



# HIGH-TIME RESOLUTION IN SITU INVESTIGATION OF MAJOR COMETARY VOLATILES AROUND 67P/C-G AT 3.1–2.3 au MEASURED WITH ROSINA-RTOF

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## ABSTRACT

Comets considered to be pristine objects contain key information about the early formation of the solar system. Their volatile components can provide clues about the origin and evolution of gases and ices in the comets. Measurements with ROSINA/RTOF at 67P/Churyumov–Gerasimenko have now allowed, for the first time, a direct in situ high-time resolution measurement of the most abundant cometary molecules originating directly from a comet's nucleus over a long time-period, much longer than any previous measurements at a close distance to a comet between 3.1 and 2.3 au. We determine the local densities of H<sub>2</sub>O, CO<sub>2</sub>, and CO, and investigate their variabilities.

**Key words:** comets: general – comets: individual (67P, Churyumov–Gerasimenko)

## 1. INTRODUCTION

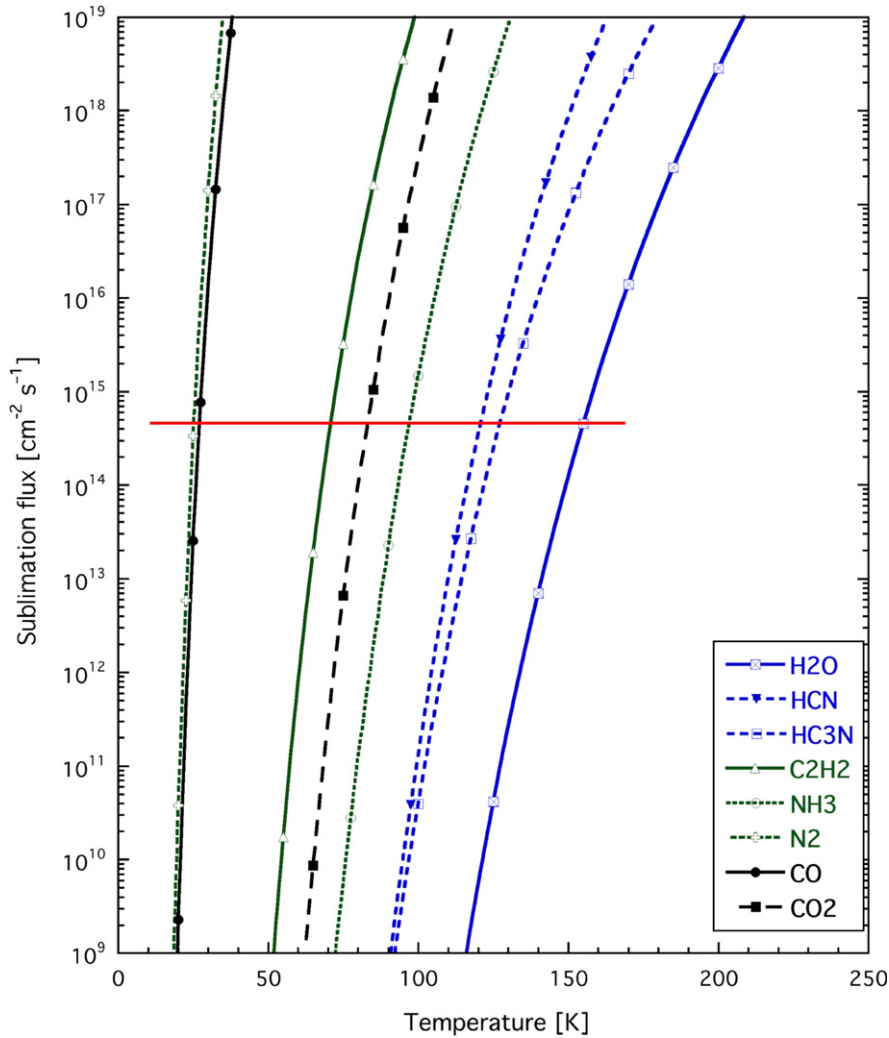
Comets are thought to be built up of icy materials and dust grains. Comets may preserve both interstellar material, as well as material from the proto-solar nebula. As comets have spent extensive time far away from the Sun under very cold conditions, they are usually considered to be pristine objects that contain key information about the early formation of the solar system. Their volatile components can provide clues about the evolution of gases and ices, as the collapsing molecular cloud transforms into a mature planetary system. For example, the abundance of CO is of particular interest, as it was predicted to be the dominant C-bearing gas in the outer parts of the solar nebula where comets formed (cf. Fegley & Prinn 1989). Due to the high volatility of CO, the CO content of ices incorporated into comets is sensitive to the local conditions where the nucleus formed, or where the coldest part of the nucleus originated, assuming there was significant radial mixing of material within the nebula. The amount of CO, therefore, can contain information on the history of origin of the comets and the conditions under which they may have formed (see, e.g., Balsiger et al. 2015; Rubin et al. 2015).

A central issue of cometary science is the question of to what extent interstellar ices were chemically processed in the solar nebula before they were incorporated into cometary nuclei. A determination of the mixing ratios of cometary ices between the interstellar and proto-stellar samples is, therefore, of particular

importance. As icy materials are not only present in the solar system but also in interstellar clouds and have probably been integrated into planetary bodies, they have been considered for a long time to be an important prerequisite for the formation of life on planets. From this perspective measuring the in situ composition of the volatile cometary material is also an important goal.

Typically, the most abundant molecules in cometary ices are water, carbon dioxide, and carbon monoxide, and, most recently detected, molecular oxygen (Bieler et al. 2015a), while other molecular species such as organics (e.g., HCN, NH<sub>3</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and CH<sub>3</sub>OH) are minor (e.g., Bockelée-Morvan et al. 2004; Mumma & Charnley 2011). It is important to note that the detection of some of these species from the ground is difficult, either due to the telluric absorption of the near-infrared (NIR) in the Earth's atmosphere or due to the absence of permanent electric dipole moments for symmetric molecules, which makes detection by radio observations impossible. As comets are shedding their volatile material into interplanetary space and are ejecting dust from their surfaces, the measurement of cometary volatiles is crucial to improve our understanding of their activity and the formation of the cometary coma.

