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CHANGES IN THE PHYSICAL ENVIRONMENT OF THE INNER COMA OF 67P/CHURYUMOV-GERASIMENKO WITH DECREASING HELIOCENTRIC DISTANCE

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ABSTRACT

The Wide Angle Camera of the OSIRIS instrument on board the *Rosetta* spacecraft is equipped with several narrowband filters that are centered on the emission lines and bands of various fragment species. These are used to determine the evolution of the production and spatial distribution of the gas in the inner coma of comet 67P with time and heliocentric distance, here between 2.6 – 1.3 AU pre-perihelion. Our observations indicate that the emission observed in the OH, OI, CN, NH, and NH₂ filters is mostly produced by dissociative electron impact excitation of different parent species. We conclude that CO_2 rather than H₂O is a significant source of the [OI] 630 nm emission. A strong plume-like feature observed in the in CN and [OI] filters is present throughout our observations. This plume is not present in OH emission and indicates a local enhancement of the CO_2/H_2O ratio by as much as a factor of 3. We observed a sudden decrease in intensity levels after March 2015, which we attribute to decreased electron temperatures in the first kilometers above the nucleus surface.

6 figures, 6 tables

Key words: comets: individual 67P/Churyumov-Gerasimenko – techniques: image processing – plasmas – radiation mechanisms: non-thermal – molecular processes – atomic processes

1. INTRODUCTION

Comets are considered relatively pristine leftovers from the early days of our Solar System. They are distinguished from other minor bodies by a coma of gas and dust produced when ices retained from the formation of the solar system sublime. Understanding the connection between the coma and the comet's nucleus is critical because observations rarely detect the nucleus directly, and its properties must often be inferred from measurements of the surrounding coma. Because measurements of the coma do not necessarily represent the characteristics of the nucleus due to spatial, temporal and chemical evolution of the emitted material, projecting the coma observations back to the nucleus requires an understanding of the processes that induce changes in the coma. Compositional studies must take into account chemical reactions and photolysis to determine how the molecular abundances measured in the coma relate to the bulk composition of the nucleus.

Direct, high-resolution observations of cometary nuclei are rare, coming only from spacecraft encounters. Connecting these measurements to the coma provides a valuable means of evaluating the techniques used in situations where the nucleus cannot be seen. Images obtained by *Giotto, Vega, Deep Space 1* and *Stardust* showed details of their targets' nuclei (Keller et al. 1987; Soderblom et al. 2002; Brownlee et al. 2004; Veverka et al. 2013), but in each case, coma observations were limited to the continuum around closest approach. The *Deep Impact* spacecraft was the first to observe both the gas and dust comae of comets 9P/Tempel 1 and 103P/Hartley 2 through a multi-wavelength filter set, while monitoring each comet for months around close approach (A'Hearn et al. 2005; A'Hearn et al. 2011).

Orbiting the comet since August 2014, the European Space Agency's *Rosetta* mission has allowed an unprecedented study of the activity and evolution 67P/Churyumov-Gerasimenko. The large heliocentric distance of the comet, its low activity levels, and the close proximity of the spacecraft to its surface allow us to sample an environment that has never been studied before and that is not accessible for observations from Earth. This paper describes observations of the dust and gas in the coma of 67P/Churyumov-Gerasimenko acquired by *Rosetta*'s Optical, Spectroscopic, and Infrared Remote Imaging System (OSIRIS). Fragment species are relatively bright and emit in wavelengths accessible from the ground. OSIRIS' narrow band filters provide an important link to ground based observations, and help to connect our detailed knowledge of 67P/Churyumov-Gerasimenko to the wider population of comets.

