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

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A B S T R A C T

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.

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1. Introduction

More than any other Solar System material, the ices contained in the nuclei of comets (i.e., their native ices)1 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 R0 > 30 AU), while those from the OC formed in the R0 ~ 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 $5 \times 10^6$ 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 ($a_0 \sim 1–3$ 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 rates of nearly isotropic comets. As a result, it was argued that a large 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 near $a_0 = 1.8$ AU pre-perihelion and 1.6 AU post-perihelion. We compare our results with other infrared studies of C/2009 P1, place them in the context of our ongoing compositional taxonomy among comets measured to date, and discuss possible implications regarding the processing history of the ices in this comet. We compare spatial emission profiles, and thereby estimate the fraction of H$_2$O released from what appear to be water-rich grains in the coma.

### 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 ($\lambda/\Delta \lambda \sim 24,000$) spectrometer (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, 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, thereby estimate the fraction of H$_2$O released from what appear to be water-rich grains in the coma.

### 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...
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: H$_2$O multiple bands (Figs. 1a, 2c and 3c; Villanueva et al., 2012a), OH $v_1$ and $v_2 - v_1$ (Figs. 1b, 2c and 3a-3c; Bonev, 2005, Bonev et al., 2006), C$_2$H$_6$ $v_7$ (Fig. 2a; Villanueva et al., 2011b), CH$_4$ $v_3$ (Figs. 1b and 3a; Gibb et al., 2003), C$_2$H$_4$ $v_3$ and $v_2 + v_4 + v_5$ (Figs. 1c and 3a), CO $v_1$ (Villanueva et al., 2011a), NH$_3$ $v_1$ and $v_3$ (Figs. 1c and 3a; Villanueva et al., 2013; Kawakita and Mumma, 2011), HCN $v_1$ (Figs. 1c and 3a; Lippi et al., 2013; Villanueva et al., 2013), H$_2$CO $v_1$ and $v_3$ (Reuter et al., 1989; DiSanti et al., 2006), and CH$_3$OH $v_2$ (Fig. 2a; DiSanti et al., 2013) and $v_3$ (Fig. 2b; Villanueva et al., 2012b). These models make use of a realistic solar flux that includes Fraunhofer lines and incorporates the cometary heliocentric velocity ($\dot{R}_h$ 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 H$_2$O lines, and so introduced correspondingly large uncertainties in line-by-line production rates retrieved from transmittance-corrected line fluxes (see Eq. 1 below). The H$_2$O 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 ($T_{\text{rot}} = 42 \pm 26$ K).

We retrieved more precise rotational temperatures independently for HCN, CH$_4$, CO, C$_2$H$_6$, and CH$_3$OH on October 13 (Table 2). Their weighted mean value ($T_{\text{rot}} = 48 \pm 4$ K; 1σ uncertainty) is consistent with $T_{\text{rot}}$ measured for C/2009 P1 near $R_h = 2.1$ AU (40 ± 7 K; Villanueva et al., 2012c) and 2.0 AU (50 K; Paganini et al., 2012). We take our weighted mean $T_{\text{rot}}$ (48 K) to be the most probable temperature, and adopt this for all molecules on October 13. From our January 8 observations, we measured $T_{\text{rot}} = 55 \pm 10$ K based on water lines in order 26 (Fig. 3c). We were unable to determine $T_{\text{rot}}$ for HCN nor CH$_4$, and therefore adopt 55 K for all molecules measured on January 8.

We note that individual values of $T_{\text{rot}}$ 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 1 σ) measured post-perihelion for H$_2$O, for example if the smaller $R_0$ on January 8 was compensated by the lower water production rate $Q$(H$_2$O). Our lower post-perihelion Q(H$_2$O) is consistent with pre-/post-perihelion asymmetries found by other observers of C/2009 P1 (Section 4.3), as well as asymmetries found by other observers of C/2009 P1 (Section 4.3). 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. 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):

$$Q_{\text{nc, line}} = \frac{4\pi d^2 F_{\text{line}}}{\tau f(x) B_{\text{line}}}$$

(1)

In Eq. (1), $\tau_1$ (s) and $g_1$ (W molecule$^{-1}$) represent the photo-dissociation lifetime and fluorescence g-factor (both evaluated at $R_0 = 1$ AU), $F_{\text{line}}$ (W m$^{-2}$) is the line flux at the top of the terrestrial atmosphere, and geocentric distance ($\lambda$) 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 $R_0$, $\lambda$, and gas outflow speed $v_{\text{gas}}$, assumed to be spherically-symmetric and equal to 800 $R_0^{0.5}$ m s$^{-1}$ (Biver et al., 2006; Biver et al., 2002). Because $f(x)$ varies approximately as $\tau_1^{-1}$ 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:

$$Q_{\text{tot}} = Q_{\text{nc}} \times \text{GF}.$$ 

(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” $\sigma T_{\text{rot}}$ ($\pm 4$ 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.