With sublimation temperatures of the major volatiles covering a wide range of temperatures ( $T_{\text{sub}}$  of H<sub>2</sub>O ice is ~150 K,  $T_{\text{sub}}$  CO<sub>2</sub> ice is ~70 K and  $T_{\text{sub}}$  CO ice is ~30 K; see Figure 1)



**Figure 1.** Sublimation fluxes for selected species relevant for Churyumov–Gerasimenko, based on Fray & Schmitt (2009). The horizontal line indicates where the sublimation flux is about 1 monolayer per second, defining the “sublimation temperature.”

the activity of comets at different heliocentric distances must be partially driven by the different cometary species. This was beautifully revealed by NASA’s EPOXY mission to the Jupiter family comet 103P/Hartley 2 (e.g., A’Hearn et al. 2011). This mission demonstrated the importance of CO<sub>2</sub> ice in lifting water ice grains at 1.07 au distance.

And yet, due to the above-mentioned observational issues there are only a few in situ measurements of H<sub>2</sub>O, CO<sub>2</sub>, and CO in comets. Therefore, the IR measurements of the AKARI IRC instrument of the 18 observed Oort cloud and Jupiter-family comets are particularly important because they provide a range of the major volatiles as a function of heliocentric distance: Ootsubo et al. (2012) not only provided the first homogenous database of the CO<sub>2</sub>/H<sub>2</sub>O ratio in more than 10 samples of comets that were compatible with earlier measurements, but also showed that the CO<sub>2</sub>/H<sub>2</sub>O production rate ratio is systematically higher for comets which are further than 2.5 au away from the Sun. They found that the CO/CO<sub>2</sub> ratio in the observed comets is smaller than unity, although they only obtained upper limits for CO in most of their observed comets. For 67P/Churyumov–Gerasimenko (67P/C–G) at 1.8 au they found a CO<sub>2</sub>/H<sub>2</sub>O value of about 7%.

With the *Rosetta* Mission exploring the Jupiter-family comet 67P/C–G, coma abundance measurements can now be improved. We are for the first time in a position not only to measure abundance ratios or abundances for a specific moment in time, but also to study the spatial and temporal evolution of the gas abundances in the coma over a very long time period at large distances from the Sun. It is of special interest to explore how our measurements are related to the illumination and the observation conditions at the comet.

Hässig et al. (2015) presented two periods of coma composition measurements made with the *Rosetta* Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA)/DFMS instrument when *Rosetta* was close to 67P/C–G with a time resolution better (>10 measurements) than the rotation period of the comet. During the first 4 day period from 2014 August 4 to 8 *Rosetta* was above the summer hemisphere and from 2014 September 18 to 19 was above the winter hemisphere. These first measurements indicated that the cometary coma is highly heterogeneous.

In this paper, we investigate the temporal evolution of the major gas species around the cometary nucleus with the ROSINA/RTOF instrument for an extended time period between 2014 October and 2015 February, at heliocentric

distances of 3.1–2.3 au. ROSINA/RTOF obtains mass spectra with a higher time resolution of 200 s and thus is better suited to resolve spatial/temporal variations in the coma than ROSINA/DFMS.

## 2. THE ROSINA INSTRUMENT

The ROSINA instrument suite on board the European Space Agency’s (ESA) *Rosetta* spacecraft consists of two mass spectrometers: the Double Focusing Mass Spectrometer (DFMS) and the Reflectron-type Time-Of-Flight (RTOF), as well as the ROSINA COmet Pressure Sensor (COPS; Scherer et al. 2006; Balsiger et al. 2007). COPS measures the total neutral particle density with the nude gauge and ram pressure with the ram gauge. Measured values are converted on board with a reference temperature of 20°C into pressure. Lower limits are  $10^{-11}$  mbar for the nude gauge and  $10^{-9}$  mbar for the ram gauge. RTOF complements the DFMS with an extended mass range from 1 to >300 amu/q. While the ROSINA/DFMS spectrometer excels in mass resolution, the ROSINA/RTOF instrument shines through its measurement frequency. RTOF can measure all cometary species in a single spectrum acquired within 200 s. This ability permits one to monitor the complete mass range of cometary volatile species simultaneously.

To measure the neutral and the ionized cometary gas components, two ion sources were implemented in RTOF: the Orthogonal extraction ion Source (OS) and the Storage ion Source (SS), both of which can use the electron impact for ionization of neutral gas. The OS is dedicated to the measurement of the ionized component of the cometary atmosphere. The OS directs incoming ionized particles into the TOF section of the mass spectrometer, while the SS, dedicated to the neutral cometary gas component, ionizes neutral particles and extracts them into the TOF analyzer. The analyzer contains the 83 cm long drift tube of the time-of-flight instrument. RTOF is able to measure, with both sources simultaneously, neutrals in the storage sources and ions in the ortho source, but also with each source alone. RTOF was originally designed to measure molecules with a mass resolution up to  $m/\Delta m > 4500$  at 50% peak height (Scherer et al. 2006). However, due to problems in flight with the 9 kV high voltage power converter, the instrument had to be operated at 2 kV, which naturally leads to a lower mass resolution for RTOF of ~300–400 at 50% peak height.

## 3. RTOF DATA ANALYSIS

### 3.1. Operational and Observational Conditions

The RTOF instrument can be operated in various operational measuring modes. In this investigation we have analyzed all spectra obtained with the OS sensor in measuring mode 523 between 2014 October 24 and 2015 February 17, a grand total of 10,750 spectra. During this period the *Rosetta* spacecraft orbited or passed the comet at distances between 8 and 77 km from its center and was able to monitor the comet’s activity for a variety of solar illumination conditions.

### 3.2. Data Processing

Ions that have been created from neutral gas in the OS are extracted from the source with a frequency (10 kHz) that is defined by a high-voltage pulser. The time of extraction starts a