2. OBSERVATIONS

OSIRIS consists of two bore-sighted cameras: a narrow angle camera (NAC, field of view 2.2 x 2.2 degrees) and a wide angle camera (WAC, field of view 11.4 x 12.11 degrees) (Keller et al. 2007). The WAC is best equipped to study the coma; its twelve narrowband and two medium width filters allow color discrimination and the imaging of emission lines and bands from gas and continuum in optical wavelengths (250–750 nm). We typically monitored gas and dust activity with the WAC, about once every two weeks for heliocentric distances greater than 2 AU, and once per week between 2 and 1.3 AU pre-perihelion. The

SEQUENCE	Date	Time	r _h	Δr_{h}	Range	Phase
	(UTC)	(UTC)	(AU)	(km/s)	(km)	(deg)
MTP12/DEEP VAC	2015 Jan 24	11:35 AM	2.47	-12.8	27.9	92.8
MTP14/DEEP VAC	2015 Mar 12,	1:27 AM	2.12	-13.3	80.7	50.6
MTP15/STP051	2015 Apr 14	4:25 PM	1.88	-13.2	170	74.5
MTP16/STP055	2015 May 12	2:11 AM	1.66	-12.5	155	71.6
MTP17/DEEP VAC	2015 June 3	8:04 AM	1.51	-10.9	232	89.3
MTP18/VAC	2015 July 3	8:19 AM	1.34	-7.77	168	89.7

Table 1 – Observing log.

nominal sequence had a set of observations once per hour for a full comet rotation (~12h25m during the observations described here; Keller et al. 2015). As both Rosetta and 67P were coming closer to Earth, the data volume available increased, allowing us to increase the observing cadence to one set of observations every 20 min, for 14h (to avoid aliasing with the comet's rotation period). Exposure times are optimized to achieve good signal-to-noise in the coma, often resulting in saturation on the nucleus and in the apparition of internal reflection artifacts (ghosts) appearing on the CCD images as a circular 'blob' to the right of the nucleus (Keller et al. 2007). The acquired images are scaled with binning (typically 4 x 4 for coma observations) and observing geometry (distance to the comet, distance to the Sun). To establish the connection with the nucleus, shortexposure, 2x2-binned images were acquired with the 375 nm and 610 nm filters along with the coma images. For this paper, we limit ourselves to data acquired during four periods when *Rosetta* conducted the so-called 'Volatile Activity Campaigns'. These campaigns were multi-instrument observations specifically designed to study the gas in the coma of 67P (including OSIRIS, VIRTIS, MIRO, and Alice), and two more dedicated OSIRIS campaigns to provide better temporal coverage. The observations discussed in this manuscript were acquired before the comet's perihelion, between 2015 January 24 and July 3 (see Table 1). During this period, the comet's distance to the Sun decreased from 2.48 AU to 1.34 AU. Because Rosetta was close to the surface in January, the nucleus fills a significant part of the field of view, whereas during the later observations the WAC maps a much larger part of the coma. For the analysis described below, we used images acquired at the approximate same diurnal phase.

3. ANALYSIS

3.1 Data Reduction and Image Processing

All images are pre-processed using the standard OSIRIS pipeline (Tubiana et al. 2015), which includes bias and dark subtraction, flat fielding, conversion from electron yield to radiance units (W $m^{-2} sr^{-1} nm^{-1}$), and bad-pixel masking.

3.1.1. Coma gas emissions in the filters

The narrowband filters were designed to sample either emission lines and bands of specific gases or continuum light at nearby wavelengths, but inevitably also sample the emission of other molecules with lines that fall within the narrowband filters' passbands at various