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3 The best-fit heliocentric dependence of $r_{\text{gas}}$ for the 4 comets in Biver et al. (2006) is $R_0^{-0.5160.12}$ km s$^{-1}$. 

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Fig. 3. Same as Figs. 1 and 2, but for January 8.
January 8.

entry (in parentheses) incorporates uncertainty in et al., 2012c; see Section 4.4, and Appendix A). We note that the GF


cies that lack a meaningful spatial profile owing to insufficient sig-
spectra and establishing nucleus-centered line intensities for spe-
tation for projected distance along the slit, and although distinct
case for comets, it ensures uniform spatial registration for all tar-
from co-measured molecular emission profiles as is generally the

spread-function (PSF, dotted trace) based on the measured stellar

c0 within each order), and a representative point-
(hard trace in each panel), the dust continuum profile (light trace,

The spatial profiles for H2O on October 13 were clearly broader

relative to

Qrot = 48 ± 4 K (first row) and at the

Trot = 48 ± 4 K (first row) and at the

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Table 2


<table>
<thead>
<tr>
<th>Molec.</th>
<th>Tem (K)</th>
<th>Qtot (1025 molec/s)</th>
<th>GF</th>
<th>Qrot (1025 molec/s)</th>
<th>XH2O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</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>21.5 ± 0.76</td>
<td>20.0 ± 2.37</td>
<td>0.236 ± 0.018</td>
</tr>
<tr>
<td>CH4</td>
<td>48 ± 4</td>
<td>52.9 ± 2.40(6.07)</td>
<td>1.407 ± 0.086</td>
<td>79.2 ± 9.84</td>
<td>0.882 ± 0.0089</td>
</tr>
<tr>
<td>N2O</td>
<td>48 ± 4</td>
<td>55.7 ± 2.53(14.3)</td>
<td>83.4 ± 21.8</td>
<td>9.13 ± 0.249</td>
<td></td>
</tr>
<tr>
<td>CH2O</td>
<td>48 ± 4</td>
<td>55.7 ± 2.53(14.3)</td>
<td>83.6 ± 23.0</td>
<td>0.914 ± 0.261</td>
<td></td>
</tr>
<tr>
<td>CH3OH</td>
<td>48 ± 4</td>
<td>6.53 ± 2.37(2.38)</td>
<td>(1.498 ± 0.071)</td>
<td>9.78 ± 3.60</td>
<td>0.115 ± 0.041</td>
</tr>
<tr>
<td>CH3N</td>
<td>48 ± 4</td>
<td>297.7 ± 9.30(5.56)</td>
<td>(1.498 ± 0.071)</td>
<td>44.5 ± 14.5</td>
<td>0.505 ± 0.16</td>
</tr>
<tr>
<td>CNH2</td>
<td>48 ± 4</td>
<td>3.36 ± 1.32(1.32)</td>
<td>(1.498 ± 0.071)</td>
<td>5.03 ± 1.99</td>
<td>0.056 ± 0.023</td>
</tr>
</tbody>
</table>

Mwidea A setting

<table>
<thead>
<tr>
<th>Molec.</th>
<th>Tem (K)</th>
<th>Qtot (1025 molec/s)</th>
<th>GF</th>
<th>Qrot (1025 molec/s)</th>
<th>XH2O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</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 ± 26.6(35.9)</td>
<td>1.52 ± 0.056</td>
<td>860 ± 63.0</td>
<td>9.12 ± 0.80</td>
</tr>
<tr>
<td></td>
<td>4810</td>
<td>565 ± 26.6(35.9)</td>
<td>1.52 ± 0.056</td>
<td>860 ± 63.0</td>
<td>9.12 ± 1.22</td>
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KL1 setting