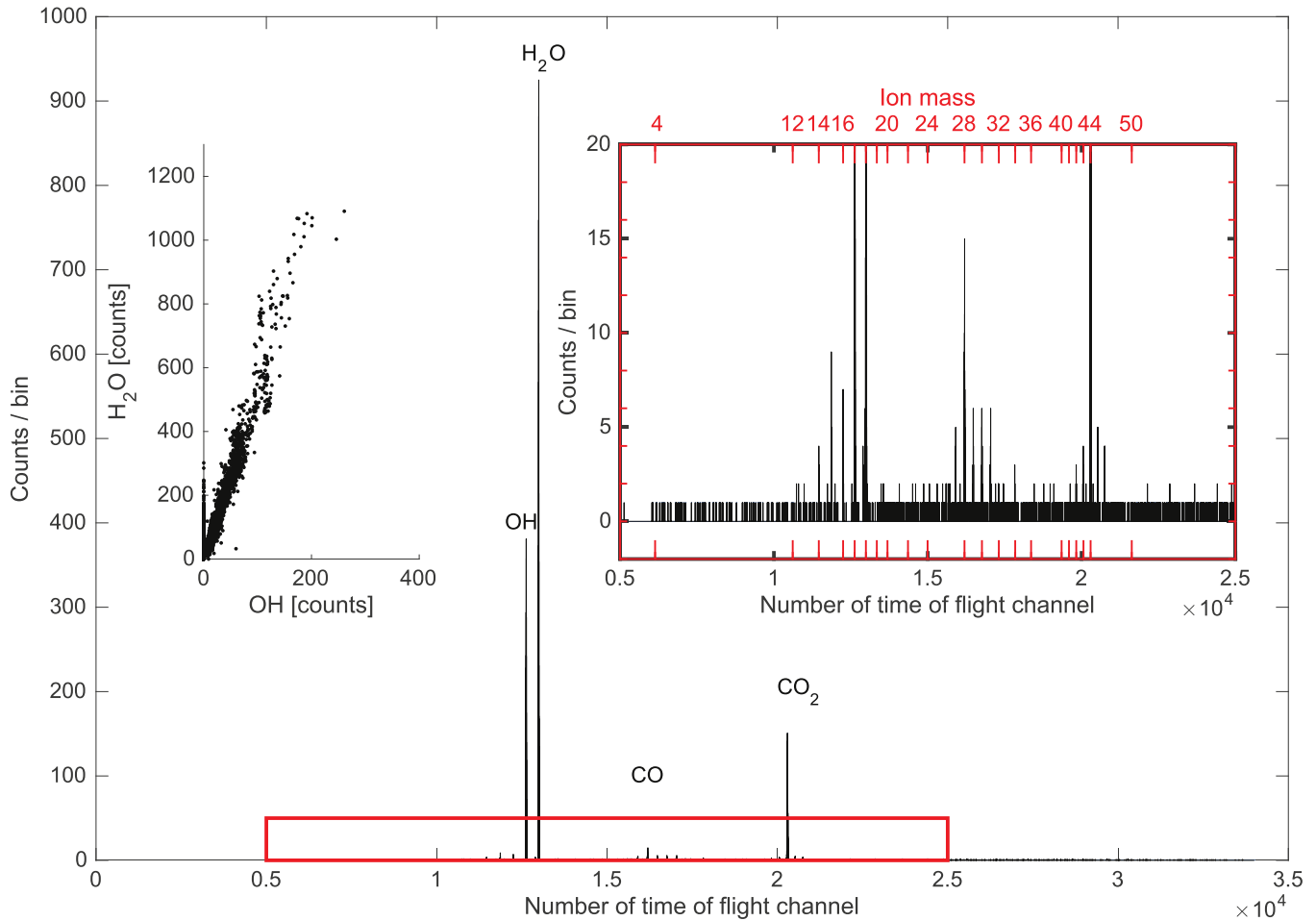
time-of-flight measurement. After traversing the drift tube, reflected at the ion mirror and returning, an ion is measured if it hits the micro channel plate (MCP) detector (Schletti et al. 2001; Siegmund et al. 2001). The MCP produces a current pulse that is processed in the OS data acquisition board ETS-L (Equivalent Time Sampler-Light). The ion is registered as detected if the amplitude of the measured detector signal surpasses a given set threshold. The corresponding time-of-flight of a detected ion is then recorded in a spectrum which has 35152 time channels with a bin length of 1.65 ns each for measuring mode 523. For a given measuring mode the RTOF on board electronics ETS-L board produces one spectrum consisting of all the TOF measurements generated during the acquisition time of 200 s.

The analysis of a single RTOF spectrum consists of integrating the count rates of the individual peaks associated with the detected ions in the corresponding TOF channels.

Due to operational and noise issues, the measured ion signals are superimposed on a varying background that is not necessarily flat. A smoothing procedure is applied to identify the background signal, which is then subtracted from the measured spectrum. The individual channels of a spectrum are associated with their corresponding ion mass/charge ratios with the help of a calibration gas mixture. During dedicated calibration measurements this calibration gas mixture is injected into the ion source to generate those mass calibration spectra with peaks at specific known masses (He, CO<sub>2</sub>, and Kr). With a procedure described by S. Gasc et al. (2016, in preparation), the accurate mass scale can then be found. The resulting mass spectra are then used to identify ion count peaks, which surpass a given threshold. We fitted exponentially modified Gaussian distributions to the individual peaks. With the parameters found, we computed the area of the identified peaks. Each spectrum acquired at a specific time at the comet is therefore characterized by a given number of peaks whose parameters we have determined. For each analyzed spectrum we computed ancillary data at the corresponding spectrum acquisition time with the help of the SPICE toolkit using ESA’s reconstructed kernels for the orbit of *Rosetta* and 67P/C–G, and the associated shape model of the comet. In the main body of Figure 2 the integrated count rate of all the RTOF spectra for the investigated data period is displayed. It is seen that the mass spectra are dominated by the three compounds, H<sub>2</sub>O, OH, CO<sub>2</sub>, and minor species like CO. As ROSINA operates in an extremely tenuous coma, great care has to be taken to ensure that ROSINA cometary gas measurements are not accidentally contaminated by gas molecules released during spacecraft maneuvers. The contamination effects on ROSINA and the identification of species originating from such maneuvers were studied in detail during the long flight of *Rosetta* from Earth to the comet (Schlappi et al. 2010). The right insert, which is marked red in the main body of Figure 2, shows an enlargement of the middle part of the spectrum (time-of-flight bin numbers from 0.5 to 2.5 times  $10^4$ ) to show the minor species. The left insert shows a correlation plot of the OH versus the H<sub>2</sub>O count rate computed for each spectrum.

### 3.3. Results

As molecules break into fragments under electron ion impact ionization in a mass spectrometer, the fragmentation patterns for RTOF need to be measured in the laboratory with the flight spare instrument under conditions duplicating the situation in



**Figure 2.** Sum of accumulated count rate of identified ion peaks in the investigated time interval (main part of figure). The right upper insert shows a zoomed fraction of the main ion histogram. The left insert shows the correlation between OH and the  $\text{H}_2\text{O}$  molecule.

flight. Gasc (2015) has done these laboratory calibration measurements. We used the sensitivity values and fragmentation calibration by S. Gasc et al. (2016, in preparation, Table 3: Relative fragmentation ratios) for the OS RTOF measurement. The relative fragmentation ratio is defined as the precursor ion intensity (taken to be 100%) over the fragment ion intensity. In our study we considered the fragmentation of  $\text{H}_2\text{O}$  (100%) into  $\text{OH}^+$  ( $23.35 \pm 0.53\%$ ) and  $\text{O}^+$  ( $1.16 \pm 0.06\%$ ), for  $\text{CO}_2$  into  $\text{CO}^+$  ( $3.86 \pm 0.21\%$ ) and  $\text{O}^+$  ( $5.07 \pm 0.22\%$ ) and  $\text{C}^+$  ( $1.20 \pm 0.10\%$ ), and for  $\text{CO}$  into  $\text{O}^+$  ( $0.08 \pm 0.04\%$ ) and  $\text{C}^+$  ( $0.77 \pm 0.02\%$ ). These values, together with an electron emission current of  $200 \mu\text{A}$  for the OS filament, are then used to convert the count rates into densities.