Filter + Name	$\lambda_{central}$	Width	Comments
	(nm)	(nm)	
21 Green	537.2	63.2	Includes C_2 Swan $\Delta v = -1,0$.
31 UV245	246.2	14.1	Isolated pinholes.
41 CS	259.0	5.6	Several overlapping pinholes.
			Samples CS $A^{1}\Pi - X^{1}\Sigma^{+}$ (0-0).
51 UV295	295.9	10.9	
61 OH	309.7	4.1	Several pinholes, one strong (at
			the lower left quadrant of the CCD
			images). Samples OH A ² Σ ⁺ –X ² Π ⁱ
			(0-0).
71 UV325	325.8	10.7	Many overlapping pinholes.
81 NH	335.9	4.1	Samples NH A ³ Π_1 –X ³ Σ ⁻ (0-0).
			Includes OH ⁺ (A ³ Π – X ³ Σ ⁻).
12 Red	629.8	156.8	Broad band filter.
13 UV375	375.6	9.8	Minor contribution C ₃ Comet Head
			Group.
14 CN	388.4	5.2	Samples CN violet system, minor
			contribution C_3 Comet Head
			Group. Includes CO_2^+ (A ² 11 – X ³ Σ^-).
15 NH2	572.1	11.5	Samples NH ₂ A ${}^2A_1 \rightarrow X {}^2B_1$
1 C N -	F00 7	4 7	(0,10,0).
16 Na	590.7	4./	Covers both Na D1 and D2
45.01	(21.6	4.0	doublets; includes C_2 Swan $\Delta v = -2$
17 01	631.6	4.0	Samples [UI] 1 D – 3 P 630 nm line
			Only. Includes $NH_2 A A_1 \rightarrow X B_1$
10 Wig(10)	6126	0.0	$[U, \nabla, U]$. Includes NIL $\tilde{\Lambda}^2 \Lambda \rightarrow V^2 D$ (0.0.0)
19 112010	012.0	9.8	Includes $NH_2 A A_1 \rightarrow X B_1 (0,9,0)$.

Table 2 - Characteristics of the WAC's filters (Keller et al. 2007).

levels. A summary of the characteristics of the WAC's filters and of the most prominent emission features within their pass bands is given in Table 2.

The WAC can map the distribution of water with its OI and OH filters. The OI filter covers the forbidden transitions from the OI ($2p^4$) ¹D state to the ground state. The OI ($2p^4$) ¹D state is populated directly by photodissociation of H₂O molecules, as is the OI ($2p^4$) ¹S state, which relaxes mostly (95%) by decay into the ¹D state (c.f. Cochran 2008). The OH filter covers the (0-0) band of the A ² Σ^+ – X ² Π transition of OH, centered at about 308.5 nm, which is excited almost entirely by fluorescence of sun light (c.f. Schleicher & A'Hearn 1988). A small fraction of the photodissociation of H₂O also leads directly to the population of OH in high rotational states of the A ² Σ^+ electronic state (A'Hearn et al. 2015), but the resulting emission falls outside the passband of the WAC's OH filter. The WAC's CN filter covers emission from B² Σ^+ – X² Σ^+ (0,0) transitions around 388 nm. The NH₂ Ã ²A₁ \rightarrow X ²B₁ (0,10,0) band is very wide and how much of the emission falls within the NH₂ filter's

FILTERS	Removal Factor ΔF						
	0%	10%	20%	30%	(%)		
OI/UV375	1.570	2.026	2.623	3.438	5		
CN/UV375	1.021	1.034	1.053	1.077	6		
OH/UV375	0.479	0.444	0.397	0.332	10		
NH/UV375	0.829	0.790	0.740	0.671	8		
NH2/UV375	1.738	2.124	2.630	3.321	5		
Na/UV375	1.673	2.080	2.614	3.343	8		
Vis610/UV375	1.648	2.127	2.753	3.609	5		

Table 3 – Continuum removal factors F for the WAC gas filters assuming different continuum reddening (% per 100 nm between 375 nm and 610 nm). ΔF is the relative, error-propagated 1-sigma standard deviations of the removal factors.

passband depends on the heliocentric distance and velocity. The NH filter covers the NH $A^{3}\Pi_{1} - X^{3}\Sigma^{-}$ (0-0) transition. While the WAC is equipped with CS and Na filters, those two filters were used only sporadically during the first half of the mission because the low SNR and pinholes (CS) and contamination by C₂ emission (Na) hampers the interpretation of observations made with these two filters.