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<tr>
<th>Molec.</th>
<th>Tem (K)</th>
<th>Qtot (1025 molec/s)</th>
<th>GF</th>
<th>Qrot (1025 molec/s)</th>
<th>XH2O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</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>HCN</td>
<td>48 ± 4</td>
<td>45.9 ± 2.43(3.79)</td>
<td>68.1 ± 5.61</td>
<td>0.644 ± 0.0989</td>
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</tr>
<tr>
<td>CH3O</td>
<td>48 ± 4</td>
<td>44.7 ± 2.32(2.49)</td>
<td>66.2 ± 6.36</td>
<td>0.621 ± 0.100</td>
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</tr>
<tr>
<td>CH3OH</td>
<td>48 ± 4</td>
<td>44.7 ± 2.32(2.49)</td>
<td>66.1 ± 6.48</td>
<td>0.626 ± 0.102</td>
<td></td>
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<tr>
<td></td>
<td>4810</td>
<td>153 ± 15.6(15.7)</td>
<td>1.482 ± 0.085</td>
<td>226 ± 26.6</td>
<td>2.14 ± 0.38</td>
</tr>
<tr>
<td></td>
<td>4510</td>
<td>151 ± 15.5(15.7)</td>
<td>224 ± 26.3</td>
<td>0.12 ± 0.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4510</td>
<td>151 ± 15.5(15.7)</td>
<td>232 ± 51.1</td>
<td>0.15 ± 0.52</td>
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</tr>
</tbody>
</table>

Post-perihelion – UT 2012 January 8

<table>
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<th>Molec.</th>
<th>Tem (K)</th>
<th>Qtot (1025 molec/s)</th>
<th>GF</th>
<th>Qrot (1025 molec/s)</th>
<th>XH2O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>55 ± 10</td>
<td>4907 ± 185(546)</td>
<td>1.478 ± 0.131</td>
<td>7253 ± 698</td>
<td>100</td>
</tr>
<tr>
<td>HCN</td>
<td>55 ± 10</td>
<td>4907 ± 185(546)</td>
<td>1.459 ± 0.178</td>
<td>7159 ± 1138</td>
<td>100</td>
</tr>
<tr>
<td>CH3O</td>
<td>55 ± 10</td>
<td>9.2 ± 0.90(1.83)</td>
<td>1.478 ± 0.131</td>
<td>13.6 ± 1.79</td>
<td>0.19 ± 0.020</td>
</tr>
<tr>
<td>CH3OH</td>
<td>55 ± 10</td>
<td>9.2 ± 0.90(1.83)</td>
<td>1.478 ± 0.131</td>
<td>14.4 ± 3.79</td>
<td>0.20 ± 0.063</td>
</tr>
<tr>
<td></td>
<td>55 ± 10</td>
<td>35.7 ± 7.35(11.5)</td>
<td>1.478 ± 0.131</td>
<td>52.8 ± 11.8</td>
<td>0.71 ± 0.152</td>
</tr>
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<td></td>
<td>55 ± 10</td>
<td>35.7 ± 7.35(11.5)</td>
<td>1.478 ± 0.131</td>
<td>52.8 ± 11.8</td>
<td>0.71 ± 0.152</td>
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<tr>
<td></td>
<td>55 ± 10</td>
<td>&lt;4.9 (3e)</td>
<td>(1.478 ± 0.131)</td>
<td>&lt;7.2</td>
<td>&lt;0.10 (3e)</td>
</tr>
<tr>
<td></td>
<td>55 ± 10</td>
<td>&lt;35.7 (3e)</td>
<td>(1.478 ± 0.131)</td>
<td>&lt;52.8</td>
<td>&lt;0.73 (3e)</td>
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<tr>
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<td>55 ± 10</td>
<td>&lt;3.8 (3e)</td>
<td>(1.478 ± 0.131)</td>
<td>&lt;5.6</td>
<td>&lt;0.077 (3e)</td>
</tr>
</tbody>
</table>

| Abundance, corresponding to the weighted mean global production rate for H2O among the three settings on October 13 (∼9430 ± 606 × 1025 molecules s−1), at Trot = 48 ± 4 K (first row) and at the Ttot measured for CO.
| The production rate listed for CH3OH is the weighted mean of those from orders 22 (232 ± 32 × 1025 molecules s−1) and 23 (216 ± 39 × 1025 molecules s−1).