Figure 3 shows in the upper panel the total COPS local density as a function of time (black line) and the deviation of the RTOF pointing direction from the Nadir pointing direction (blue line).

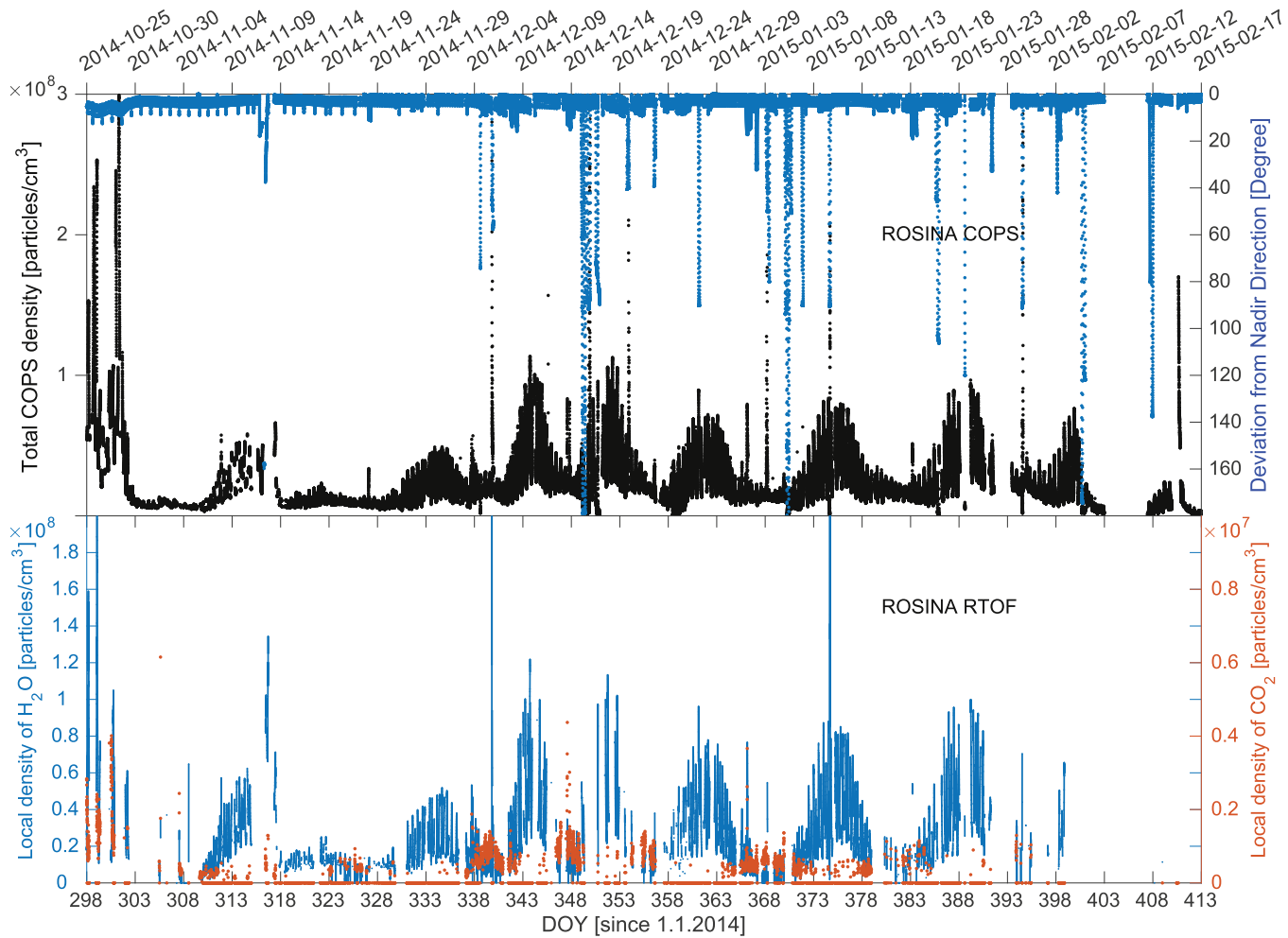
The COPS data shown have been cleaned from COPS measurements made during routine spacecraft maneuvers (e.g., wheel off-loading time periods). To identify additional non-routine maneuvers, which could contaminate measurements, Figure 3 also shows in the top panel the deviation from the RTOF FOV looking direction and its Nadir pointing direction. The lower panel in Figure 3 contains as a time series the local density of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . The RTOF time series, unlike the COPS measurements, have data gaps, which occurred when

RTOF was switched to SS mode or RTOF was simply not in operation due to reaction wheel offloading. Both sensors have also been switched off during most (COPS) or all (RTOF) orbital correction maneuvers, occurring approximately twice per week for the time period reported here.

Investigating the correlations between the different observed species in the RTOF mass spectra, we find only the clear correlation between  $\text{H}_2\text{O}^+$  and  $\text{OH}^+$  signals. This correlation, shown in the left insert of Figure 2, demonstrates that the  $\text{OH}^+$  peak seen in the spectra is a fragment of an  $\text{H}_2\text{O}$  molecule; the measurements were taken so close to the nucleus that the contribution of OH from photo-dissociation in the coma is negligible. The correlation shows the fragmentation ratio found by S. Gasc et al. (2016, in preparation) of  $\sim 23\%$ .

The more or less continuous COPS total density measurements around the comet clearly show the total density fluctuating with a cometary rotation period of 12.4 hr. To visualize that RTOF indeed sees molecules from the comet, Figure 4 zooms in on the 8 day period from DOY 371 to DOY 379, superimposed on the COPS data. In this time interval RTOF observed mostly  $\text{H}_2\text{O}$  molecules. It is important to point out that COPS measures the local total particle density, i.e., including all major and minor species, as it is not possible to separate those with COPS. Most of the time the coma is dominated by neutral water and therefore a close match can be expected to the RTOF  $\text{H}_2\text{O}$  observations. The figure shows the





**Figure 3.** Time series of COPS total pressure measurements (upper panel) and H<sub>2</sub>O (blue) and CO<sub>2</sub> (red) measurements with RTOF OS (lower panel).