The WAC is also equipped with several filters that can sample the continuum. Comparing the 375 nm and 610 nm narrowband filters illustrates the level of contamination of the latter filter by gas emission features. In WAC observations of 16Cyg, a system of two solar analogs, we measured a flux ratio Vis610/UV375 = 1.648 ± 0.08, whereas for the dust surrounding 67P this ratio was between 2.8 and 5.6 (Jan/March) and 2.5 – 3.3 (June/July). Such values would require a reddening between 20-40% per 100 nm between the two filters, while we determined from the NAC images that the average reddening of the dust was between 375 and 610 nm was around 18% per 100 nm (Sec. 3.1.2.). This suggest that in the January/March data, up to 50% of the flux in the 610 nm filter might come from gaseous emission, probably mostly due to the emission from the NH₂ Ã ²A₁ \rightarrow X ²B₁ (0,9,0) and C₂ d³\Pig – a³\Pi_u ($\Delta v = -2$) transitions. As will be discussed below, the Vis610/UV375 ratio measured in June and July is close to what is expected based on the NAC reddening measurement, suggesting that the relative contribution of gaseous emission to the flux measured in the Vis610 decreased.

To further assess the gas contamination in other filters, we show the transmission of the WAC filters on a high-resolution spectrum of comet 122P/DeVico; Cochran 2002); Fig 1a). The spectrum of this comet is not a particularly good proxy for that of 67P; the comet was observed very close to the Sun (0.7 AU), was extremely dust-poor, and the two comets have different compositions (67P is depleted in its carbon chain molecules while 122P has a 'typical' composition; Fink 2009). However, the high-quality spectrum and line catalogue demonstrate the extent of the contamination and the identification of the gases responsible for it. An example is shown in Fig 1b, where we show the transmission of the OI filter overlaid on comet 122P/DeVico's spectrum. The filter was designed to sample emission from the [OI] ${}^{1}D \rightarrow {}^{3}P$ line at 630 nm, but also contains several emission lines of the NH₂ molecule, notably the $\tilde{A} {}^{2}A_{1} \rightarrow X {}^{2}B_{1}$ (0,8,0). The WAC is equipped with a narrow band filter designed specifically to observe the NH₂ $\tilde{A} {}^{2}A_{1} \rightarrow X {}^{2}B_{1}$ (0,10,0) band, which can be used to



Fig. 1a – OSIRIS/WAC filter transmission profiles overlaid on a high-resolution spectrum of comet 122P/DeVico (Cochran et al. 2002). Profiles are not convolved with the quantum efficiency of the detector.



Fig. 1b – As above - close up on the OI filter transmission.

remove NH₂ emission from the 610 nm (NH₂ $\tilde{A} {}^{2}A_{1} \rightarrow X {}^{2}B_{1}$ (0,9,0) transition) and OI narrow band filters (NH₂ $\tilde{A} {}^{2}A_{1} \rightarrow X {}^{2}B_{1}$ transition's (0,8,0)) if the relation between the three different emission bands of NH₂ is known. To calculate the contribution of NH₂ emission to the flux measured in the NH₂, Vis610, and OI filters we weighted the archival spectrum *S*(λ) of 122P with OSIRIS' CCD quantum efficiency *Q*(λ), the reflectivity *R*(λ), and transmission of its filters *T*(λ):

$$S'(\lambda) = \frac{\int Q(\lambda) \cdot R(\lambda) \cdot T(\lambda) \cdot S(\lambda) \cdot d\lambda}{\int Q(\lambda) \cdot R(\lambda) \cdot T(\lambda) \cdot d\lambda}$$
[1]

For comet DeVico we find that the ratio between NH_2 emission in the OI and NH_2 filters is 1.389, and 0.45 for the ratio between NH_2 emission in the Vis610 and NH_2 filters. Using this band ratio, we find that NH_2 typically contributed between 10-20% to the flux measured in the OI filter (after continuum subtraction); however, as we will discuss in Sec. 5, this assumes that band ratios between photo fluorescent excitation and electron impact excitation are similar, which may not be the case.

Fluorescence efficiencies for NH_2 have been calculated by Kawakita & Watanabe (2002). Their model shows that the ratio between fluorescence efficiencies of even and odd transitions is strongly dependent on the heliocentric distance and heliocentric velocity, but that the ratio between even bands is constant. NH_2 emission in the NH_2 and OI filters is thus coupled and can be removed with a constant factor that is independent of heliocentric distance and velocity, and this factor should be the same for both 122P and 67P. The Vis610 filter however includes emission from an odd band, (0,9,0), which has a much more complex relation to the emission in the even (0,10,0) band sampled by the NH_2 filter. We therefore did not attempt to remove the contribution of NH_2 to the images acquired with the Vis610 filter.