* Relatively precise rotational temperatures were measured for five primary volatiles on October 13 (HCN, CH4, CO, CH3O, and CH3OH). Their weighted mean (48 ± 4 K, adopted for all molecules), and (in a second row) individually measured Qrot are listed. On January 08, the value measured for H2O 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.

* Scaling factor (growth factor, GF) for Q outside the seeing-dominated region, relative to Qtot. Values in parentheses indicate that GF was adopted from measurements of other molecules.

* Total production rate (Eq. (2)). For each molecule, the uncertainty includes both those in mean GF and Qrot, with GF from October 13 based on HCN and CH4 in KL2, and on CH3O and CH3OH in KL1. For these four molecules, the third row of entries includes uncertainties in both individually measured Qrot and − in all cases Qrot and Qtot on October 13 agree (within 1σ uncertainty) with their values at 48 K and (for Qrot) with their values using the relevant mean growth factors.

* Abundance, corresponding to the ratio of molecular production rates to H2O. All molecules are assumed to have the same Ttot, hence both pre- and post-perihelion, σQtot 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.

* CO abundance, compared to the weighted mean global production rate for H2O among the three settings on October 13 (∼9430 ± 606 × 1025 molecules s−1), at Trot = 48 ± 4 K (first row) and at the Ttot measured for CO.

* If in a “complex” rotation state, the actual period for C/2009 P1 would be a multiple of the reported 10-h period.
tions. 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.
4.2. Comparison with optical observations of C/2009 P1

D. Schleicher (private communication, 2011) reported water production rates \(1.5 \times 10^{29} \text{ molecules s}^{-1}\) from narrow-band photometry at \(R_h = 1.97\) AU (September 24) and 1.80 AU (October 18 and 20) that are approximately 50% larger than the values reported from the IR studies (Paganini et al., 2012; Villanueva et al., 2012c). The lower limit for the abundance of \(\text{H}_2\text{O} \) at \(-2.4\) AU corresponds to the upper limit (3σ) found for \(\text{H}_2\text{O}\), which had not yet fully activated at that heliocentric distance.

4.3. Pre-/post-perihelion comparisons

Six of nine primary volatiles measured in C/2009 P1 on October 13 were also measured on January 8. Abundance ratios of HCN and \(\text{CH}_4\) (relative to \(\text{H}_2\text{O}\)) were unchanged (within 1σ uncertainties), and upper limits (3σ) for \(\text{H}_2\text{CO}, \text{NH}_3\), and \(\text{C}_2\text{H}_2\) 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 – for 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: \(Q_{\text{tot}}\) for \(\text{H}_2\text{O}\) was lower by ~23% relative to its mean value among settings on October 13 (Table 2, see note ‘f’). Subsequent observations of C/2009 P1 by EPOXI/MRI on UT 2012 February 23 \((R_h = 1.7\) AU) and April 06 \((R_h = 2.1\) AU) yielded values for \(Q(\text{OH})\) (2.3 and 1.4 \(\times 10^{28} \text{ molecules s}^{-1}\)), 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 \((R_h^{-1-2})\) post-perihelion decrease in \(Q(\text{H}_2\text{O})\). This followed larger, relatively constant pre-perihelion production of \(\text{H}_2\text{O}\) from \(R_h \approx 2.1\) 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 \(\text{H}_2\text{O}\) 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 \(\text{H}_2\text{O}\), such that the production rates of \(\text{H}_2\text{O}\) and measured trace species decreased by similar amounts.

4.4. Comparison of spatial profiles – establishing pre-perihelion “excess” \(\text{H}_2\text{O}\) emission

On October 13, the weighted mean intensities for both \(\text{H}_2\text{O}\) and \(\text{CH}_3\text{OH}\) were in the sunward-facing hemisphere (Fig. 4), yet only \(\text{H}_2\text{O}\) 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

![Figure 5](image-url)  
**Fig. 5.** Abundances of several primary volatiles in C/2009 P1 (Garradd), expressed in percent relative to \(\text{H}_2\text{O}\) (panel a) and HCN (panel b) and retrieved using high-resolution IR spectroscopy. Note that for clarity, the points for CO and \(\text{C}_2\text{H}_6\) are encompassed by the (very narrow) IR slits.
water-rich grains having a larger characteristic scale for release of H$_2$O in the sunward-facing hemisphere.