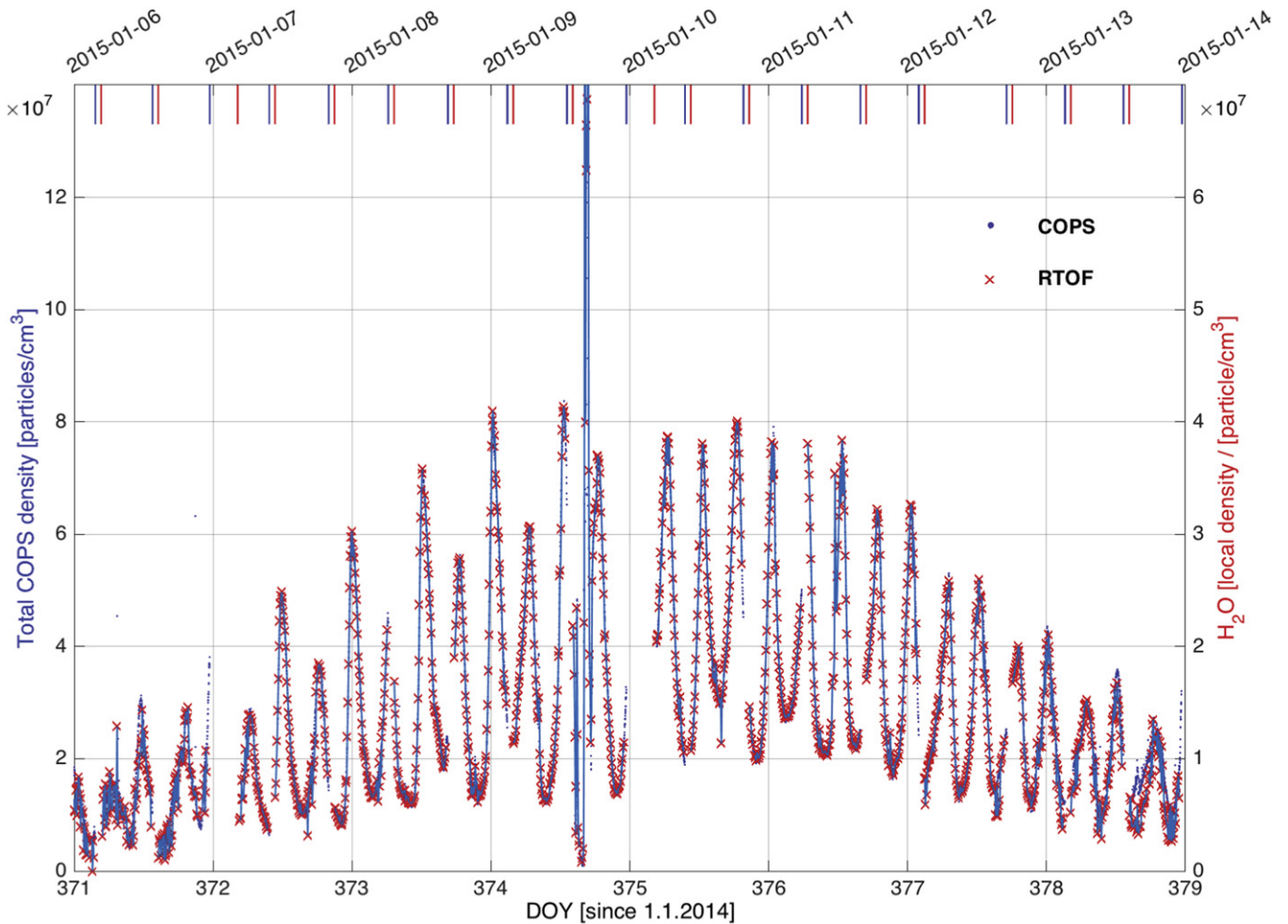
synchronous variations of the two independent measurements, which in turn implies that during this period, H<sub>2</sub>O was indeed the dominating gas species in the coma. Clearly visible in the figure is an additional space manoeuvre, which generates the spike in the observed densities.

The RTOF local density time series from Figure 3 suggest that the H<sub>2</sub>O and CO<sub>2</sub> densities are anti-correlated. We show in Figure 5 the density ratio CO<sub>2</sub>/H<sub>2</sub>O for the data period displayed in Figure 3.

As all measurements in the time ordered sequence shown in Figure 3 are made at different locations around the comet, we investigated which part of the comet is in the field of view of the RTOF instrument at a particular point in time. Under the assumption that RTOF detects neutral gas species, always originating from the surface of the comet, and flying into the center of the RTOF field of view direction, we can compute for each measurement the corresponding latitude and longitude values on the comet (sub-spacecraft footpoint). It must be very clear that such a simple mapping procedure can only give a rough idea about the place of origin of the measured neutrals. Bieler et al. (2015b) have investigated this issue by modeling the neutral coma of 67P/C-G with 3D kinetic and hydrodynamic codes. The large collisional mean free path of the particles leaving the cometary surface, the large fractions of concave surfaces of the nucleus shape and a rapidly changing temperature distribution of the particle emitting surface area

make this tracking to the surface origin a complex problem. Furthermore, RTOF's projected field of view was always larger than the comet itself, which means that gas can come from almost everywhere on the nucleus facing *Rosetta*. However, the fact that the overall longitude, latitude distribution pattern of the investigated ion species remains relatively constant when the studied time interval is subdivided into smaller time intervals, lends some credibility to the employed method of projection. We conclude, therefore, that the analysis shows that under the given assumptions H<sub>2</sub>O molecules are preferentially observed on the Northern Hemisphere, while CO<sub>2</sub> is leaving the comet more on the Southern Hemisphere (compare these figures with the results (Figure 4) from the DFMS instrument by Hässig et al. 2014). Note that RTOF's high time resolution translates into a high spatial resolution, especially in the longitudinal dimension. A much more sophisticated spatial analysis is in progress and will be published in a separate paper.