Concluding, we deem the filter centered at 375 nm best suited to image the continuum light, although its transmission includes some emission lines from C_3 ($\tilde{A} \ ^1\Pi_u \rightarrow X^1\Sigma_g^+$) transitions. There are fewer emission lines at shorter wavelengths, but the three near-UV continuum filters centered on 245, 295, and 325 nm suffer heavily from pinholes (circular defects in the filters' coatings from impurities in the production process) which represent an increased light flux at shorter and longer wavelengths than those in the filter width bandpass. The disadvantage of using the UV375 filter to remove the continuum from all the gas filters is that since we use only one filter, we do not measure coma colors, and have to assume a linear reflectance with respect to the wavelength. The assumed reddening has a large impact on the continuum removal factor used with increasing wavelength difference.

3.1.2. Continuum removal and reddening

To measure the gaseous emission line flux, the contribution of the reflected continuum needs to be removed (see e.g. Farnham et al. 2000). We used OSIRIS observations of the solar analogues of the 16Cyg system (the two stars are not spatially resolved by the WAC) to determine the ratio of narrowband continuum fluxes in all filters for a solar spectrum. These ratios α are the weight factors needed to remove the flux contribution of 'grey' dust from the total flux F_{tot} measured in a narrow band using the flux F_{375} measured in the UV375 filter in order to measure the flux contribution by the gas of interest:

BODEWITS ET AL. - PHYSICAL PROCESSES IN THE INNER COMA OF 67P (ARXIV)

$$F_{gas} = F_{tot} - \alpha \cdot F_{375}$$
^[2]

The signal-to-noise ratio in the OH and NH filters is poor because UV fluxes from solar analogs are low and the CCD's quantum efficiency drops significantly below 400 nm (Magrin et al. 2015). In addition, the long exposures required in these filters increases the chance of cosmic rays affecting the measurement, reducing the number of useable images. Average filter ratios and $1-\sigma$ standard deviations are given in Table 2.

To calculate the effect of spectral reddening *P* (in percent per 100 nm) on the flux ratios we first calculated the resulting, reddened spectrum by weighting a solar spectrum with the reddening $R(\lambda)$ as a linear function of wavelength λ between $\lambda_1 = 375.6$ nm and $\lambda_2 = 612.6$ nm (the central wavelengths of two of the WAC's continuum filters), normalized at 494 nm:

$$R(\lambda) = 1 + 0.01 \cdot P \cdot (\lambda - 0.5 \cdot (\lambda_2 - \lambda_1))$$
[3]

We used the ratios of the fluxes of the reddened spectrum and the original solar spectrum to calculate continuum removal factors for increasing reddening, which are given in Table 3. To estimate the average reddening of the continuum of 67P we performed a deeper investigation of the colors of the coma using NAC medium-band filters observations, for which the contributions of extraneous emission lines should be less important. For this, we choose a dataset that had good coverage of the coma around the nucleus using a large number filters. The selected images have been acquired on 2015 February 18 in five filters: Near-UV, Blue, Orange, Red, Infrared. The comet was at about 2.3 AU from the Sun and the phase angle was about 85 deg. The spacecraft was at 220 km from the comet and the NAC's field of view was about 9 km around the nucleus.

We constructed a map of radial distance from the nucleus limb and computed the average coma surface brightness over an azimuthal region generally free of gas jets and ghosts. Assuming that in the broad NAC filters (mostly ~ 50 nm) the contribution of the gas emission is small with respect to the dust contribution, we derived the colors of the dust coma. We found that the coma has an average reddening of 19% per 100 nm in the wavelength range 360 – 649 nm, the closest to the 375 – 610 nm range obtained with WAC filters.