In contrast, CH$_4$, CO, C$_2$H$_6$, and HCN exhibited similar distributions, albeit with subtle differences: CH$_4$ and CO peaked (slightly) toward the anti-sunward-facing hemisphere and showed slight degrees of asymmetry in that direction, perhaps indicating "night-side" release. C$_2$H$_6$ 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 H$_2$O attributable to the "excess" emission through comparison with the combined profiles of C$_2$H$_6$ and HCN. We postulate its origin in H$_2$O-rich particles in the coma that contributed 25–30% of the total water within our slit (see Appendix A for details).

Evidence for excess H$_2$O was also observed in C/2009 P1 using NIRSPEC on UT 2011 September 9 ($\beta = 26^\circ$, $R_h = 2.1$ AU; Villanueva et al., 2012c). For those observations, the slit was oriented approximately 45$^\circ$ from the Sun-comet direction. The excess was most pronounced in the sunward-facing hemisphere (see Fig. 2C in Villanueva et al., 2012c) 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 $R_h = 2.0$ 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 H$_2$O may have persisted and was/were illuminated similarly for at least the

### Table 4

<table>
<thead>
<tr>
<th>No.</th>
<th>Comet</th>
<th>Origin</th>
<th>CO/H$_2$O</th>
<th>C$_2$H$_6$/H$_2$O</th>
<th>CH$_3$OH/H$_2$O</th>
<th>C$_2$H$_4$/H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C/2001 A2 (LINEAR)</td>
<td>NIC/OC</td>
<td>3.9 ± 1.1$^c$</td>
<td>0.5 ± 0.1$^d$</td>
<td>3.0 ± 0.1$^d$</td>
<td>1.7 ± 0.2$^d$</td>
</tr>
<tr>
<td>2</td>
<td>C/1996 B2 (Hyakutake)</td>
<td>NIC/OC</td>
<td>14.9 ± 1.9$^e$</td>
<td>0.16 ± 0.08$^f$</td>
<td>1.7 ± 0.4$^b$</td>
<td>0.62 ± 0.07$^b$</td>
</tr>
<tr>
<td>3</td>
<td>C/1995 O1 (Hale–Bopp)</td>
<td>NIC/OC</td>
<td>12.0 ± 0.4$^g$</td>
<td>0.31 ± 0.10$^h$</td>
<td>1.7 ± 0.4$^b$</td>
<td>0.56 ± 0.04$^b$</td>
</tr>
<tr>
<td>4</td>
<td>C/1999 H1 (Lee)</td>
<td>NIC/OC</td>
<td>1.8 ± 0.2$^i$</td>
<td>0.27 ± 0.03$^m$</td>
<td>2.02 ± 0.48$^n$</td>
<td>0.67 ± 0.07$^m$</td>
</tr>
<tr>
<td>5</td>
<td>153P/Keya–Zhang</td>
<td>HTC/OC</td>
<td>4.7 ± 0.8$^o$</td>
<td>0.18 ± 0.05$^p$</td>
<td>1.75 ± 0.35$^b$</td>
<td>0.62 ± 0.18$^b$</td>
</tr>
<tr>
<td>6</td>
<td>1P/Halley</td>
<td>HTC/OC</td>
<td>3.5$^q$</td>
<td>0.3$^r$</td>
<td>1.7 ± 0.4$^b$</td>
<td>0.4$^r$</td>
</tr>
<tr>
<td>7</td>
<td>C/2004 Q2(Machholz)</td>
<td>NIC/OC</td>
<td>5.1 ± 0.51$^s$</td>
<td>0.09 ± 0.01$^t$</td>
<td>1.58 ± 0.06$^u$</td>
<td>0.56 ± 0.03$^u$</td>
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<tr>
<td>8</td>
<td>8P/Tuttle</td>
<td>HTC/OC</td>
<td>0.45 ± 0.09$^v$</td>
<td>&lt;0.04$^w$</td>
<td>1.94 ± 0.10$^x$</td>
<td>0.25 ± 0.03$^u$</td>
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<tr>
<td>9</td>
<td>C/2001 WM (LINEAR)</td>
<td>NIC/OC</td>
<td>0.52 ± 0.12$^y$</td>
<td>&lt;0.05$^z$</td>
<td>1.12 ± 0.07$^z$</td>
<td>0.47 ± 0.03$^z$</td>
</tr>
<tr>
<td>10</td>
<td>C/1999 S4 (LINEAR)</td>
<td>NIC/OC</td>
<td>0.9 ± 0.3$^{</td>
<td>}$</td>
<td>&lt;0.12$^{</td>
<td>}$</td>
</tr>
<tr>
<td>11</td>
<td>73P/S-W 1$^A$</td>
<td>JFC/KB</td>
<td>0.5 ± 0.13$^B$</td>
<td>0.23 ± 0.06$^C$</td>
<td>&lt;0.03$^D$</td>
<td>0.14 ± 0.02$^D$</td>
</tr>
<tr>
<td>12</td>
<td>103P/Hartley 2$^A$</td>
<td>JFC/KB</td>
<td>0.15–0.45$^E$</td>
<td>0.11 ± 0.01$^F$</td>
<td>1.78 ± 0.08$^G$</td>
<td>0.73 ± 0.03$^G$</td>
</tr>
<tr>
<td>13</td>
<td>C/2007 N1 (Lulin)</td>
<td>NIC/OC</td>
<td>2.19 ± 0.10$^H$</td>
<td>0.076 ± 0.008$^I$</td>
<td>3.6 ± 0.18$^J$</td>
<td>0.65 ± 0.08$^J$</td>
</tr>
<tr>
<td>14</td>
<td>C/1999 T1(McNt-Hartley)</td>
<td>NIC/OC</td>
<td>17 ± 4$^K$</td>
<td>0.13 ± 0.03$^L$</td>
<td>3.0 ± 0.3$^M$</td>
<td>0.67 ± 0.03$^M$</td>
</tr>
<tr>
<td>15</td>
<td>C/2007 W3 (Boattini)</td>
<td>NIC/OC</td>
<td>4.5 ± 0.51$^N$</td>
<td>0.29 ± 0.02$^O$</td>
<td>3.67 ± 0.11$^P$</td>
<td>1.96 ± 0.04$^P$</td>
</tr>
<tr>
<td>16</td>
<td>C/2009 P1 (Garradd)</td>
<td>NIC/OC</td>
<td>9.12 ± 0.80$^Q$</td>
<td>0.056 ± 0.023$^R$</td>
<td>2.1 ± 0.4$^R$</td>
<td>0.64 ± 0.09$^R$</td>
</tr>
</tbody>
</table>