CO abundance measurements either inferred from ground-based or in situ measurements have shown a wide range of values. CO in the coma could originate either as a primary species or as a dissociation product from CO<sub>2</sub>. Carbon monoxide was first detected in comet C/1975 V1 (West) by rocket UV observations (Feldman & Brune 1976). Highly different CO abundances were observed: from 2% in C/1979 Y1 (Bradfield) to 15%–20% in comets C/1975 V1 (West) and 1P/Halley. More recently, Paganini et al. (2015) reported



**Figure 4.** COPS total density and H<sub>2</sub>O count rate for an 8 day period. Vertical lines at the top of the figure display the times of spacecraft maneuvers (blue: start, red: end of maneuver).

measurements of C/2013 R1 (Lovejoy) at pre-perihelion distances from 1.35 to 1.16 au with the Near InfraRed SPECTrometer (NIRSPEC) at the Keck Observatory. Their findings indicate that C/2013 R1, with a measured mean abundance ratio of CO/H<sub>2</sub>O of  $9.89 \pm 2.03$ , is enriched in CO. From their compilation of the CO/H<sub>2</sub>O abundance ratios in 23 Oort Cloud comets ranging from 0.4% to 28% they compute a median value of  $\sim 4\%$  and arbitrarily define comets with abundances larger than twice the median CO abundance (i.e.,  $>8\%$ ) to represent “CO-rich” comets.

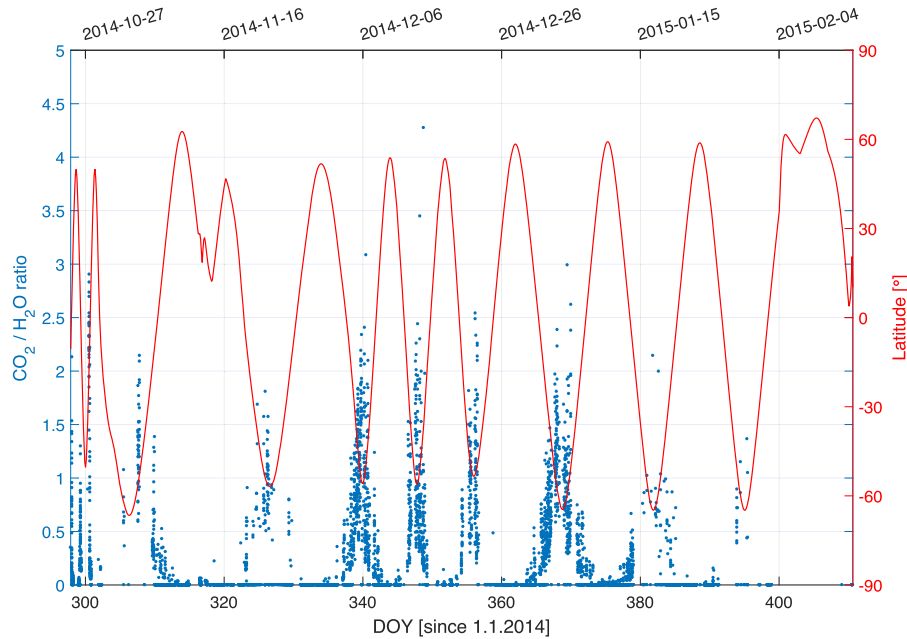
Analyses of UV observations made with different fields of view, as well as the CO density evolution observed in situ by the Neutral Mass Spectrometer (NMS) on Giotto at 1P/Halley, show that the origin of CO is twofold: one part is coming from the nucleus region, and another one is from a distributed source within the coma with a scale length of the order of  $10^4$  km (Eberhardt et al. 1999; Cottin & Fray 2008; Mumma & Charnley 2011).

On *Rosetta*, Feldman et al. (2015) reported the detection of a weak emission from atomic CO. We have examined in the investigated data period the occurrence of RTOF spectra that show a clear CO signal. Figure 6 displays the CO local density for this time period. Also plotted are the distance of the spacecraft from the comet and the sub-solar-latitude. Unlike observations at Hyakutake and Hale-Bopp (e.g.,

Bockelee-Morvan 1997), where a high CO abundance was observed, we could identify only a few mass spectra that revealed a clear CO signal. Extreme care had to be taken to separate spectra taken adjacent to spacecraft maneuvers, to ensure that RTOF is not detecting the CO fragmentation remnants of spacecraft contaminations sticking to the spacecraft structure, which are released when the thermal environment changed.

#### 4. DISCUSSION

The composition of cometary volatiles contains basic information on the nature of comets and their formation mechanisms. This information originated for a long time only from measurements of the cometary dissociation products, observed mostly from far away. Cometary in situ exploration with the possibility for close fly-bys has changed this situation drastically. As comets display huge variation in the abundance of volatiles, high-resolution mass spectrometry is now able to provide the necessary information to come up with an accurate chemical inventory for individual comets, thereby removing a lot of ambiguities. Abundance measurements of cometary volatiles are often quoted as ratios. Such ratios are used in various classification schemes of comets (e.g., A’Hearn 1995; Fink 2009; Mumma & Charnley 2011; Le Roy et al. 2015). The variability of these ratios is therefore important. Many of these



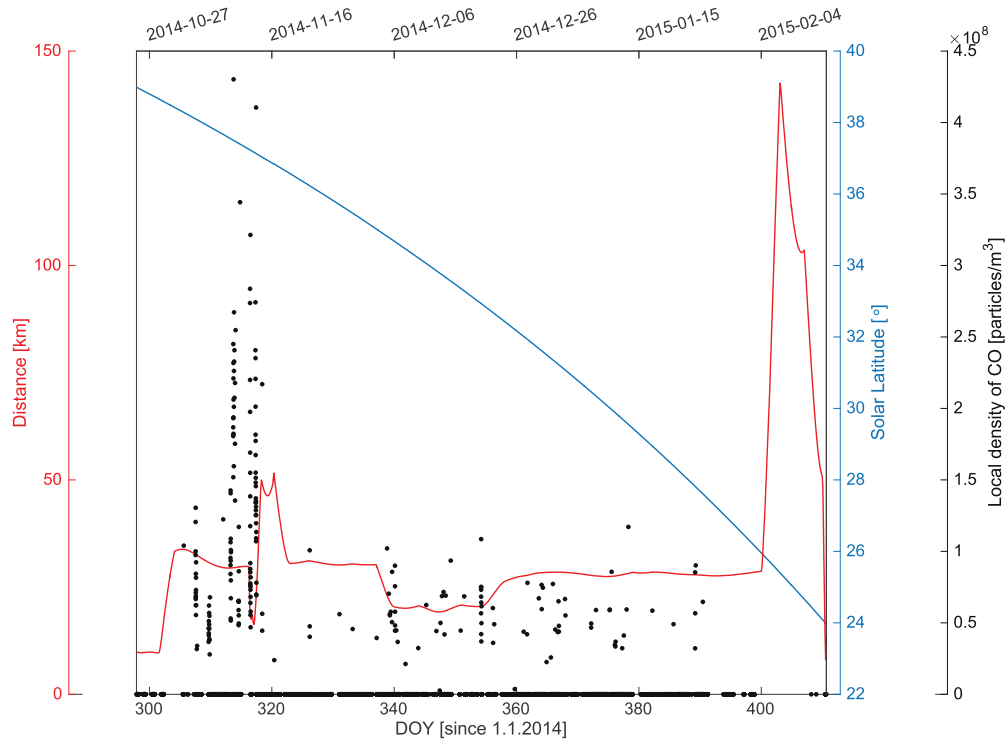
**Figure 5.**  $\text{CO}_2/\text{H}_2\text{O}$  ratio (left) and the latitude of the sub-spacecraft point (right) for the investigated time period.

