted,” or “organics enriched,” based on their abundances of the four organic molecules C$_2$H$_6$, CH$_3$OH, HCN, and C$_2$H$_2$ relative to H$_2$O, with “normal” values being approximately 0.6%, 2%, 0.2%, and 0.2%, respectively (e.g., see Mumma and Charnley, 2011, and references therein). In C/2009 P1, the abundance ratios (relative to H$_2$O) we measured for C$_2$H$_6$ (0.64%), CH$_3$OH (2.1%), and HCN (0.24%) were consistent with “organics-normal,” however C$_2$H$_2$ (0.06%) was well below its normal value.

The abundance of NH$_3$ (0.5%) fell within the range measured in comets (Magee-Sauer et al., 2008a), and H$_2$CO (0.11%) was similar to that found in several comets (0.1–0.3%); e.g., C/2004 Q2 (Machholz; Bonev et al., 2009), C/2001 WM$_1$ (LINEAR; Radeva et al., 2010), and C/2007 N1 (Lulin; Gibb et al., 2012). It was however well below that found in C/2002 T7 (LINEAR; DiSanti et al., 2006) or C/2002 C1 (Ikeya–Zhang; DiSanti et al., 2002). Whether a “dichotomy” in (native) H$_2$CO/H$_2$O (i.e., >0.5%, versus significantly below 0.5%) extends to the overall comet population is an open question that can only be answered by measuring its abundance in the nuclei of a significantly larger number of comets.

Our abundance ratio CH$_4$/H$_2$O in C/2009 P1 (0.8–0.9%) was close to its median value found among comets (0.9–1%). Our measured abundance ratio for CO (9.1%) was within the range found in comets, which span <0.5% (Weaver et al., 2011) to ~30% (e.g., see Bockelée-Morvan et al., 2005), but significantly above its median value among comets (~4%). Only C/1996 B2 (Hyakutake; DiSanti et al., 2003), C/1995 O1 (Hale–Bopp; Bockelée-Morvan et al., 2009; DiSanti et al., 2001), and C/1999 T1 (McNaught–Hartley; Mumma et al., 2001c) had CO/H$_2$O exceeding 10%. The abundance of CO in C/2009 P1 was also well above that found for the majority of comets observed within $R_h \approx 2.5$ AU in the Akari survey (Ootsubo et al., 2012). This classifies C/2009 P1 as a CO-rich comet, as noted from other studies (Paganini et al., 2012; Villanueva et al., 2012c; Biver et al., 2012; McKay et al., 2012, Feaga et al., 2012).

6. Redox chemistry of grain surface reactions

6.1. Molecular abundances in comets as a possible test for redox chemistry

The combined reactions of condensed interstellar molecules (e.g., CO and C$_2$H$_2$) on grain surfaces with hydrogen (reduction reactions) and oxygen (or OH; oxidation reactions) are known to produce more complex molecular species that can then be stored as ices in cometary nuclei. In the infrared, comparing measured abundances (among comets) of CO and C$_2$H$_2$ to species produced through their reduction on grain surfaces (CH$_3$OH and C$_2$H$_6$,
Hydrogen atom addition to \( \text{C}_2\text{H}_2 \) on the surfaces of interstellar grains as a means of producing \( \text{C}_2\text{H}_4 \) and then to \( \text{CH}_3\text{OH} \). This was addressed theoretically (Charnley and Rodgers, 2009), and also was demonstrated observationally as a far more efficient means of accounting for methanol abundances in interstellar sources compared with gas-phase ion-neutral chemistry (Wirström et al., 2011; Bottinelli et al., 2010). Laboratory irradiation experiments (Watanabe et al., 2004; Hudson and Moore, 1999) showed such surface reactions to be viable, providing significant product yields at very low temperatures (10–20 K), but with virtually no production at (or above) ~25 K (Watanabe et al., 2004). Irradiation of \( \text{H}_2\text{O} \) and CO ice mixtures at 10 K using energetic electrons (Bennett et al., 2011) and at 16 K with 0.8-MeV protons (Hudson and Moore, 1999) also produced formic acid (HCOOH). The relative abundances of \( \text{CO}_2\text{H}_2\text{O} \) and \( \text{CH}_3\text{OH} \) in comets can test their inter-relationship, and the laboratory yields provide a comparison in assessing natal conditions.