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*ID numbers for comets refer to points in Fig. 6. Abundances are relative to H$_2$O = 100.

*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).

*Previously published values for Q(CH$_3$OH) from IR observations using the $\nu_3$ Q-branch intensity have been inter-normalized to g(Q-br) = 1.5 × 10$^{-5}$ ph s$^{-1}$ molecule$^{-1}$ (Villanueva et al., 2012b).

Magee-Sauer et al. (2008b).

DiSanti et al. (2003).

Magee-Sauer et al. (2002a).

Biver et al. (1999a).

DiLollo et al. (2002a).

DiSanti et al. (2001).

Magee-Sauer et al. (1999).

DiSanti et al. (2002).

Magee-Sauer et al. (2002b).

Dello Russo et al. (2002b).

Eberhardt (1999).

Eberhardt et al. (1994).

Bonev et al. (2009).

Bönhardt et al. (2008).

Bonev et al. (2008).

Radeva et al. (2010).

Mumma et al. (2001a).

DiSanti et al. (2007).

Villanueva et al. (2006).

Dello Russo et al. (2007).

Weaver et al. (2011).

Dello Russo et al. (2011).

Mumma et al. (2011).

Gibb et al. (2012).

Mumma et al. (2001c) and DiSanti et al. (in preparation).

Villanueva et al. (2011a).

This work.

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_2H_6, CH_3OH, HCN, and C_2H_2 relative to H_2O, 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_2O) we measured for C_2H_6 (0.64%), CH_3OH (2.1%), and HCN (0.24%) were consistent with "organics-normal," however C_2H_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_2CO (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_2CO/H_2O (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_2O 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_2O exceeding 10%. The abundance of CO in C/2009 P1 was also well above that found for the majority of comets observed within R<sub>n</sub> ~ 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_2H_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_2H_2 to species produced through their reduction on grain surfaces (CH_3OH and C_2H_6, respectively)
respectively) provides a potential means of testing the relative influence of oxidation.