observations have been the result of relatively short period measurements with remote sensing instrumentation, taking into account the integrated coma along the viewing direction. Some of these ratios also result from measurements over large areas of the inner coma, thus providing a global average of the production rate of these species, and also include molecular species that sublimated from the nucleus and those that were generated in subsequent chemical processes in the coma. From the in situ measurement of the CO density in the coma of Comet Halley we know, for example, that for this comet only about 1/3 of the CO originates directly from the nucleus (Eberhardt et al. 1987). The remainder of the CO comes from an extended source located in the innermost 25,000 km of the coma (for a review of distributed sources in comets, see, e.g., Cottin & Fray 2008). No suitable parent molecule for this extended source could be identified at that time, and Eberhardt et al. (1987) concluded that the CO evaporated from CHON-type dust grains in the coma either as CO or as a short-lived parent. In the case of 67P/C-G not much dust was observed (Rotundi et al. 2015).

ROSINA/RTOF has now allowed, for the first time, a direct in situ high-time resolution measurement of cometary molecules originating directly from a comet's nucleus over a long time-period, much longer than any previous measurements at a close distance to the comet. With the present study we have made with ROSINA/RTOF the first step to record precisely the heliocentric variation of cometary abundances to investigate processes responsible for the production of the most abundant cometary parent molecules. These and the forthcoming measurements at 67P/C-G have then to be used to investigate the question of to what extent molecular abundance ratios vary and what causes the observed variability in the coma. The presented RTOF measurements indeed reveal a high variability but also a distinct pattern. Our measurements show a clear north-south asymmetry in the abundance of the major volatiles (see Figure 5). The ultimate issue to be resolved is the question of whether this asymmetry can arise from a comet whose building blocks originated from a single reservoir or whether

the comet was formed through fusion of material from a different origin. To answer this question we need to draw inferences from the measured volatile inventory in the coma to the composition of the volatiles in the nucleus; we have to turn our attention to the question of whether we can infer from a measurement of released trapped gases in the ice the amount of original available gas when the comet ice was formed. The underlying physics of this question was addressed in a series of laboratory experiments (see, e.g., Bar-Nun & Laufer 2003) with the goal to understand how much gas relative to its abundance in the gas phase can be trapped in water ice at a particular pressure-temperature range and how the trapped gas is then released again. Two major insights were the recognition that water ice in comets formed in the amorphous state at temperatures below  $\sim 50$  K, and that amorphous water ice has a very high capacity for trapping various gases (Bar-Nun et al. 1985, 2007). It was found that when amorphous ice is warmed trapped gases are released in eight distinct temperature ranges as a pure manifestation of the change in the ice structure at very specific temperatures (e.g., Laufer et al. 1987).

To understand our RTOF measurements we ask what would be observable by a mass spectrometer from an amorphous icy homogenous sphere made out of equal parts of intrinsically mixed  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , which is illuminated from a fixed point in space with light. The very low albedo of comets indicates that the volatile ices must be definitely mixed with dust at the surface of the comet, although the relationship is complex (e.g., Lucey & Clark 1985). Moreover, hydrocarbon molecules on the surface will be transformed to a dark non-volatile carbonaceous crust by UV light (Riedo et al. 2010). Sunlight gets absorbed to a very large extent and heats the surface layer of the comet. Due to the low thermal conductivity of the cometary surface (Gulkis et al. 2015; Spohn et al. 2015), a good fraction of the incoming sunlight is reemitted in the NIR wavelength range back to space. The remaining part penetrates the cometary surface up to a few meters and heats the volatile material. After some time the illuminated surface reaches the necessary temperature to release the  $\text{CO}_2$ . A mass spectrometer



**Figure 6.** CO local density for the investigated time period. Also plotted are the distance of the spacecraft from the comet and the solar-latitude.

at a fixed position relative to the surface would measure during the heating process an increasing flux of the sublimating  $\text{CO}_2$  molecules. If the surface temperature would be additionally increased to the point where the sublimation temperature of  $\text{H}_2\text{O}$  is reached, an increasing  $\text{H}_2\text{O}$  component would be seen as well. The measured ratio  $\text{CO}_2/\text{H}_2\text{O}$  could vary over a wide range depending on the particular temperature of the ice, despite the fact that the amorphous ice was formed with a fixed  $\text{CO}_2/\text{H}_2\text{O}$  vapor ratio. Comet Simulation (KOSI) experiments (see, e.g., Grün et al. 1991), which simulated cometary heating processes, showing that already on a sample surface of a few hundreds of  $\text{cm}^2$  the temperature was not homogeneous and that the temperature pattern could change quickly in unexpected ways. At places where the ice was covered by dust, the surface temperature was significantly above 300 K. When dust was blown off, the local surface cooled down rapidly. The cover layer of dust developed during these experiments remained thin, however ( $<2.5$  millimeters). KOSI-3 and KOSI-4 experiments revealed that inward diffusion of  $\text{CO}_2$  can occur, which can even produce a variation of the chemical composition depending on the depth (Hsiung & Roessler 1989). It becomes clear that despite having accurate long-term local abundance measurements of the  $\text{H}_2\text{O}$  and  $\text{CO}_2$  components of 67P/C-G's coma, we are still at the moment missing vital information to make a link to the composition of the nucleus.