Among the sample of comets measured at IR wavelengths, \( \text{C}/2009 \text{ P1} \) exhibited the most pronounced difference between abundances of \( \text{CO} \) (enriched) and \( \text{C}_2\text{H}_2 \) (strongly depleted). Given the preceding discussion, this appears at odds with our results indicating approximately “normal” abundances of \( \text{C}_2\text{H}_4 \) and \( \text{CH}_3\text{OH} \). One possible explanation is more efficient conversion of initially less abundant \( \text{C}_2\text{H}_2 \) relative to \( \text{CO} \) on its pre-cometary grains (see Fig. 4 of Hiraoka et al., 2000 for temperature-dependence).

### 6.3. Oxidation on grains

Perhaps a more likely explanation includes oxidation reactions on icy grain mantles. Surface reactions of \( \text{CO} \) with \( \text{OH} \) are efficient at producing \( \text{CO}_2 \) (Oba et al., 2010; Garrod and Pauly, 2011). This is supported by the preponderance of \( \text{CO}_2 \) ice toward interstellar sources observed with ISO (Ehrenfreund et al., 1997; Gibb et al., 2004), and the detection of \( \text{CO}_2 \) in 17 of 18 comets surveyed by AKARI (Ootsubo et al., 2012) and in three comets measured by Deep Impact/DIXI (9P/Tempel 1; Feaga et al., 2007, 103P/Hartley 2; A’Hearn et al., 2011, 2012, C/2009 P1; Feaga et al., 2012). It was recently postulated that a significant fraction of comets from both KB and OC reservoirs formed in overlapping regions between CO and \( \text{CO}_2 \) snow lines (A’Hearn et al., 2012).

### 6.4. Combined reduction and oxidation (“redox”) on grains

Hydrogen-atom addition to \( \text{C}_2\text{H}_2 \) produces the vinyl radical (CH\(_2\)CH). Subjecting this to subsequent oxidation/reduction leads to three isomers of \( \text{C}_2\text{H}_3\text{O} \): ethylene oxide (\( \text{C}_2\text{H}_4\text{O} \)), vinyl alcohol (\( \text{CH}_2\text{CHOH} \)), and acetaldehyde (\( \text{CH}_2\text{CHO} \)) (Ward and Price, 2011). Hydrogenation of the latter two isomers provides a viable means of producing ethanol (\( \text{CH}_3\text{CHOH} \)) (see Charnley, 2004). These studies together with our findings for \( \text{C}/2009 \text{ P1} \) and perhaps other comets with high \( \text{CO}/\text{C}_2\text{H}_2 \) (e.g., C/1999 T1 and C/1996 B2; see Table 4, Fig. 6, and discussion below) suggest that in general both oxidation and reduction should be considered.

Our results for \( \text{C}/2009 \text{ P1} \) may represent a case in point. If its pre-cometary ices were subjected to processing that included significant oxidation reactions, this could help explain its high \( \text{CO}/\text{C}_2\text{H}_2 \) abundance ratio together with its “normal” \( \text{CH}_3\text{OH} \) and \( \text{CH}_3\text{OH} \). The depleted acetylene in \( \text{C}/2009 \text{ P1} \) could result from its conversion not only to ethane but also to the above \( \text{C}_2\text{H}_4\text{O} \) isomers and perhaps to \( \text{CH}_3\text{CHOH} \). Furthermore, its high \( \text{CO}_2/\text{H}_2\text{O} \) abundance ratio (Feaga et al., 2012) suggests its “initial” \( \text{CO} \) endowment (i.e., the amount of \( \text{CO} \) condensed onto its pre-cometary grains)
may have been considerably larger than the value we observe (9.1%).

6.5. Comparison among comets

Fig. 6 compares abundance ratios CO/C2H2 versus CH3OH/C2H6 in 16 comets identified by number in Table 4. Points well above the horizontal dotted line (median CO/H2O, “normal” C2H2/H2O) and near or to the left of the vertical dotted line (“normal” CH3OH/H2O and C2H6/H2O) could indicate a relatively more important role for oxidation reactions, and correspondingly that the ices incorporated into such comets were subjected to processing in relatively oxygen-rich environments. Considering the CH3CHO observed in star forming regions (Charnley, 2004), measuring or stringently constraining its abundance in comets6 having high CO/C2H2 yet modest CH3OH/C2H6 can test this hypothesis. However, it is important to bear in mind that, considering the aforementioned caveats (Section 6.1), comets with lower CO/C2H2 must also be considered, for example if a significant fraction of their “initial” (i.e., condensed interstellar) CO is incorporated into unaccounted-for polymers (e.g., formaldehyde polymers) and/or CO2.