However, compositional measurements provide only the net processing history of ices as opposed to their initial abundances on grain surfaces. Their interpretation is therefore subject to caveats, for example: (1) Oxidation of CO leads to CO2, which has recently been measured with surprisingly high abundance in a significant fraction of comets, frequently higher than the CO abundance (Ootsubo et al., 2012). Directly measuring CO2 requires observations from space and, including C/2009 P1 (Feaga et al., 2012), CO2 has been measured in only three comets for which the suite of primary volatile abundances have also been characterized using IR spectroscopy, the others being 9P/Tempel 1 (Mumma et al., 2005; Feaga et al., 2007) and 103P/Hartley 2 (Dello Russo et al., 2011; Mumma et al., 2011; Weaver et al., 2011, A'Hearn, 2011). (2) H-atom addition to CO produces H2CO in addition to CH3OH. Native, monomeric formaldehyde (H2CO) has been measured in a number of comets,5 however the amount contained in polymers is typically unknown, and where measured – in 1P/Halley (Eberhardt, 1999, and references therein) and C/1995 O1 Hale–Bopp (Wink et al., 1999) – its abundance dominates that of monomeric H2CO in the nucleus.

A complete assessment must investigate all viable formation pathways for oxidized carbon compounds, including gas-phase production of species like CO2 and H2CO (Walsh et al., 2012) and also addition reactions on the surfaces of (interstellar) grains. Surface reactions of CO with OH are efficient (i.e., the amount of CO condensed onto its pre-cometary grains) and H-atom addition as both common and significant in the evolution of pre-cometary ices.

Similarly, H-atom addition to CO on grains produces the highly-reactive formyl radical (HCO), which readily converts to H2CO and then to CH3OH. 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 H2O 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 CO, H2CO and CH3OH 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, C/2009 P1 exhibited the most pronounced difference between abundances of CO (enriched) and C2H2 (strongly depleted). Given the preceding discussion, this appears at odds with our results indicating approximately “normal” abundances of C2H4 and CH3OH. One possible explanation is more efficient conversion of initially less abundant C2H2 relative to CO on its pre-cometary ices (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 CO with OH are efficient at producing CO2 (Oba et al., 2010; Garrod and Pauly, 2011). This is supported by the preponderance of CO2 ice toward interstellar sources observed with ISO (Ehrenfreund et al., 1997; Gibb et al., 2004), and the detection of CO2 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, 2011, and 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 CO2 snow lines (A'Hearn et al., 2012).

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

Hydrogen-atom addition to C2H2 produces the vinyl radical (CH2CH). Subjecting this to subsequent oxidation/reduction leads to three isomers of C2H4O: ethylene oxide (c-C2H4O), vinyl alcohol (CH2CHOH), and acetaldehyde (CH3CHO) (Ward and Price, 2011). Hydrogenation of the latter two isomers provides a viable means of producing ethanol (CH3CH2OH) (see Charnley, 2004). These studies together with our findings for C/2009 P1 and perhaps other comets with high CO/C2H2 (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 C/2009 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 CO/C2H2 abundance ratio together with its “normal” C2H6 and CH3OH. The depleted acetylene in C/2009 P1 could result from its conversion not only to ethane but also to the above C2H4O isomers and perhaps to CH3CH2OH. Furthermore, its high CO2/H2O abundance ratio (Feaga et al., 2012) suggests its “initial” CO endowment (i.e., the amount of CO condensed onto its pre-cometary grains)

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5 The combination of small (sub-arc-second) beam sizes of modern IR spectrometers such as NIRSPEC, together with the relatively small distance between A- and B-beam positions (Section 2) favors measurement of species released directly from the nucleus (i.e., of “native” abundances as defined previously).

### Table A1

<table>
<thead>
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<tbody>
<tr>
<td></td>
<td>Excess/total</td>
</tr>
<tr>
<td>(1) Summing over residual and total profilesa</td>
<td>KL1 0.248</td>
</tr>
<tr>
<td></td>
<td>KL2 0.311</td>
</tr>
<tr>
<td></td>
<td>KL12 0.289</td>
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<tr>
<td>(2) Based on Q-curve analysisb</td>
<td>KL1 0.263</td>
</tr>
<tr>
<td></td>
<td>KL2 0.304</td>
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</tbody>
</table>

a Fraction of total H2O attributable to the excess emission at projected distance 1300–1500 km sunward of the nucleus, along with its 1σ error, based on summing over its central 3000 km, corresponding approximately to the range in projected distance ~100–2000 km in Fig. A1. Weighted mean from KL1 and KL2 is listed to the right. The entries for KL12 correspond to summing over the residual excess profile in Fig. A1c, representing the weighted mean of those from KL1 (Fig. A1a) and KL2 (Fig. A1b). The corresponding weighted mean fraction obtained by summing over the central 4000 km is 0.268 ± 0.049, consistent with the “Mean KL1, KL2” value (0.289) listed in the table.