Despite this, the qualitative picture holds that due to the  $52^\circ$  obliquity and the orientation of the spin axis of 67P/C-G strong seasonal effects exist, which leads to a highly asymmetric insolation condition. During the long time when the comet is far from the Sun, the northern cometary surface areas are only weakly illuminated during the northern summer, while during the short perihelion passage of 67P the southern regions, during the southern summer, will receive a lot of sunlight for a brief period. This leads to a highly asymmetric

temperature and heat distribution on and in the upper cometary surface layers. We display in Figure 6 the solar latitude in the 67P/C-G reference frame, together with the distance between the comet and *Rosetta*. As a result of the different insolation of the Northern and Southern Hemispheres, sublimation has eroded all  $\text{CO}_2$  from the surface on the northern side of the comet. Therefore, the observed asymmetry need not be taken necessarily as evidence that the cometary material originated from more than one reservoir. However, it becomes clear that we need precise information on the heat distribution in the upper cometary surface layers and on the erosion rate that refreshes the cometary surface layer, if we want to use two molecular species with very different sublimation temperatures to make inferences about the relative abundances of the species in the cometary surface.

Measurements with the Akari space observatory have shown that the  $\text{CO}_2/\text{H}_2\text{O}$  ratios of the investigated comets are ranging from 0.05 to 1.1 at heliospheric distances between 1.3 and 3.7 au. At distances beyond 2.7 au the ratios increase to the upper end of the interval due to the decreasing volatility of the water ice (Mumma & Charnley 2011). The RTOF measurements for Jupiter-family comet 67P/C-G reveal at heliospheric distances from 3.1 to 2.3 au a stable periodic pattern of the  $\text{CO}_2/\text{H}_2\text{O}$  ratio, which reaches from 0 to a maximum of 3–4 (see Figure 5). Clearly visible are the time variations of the observed  $\text{CO}_2/\text{H}_2\text{O}$  ratio in the view direction of the RTOF observations. The observed time variability of the measured neutral abundances is understandable when one recalls that the volatility of different ices is very different. We have also identified a weak CO component, which can vary from  $\sim 0.4\%$  to  $\sim 30\%$  in 23 investigated comets (see Figure 5 in Paganini et al. 2014). As our measurements were all made close to the comet, we can safely assume that we are measuring molecules originating directly from the cometary nucleus.



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## REFERENCES

- A’Hearn, M. A. 1995, *Icar*, **118**, 223
- A’Hearn, M. A., Belton, M. J. S., Delamere, W. A., et al. 2011, *Sci*, **332**, 1396
- Balsiger, H., Altwegg, K., Bar-Nun, A., et al. 2015, *SciA*, e1500377
- Balsiger, H., Altwegg, K., Bochsler, P., et al. 2007, *SSRv*, **128**, 745
- Bar-Nun, A., Herman, G., Laufer, D., & Rappaport, M. L. 1985, *Icar*, **63**, 317
- Bar-Nun, A., & Laufer, D. 2003, *Icar*, **161**, 157
- Bar-Nun, A., Notesco, G., & Owen, T. 2007, *Icar*, **190**, 655
- Bieler, A., Altwegg, K., Balsiger, H., et al. 2015a, *Natur*, **526**, 679
- Bieler, A., Fougere, N., Toth, et al. 2015b, *A&A*, **583**, A7
- Bockelee-Morvan, D. 1997, in *IAU Symp.* 178, *Molecules in Astrophysics: Probes 46 and Processes*, ed. E. F. van Dishoeck (Dordrecht, NL: Kluwer), 447
- Bockelee-Morvan, D., Crovisier, J., Mumma, M. J., & Weaver, H. A. 2004, in *Comets II*, ed. M. C. Festou, H. U. Keller, & H. A. Weaver (Tucson: Univ. Arizona Press), 391
- Cottin, H., & Fray, N. 2008, *SSRv*, **138**, 179
- Eberhardt, P. 1999, *SSRv*, **90**, 45
- Eberhardt, P., Krankowsky, D., Schulte, et al. 1987, *A&A*, **187**, 481
- Fegley, B., Jr., & Prinn, R. G. 1989, in *The Formation and Evolution of Planetary Systems*, ed. H. A. Weaver, & L. Danly (Cambridge: Cambridge Univ. Press), 171
- Feldman, P. D., A’Hearn, M. F., Bertaux, J.-P., et al. 2015, *A&A*, **583**, A8
- Feldman, P. D., & Brune, W. H. 1976, *AJ*, **209**, L45
- Fink, U. 2009, *Icar*, **201**, 311
- Fray, N., & Schmitt, B. 2009, *P&SS*, **57**, 2053
- Gasc, S. 2015, PhD thesis, Univ. Bern
- Grün, E., Bar-Nun, A., Benkhoff, J., et al. 1991, in *Comets in the Post-Halley Era*, ed. R. L. Newburn et al. (Dordrecht, NL: Kluwer), 277
- Gulkis, S., Allen, M., von Allmen, P., et al. 2015, *SciA*, **347**, aaa0709
- Hässig, M., Altwegg, K., Balsiger, H., et al. 2015, *Sci*, **347**, 276
- Hsiung, P., & Roessler, K. 1989, in *Proc. Int. Workshop on Physics and Mechanics of Cometary Materials*(ESA SP-302), 191
- Laufer, D., Kochavi, E., & Bar-Nun, A. 1987, *PhRvB*, **36**, 9219
- Le Roy, L., Altwegg, K., Balsiger, H., et al. 2015, *A&A*, **583**, A1
- Lucey, P. G., & Clark, R. 1985, in *Ices in the Solar System*, ed. J. Klinger et al. (Dordrecht: Reidel), 155
- Mumma, M. J., & Charnley, S. B. 2011, *ARA&A*, **49**, 471
- Ootsubo, T., Kawakita, H., Hamada, S., et al. 2012, *ApJ*, **752**, 15
- Paganini, L., Mumma, M. J., Villanueva, G. L., et al. 2014, *ApJ*, **791**, 122
- Paganini, L., Mumma, M. J., Villanueva, G. L., et al. 2015, *ApJ*, **801**, 1
- Riedo, P., Wahlström, J. A., Scheer, et al. 2010, *JAP*, **108**, 114915
- Rotundi, A., Sierks, H., Della Corte, V., et al. 2015, *Sci*, **347**, aaa3905
- Rubin, M., Altwegg, K., Balsiger, H., Bar-Nun, et al. 2015, *Sci*, **348**, 232
- Scherer, S., Altwegg, K., Balsiger, et al. 2006, *IUMSp*, **251**, 73
- Schläppi, B., Altwegg, K., Balsiger, et al. 2010, *JGRA*, **115**, 12313
- Schletti, R., Wurz, P., Scherer, S., & Siegmund, O. H. 2001, *RScI*, **72**, 1634
- Siegmund, O. H. W., Kromer, K., Wurz, et al. 2001, *Proc. SPIE*, **4140**, 229
- Spohn, T., Knollenberg, J., Ball, A. J., et al. 2015, *Sci*, **349**, aab0464