7. Summary

On UT 2011 October 13 (Rn = 1.836 AU pre-perihelion) we measured nine primary volatiles (H2O, CO, CH4, C2H2, C2H6, H2CO, CH3OH, HCN, and NH3) in Comet C/2009 P1 (Garradd). On 2012 January 8 (Rn = 1.566 AU post-perihelion) we measured three of these (H2O, HCN, and CH4) and obtained meaningful upper limits for three others (H2CO, NH3, and C2H2). Our measured abundance ratios relative to H2O did not change pre- and post-perihelion, suggesting compositional homogeneity among species measured on both dates, to the depths among active regions sampled. However, despite its smaller heliocentric distance, production on January 8 suggests loss of the source of icy grains. Along with C/2007 W1 (Boattini) and C/2010 X1 (PanSTARRS), we compared spatial profiles revealed differences in outgassing among volatiles in C/2009 P1. Pre-perihelion profiles for CH4, CO, C2H2, and HCN showed fairly similar spatial distributions, suggesting these four species originated from one or more active regions composed predominantly of a-polar ice. Most pronounced was the sunward-hemisphere-facing excess in H2O emission on October 13 having peak intensity at projected distance 1300–1500 km from the nucleus. This was not seen in other profiles, consistent with release from relatively pure, polar (water-rich) ice particles liberated from the nucleus, perhaps in a directed flow. We estimate that 25–30% of the total H2O encompassed in our slit was released in the coma and contained within our slit. We took two independent approaches to quantifying this fraction (excess water/total water): (1) We summed the residual H2O profile intensities in KL1 and KL2 from approximately –100 to +2900 km, and compared these to the corresponding sums for the total H2O profile. (2) We applied our standard “Q-curve” analysis to the residual H2O profiles (for details of this formalism, see discussions in Dello Russo et al., 1998; DiSanti et al., 2001; Bonev et al., 2005), and relatively oxygen-rich environment prior to their incorporation into the nucleus.

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Appendix A. Distinguishing pre-perihelion sources of H2O in C/2009 P1

A.1. Quantitative estimate of coma source contribution

Fig. A1 illustrates the approach we used for quantitatively estimating the fraction of water released in the coma of C/2009 P1. We express the H2O profiles in terms of column density Nbeam (H2O molecules m−2) averaged within a beam centered approximately 350 km sunward of the nucleus – corresponding to the approximate peak position of Gaussian fits to the water profiles – and having area Abeam, corresponding to 2400 × 580 km at the comet. This is related to the “nucleus-centered” production rate (Qnc) as (see DiSanti et al., 2009 for formalism):

\[ N_{\text{beam}} = \frac{Q_{\text{nc}}}{A_{\text{beam}}} \times \mathcal{F}(x) \times R_{\text{H}_2O}^2 \]  

\[ \text{(A1)} \]

where Rn is expressed in AU.

We isolated the fraction of water released in the coma as follows. We combined the profiles for HCN (Fig. 4b) and C2H6 (Fig. 4f), after scaling each to a common level when averaged over ±1200 km from the nucleus. Both C2H6 and HCN profiles had very similar growth factors (~1.5) and showed relatively large degrees of sunward/anti-sunward symmetry. We take this combined profile to closely approximate purely native release of primary volatiles, and refer to it as our “representative native profile.” We separately scale this to the total H2O intensity over the range 0 to −4000 km in the KL1 and KL2 settings; this range is indicated by the horizontal bar in each panel of Fig. A1.

The residual profile obtained by subtracting this scaled representative native profile provides a measure of the excess H2O released in the coma and contained within our slit. We took two independent approaches to quantifying this fraction (excess water/total water): (1) We summed the residual H2O profile intensities in KL1 and KL2 from approximately −100 to +2900 km, and compared these to the corresponding sums for the total H2O profile. (2) We applied our standard “Q-curve” analysis to the residual H2O profiles (for details of this formalism, see discussions in Dello Russo et al., 1998; DiSanti et al., 2001; Bonev et al., 2005), and...
Section 4.2 and pre-perihelion SOHO H-Ly

$H_2O$ to total $H_2O$ could represent a lower bound. If larger, such a study of $HDO$ in C/2009 P1 with HIFI on the Herschel space

craft provided the most consistent match to observed line profiles if a comparable fraction of water (30%) was adopted for release from icy grains in the coma (Bockelée-Morvan et al., 2012). However, given the much larger Herschel aperture, comparisons with our results may not be meaningful.