b Fraction of total H2O from symmetrized Q-curves. Localized isotopic release is assumed, as would be expected from large and therefore slow-moving particles, although this could be realized even for a distribution of particle sizes (see Appendix A).
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 comets$^6$ 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 ($R_h = 1.836$ 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 ($R_h = 1.566$ 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, $R_h$ was lower by approximately 23% on January 8 compared with October 13, qualitatively similar to pre-/post-perihelion differences in water production revealed by SOHO/SWAN observations of C/2009 P1.

Comparison of spatial profiles revealed differences in outgassing among volatiles in C/2009 P1. Pre-perihelion profiles for CH4, CO, C2H6 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. Along with C/2007 W1 (Boattini) and 103P/Hartley 2, C/2009 P1 is the third recent comet to show evidence for (at least) two distinct phases of ice within the nucleus.

The lack of excess H2O emission together with its lower water production on January 8 suggest loss of the source of icy grains. This plus similar decreases in production of HCN and CH4 may result from depletion of ice in, or covering of, one or more active regions on the nucleus, or perhaps more likely from pre-/post-perihelion differences in orientation relative to the incident solar radiation.

Our results for comet C/2009 P1 add a unique signature to our growing taxonomy of primary volatile abundances in comets. Its enriched CO and severely depleted C2H2, together with “normal” C2H6 and CH3OH, could indicate that its ices were processed in a 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 $N_{beam}$ (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 ($A_{beam}$) corresponding to $2400 \times 580$ km at the comet. This is related to the “nucleus-centered” production rate ($Q_{nc}$) as (see DiSanti et al., 2009 for formalism):

$$N_{beam} = \frac{Q_{nc}}{A_{beam}} \pi R_h^2 f(x)$$

(A1)

where $R_h$ 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

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$^6$ An abundance ratio CH3CHO/H2O = 0.02% was reported for C/1995 O1 (Hale–Bopp) (Crovisier et al., 2004).
compared the terminal Q to that obtained from the total H$_2$O profile (the latter corresponding to $Q_{\text{tot}}$ for H$_2$O in the KL1 and KL2 settings on October 13; Table 2). The resulting fractions are summarized in Table A1. These indicate agreement between approaches (1) and (2), with both contributing 25–30% of the total water production we observe in C/2009 P1 on October 13 being released in the coma and peaking in the sunward-facing hemisphere at projected distance 1300–1500 km from the nucleus. Interestingly, 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$_2$O in the coma but not encompassed in the slit, this fraction of “excess” H$_2$O to total H$_2$O 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 per-observation SOHO H-lyx measurements (Section 4.3).

A2. Possible interpretation of excess H$_2$O release

The most straightforward explanation for the observed excess water in C/2009 P1 is release from H$_2$O-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$_2$O.

The excess H$_2$O 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):

$$a_{\text{max}} = \frac{9}{16\pi} \frac{m_{\text{gas}} Z}{\sqrt{G \rho_c \rho_g}} \tag{A2}$$

In Eq. (A2), $m$ 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 $a_{\text{max}} \sim$ 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 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 2011 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 $X_1 (=m_{\text{water–ice}}/m_{\text{grain}})$, Beer et al. predict the lifetime of pure water ice grains ($X_1 = 1$) to be about $10^5$ s at 1.8 AU, even for small grains of size $a = 0.1$ μm. 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 release H$_2$O in the coma on the observed scale provided their outflow speed is, as one would expect, much lower (20–30 m s$^{-1}$). If associated with a nucleus rotation period of 10.4 h (see Section 3.3), the “distance doubling” seen in the KL2 water profile (Fig. 4a) implies a similar mean (projected) particle speed of ~40 m s$^{-1}$. In this manner, our observations of “excess” H$_2$O in C/2009 P1 can be explained by relatively localized release from relatively pure-water icy grains ($0.9 < X_1 < 1.0$) spanning a wide range of sizes.

References