Because we must allow for possible additional release of $H_2O$ in the coma but not encompassed in the slit, this fraction of “excess” $H_2O$ to total $H_2O$ could represent a lower bound. If larger, such additional release may explain the difference in water production reported here versus those from optical observations (Section 4.2) and pre-perihelion SOHO H-Ly measurements (Section 4.3).

A.2. Possible interpretation of excess $H_2O$ release

The most straightforward explanation for the observed excess water in C/2009 P1 is release from $H_2O$-rich icy particles. These could arise from one or more active regions on the nucleus that contain an over-abundance of polar (specifically, water-rich) ice compared with the source(s) of activity giving rise to the ambient coma gas. This could be part of a directed outflow that releases predominantly the water-rich ice component giving rise to the observed excess $H_2O$.

The excess $H_2O$ peaks at a relatively localized projected distance from the nucleus (−1300−1500 km). If polar-ice-dominated particles are the explanation, the distance at which they release water is determined by the product of their outflow speeds and their sublimation lifetimes. We consider a range of particle sizes, from sub-micron to the largest particles that can be lifted off the nucleus by the sublimation process. This maximum particle size can be estimated by balancing gravitational and gas drag forces at the surface of the nucleus (see Delsemme and Miller, 1971):

$$Q_{\text{max}} = \frac{9}{16\pi G \rho_c \rho_g} \frac{m_v \mu_s Z}{R_c} \left(1 - \frac{R_c}{q_{\text{ex}}} \right)$$

In Eq. (A2), $m_v$ is the mean molecular mass of the coma gas (taken to be ~20 amu), $Z$ is the gas sublimation rate (molecules s$^{-1}$ cm$^{-2}$), $R_c$ is the radius of the nucleus (km), and $\rho_c$ and $\rho_g$ are densities (gm cm$^{-3}$) of the bulk nucleus and the particle, respectively. Assuming reasonable values ($R_c$ = 2 km, a native gas production rate of $8 \times 10^{18}$ molecules s$^{-1}$, and $\rho_c = \rho_g = 1$) leads to $Q_{\text{max}} \sim 5$ cm. Particles this large would remain very close to the surface of the nucleus and move very slowly. Indeed, the clumps of water–ice particles this large would remain very close to the surface of the nucleus and move very slowly. Indeed, the clumps of water–ice

$\frac{\text{gas}}{\text{sub}}$ observed during the EPOXI flyby of 103P/Hartley 2 had extremely low velocities (<2 m s$^{-1}$), with only one of 50 tracked in space craft images found beyond 15 km from the nucleus (A'Hearn, 2011).

The smallest particles will maintain an outflow speed closer to (but still below) $v_{\text{gas}}$, assumed to be 0.59 km s$^{-1}$ at $R_0 = 1.83$ AU (Section 3.2), thereby requiring a lifetime of approximately 2200−2600 s for release in the region of peak excess water emission. (We note the relatively small phase angle of 31.6° on UT October 13 means that if release occurs along the actual comet-Sun direction, this distance and therefore the required particle lifetimes are approximately doubled.) This lifetime is consistent with grains dominated by water ice, as predicted by modeled sublimation of grains composed of admixtures of water ice and rocky material (i.e., “dirty” grains; Beer et al., 2006). Using a parameter $X_1$ ($= \text{mass}_{\text{water–ice}}/\text{mass}_{\text{grain}}$), Beer et al. predict the lifetime of pure water ice grains ($X_1 = 1$) to be about 10$^{\pm}$ s at 1.8 AU, even for small grains of size $a = 0.1$ mm. However, the predicted lifetime drops precipitously when even a small fraction of refractory material is present (e.g., to $10^2$ s for $X_1 = 0.9$). Large grains (but still much smaller than $a_{\text{max}}$; e.g., $a = 1$ mm) having $X_1 = 0.9$ are predicted to survive for $\sim 10^2$ s, and these could rele-

References