However, NAC imaging is not available concurrent with most WAC gas observations, and it may or may not sample the relevant region of the coma given the instrument's small field of view. Therefore, we devised a second, empirical method to determine the reddening of the dust in the coma. We assumed that NH_2 emission comes predominantly from fragment species in the coma. Thus, for the images of 67P acquired with the NH_2 filter the underlying continuum subtraction was done by varying the continuum removal factor until jets disappeared from the NH_2 filter image leaving a rather isotropic NH_2 coma. This method typically yields factors that correspond to 17-20% per 100 nm between 375 and 610 nm, somewhat larger than reported from ground-based observations of the comet in previous apparitions ($11 \pm 2\%$ per 100 nm between 436 and 797 nm; Tubiana et al. 2011) but consistent with ground-based observations acquired during this apparition (20% between B and V; Snodgrass et al. 2015). We therefore used a constant reddening of 18% per 100 nm for the data discussed in this paper.

3.2 Column Densities and Production Rates

We identified observations in each sequence that were acquired at the same diurnal phase, extracted surface brightness profiles in two directions, and measured the surface brightness at a fixed position 3 km in the sunward direction above the surface.

When the formation and excitation processes of the fragment species are known, the measured surface brightnesses S(x,y) can be converted into column densities N_{col} by assuming fluorescence efficiencies g of each species:

$$N_{col}(x,y) = \frac{4\pi \cdot S(x,y) \cdot \Delta \lambda}{E_p \cdot g}$$
[4]

where $\Delta\lambda$ is the FWHM of the filter (Table 2) and E_p the energy of the photons at the wavelength of the emission feature considered. [OI] surface brightnesses can be converted into H₂O column densities using reaction rates for prompt excitation of the ¹S and ¹D states (Bhardwaj & Raghuram 2012), weighed by the branching ratios of the transitions leading to emission at 630 nm (the 2nd line of the doublet at 636 nm is at the edge of the OI filter where the transmission is below 6% of the peak transmission; see Fig. 1b). The CN, OH, and NH surface brightnesses were converted into column densities using a standard Haser model for easier comparison with other observations. Assumed outflow velocities and lifetimes for parents and daughters can be found in the Appendix (Table A1). To better evaluate the column densities, we also calculated production rates with a modified Haser model that takes the gas acceleration, collisional quenching of the long-lived 1D state of the oxygen atom, and the effect of the oxygen atom moving out of the field of view before it can decay to the ground state into account. This model is described in Appendix A.

3.3 Uncertainties

The results are subject to several possible systematic uncertainties. The absolute calibration of OSIRIS is better than 1% for most filters, but the calibration constant for the OH filter (and continuum filters <300 nm) has an uncertainty of $\sim 10\%$ (Tubiana et al. 2015). Bias levels are temperature dependent and have gradually changed over time because the spacecraft approached the Sun. From the 16Cyg observations (where we can see the background), we estimate that the bias level is now constrained to within 1 DN. Because the bias is individually determined for each hardware configuration, the error remains 1 DN independent of binning. The resulting gas detections typically had a SNR of 4 or better per 4x4 pixel at 100 pixels from the nucleus. The continuum removal is the largest systematic and statistical uncertainty in our data analysis. For example, in the data acquired in March, at a distance of 100 pixels, i.e., 0.82 km, from the nucleus, the continuum contributes 10% to the total signal in CN, ~20% in OI, ~30% in OH, and as much as 65% of the signal in the NH₂ filter. We have also tried to optimize the quality of the continuum removal factors by averaging repeated observations of 16Cyg, and these coefficients are now constrained within 5 - 10% (Table 3). As discussed above, we only use the UV375 filter to observe the continuum emission, and have to infer the color of the coma. We do not account for spatial gradients and temporal variations in the color of the coma. Assuming that the reddening is typically between 0 – 30%, differences in reddening could result in

Uncertainties in the assumed fluorescence efficiencies can affect the results systematically. Even more so, the use of those factors rests on the premise that the dominant processes are photo-processes, which we deem not be the case (Sec. 5).

4. **RESULTS**

Continuum and contaminant removed narrowband images for March and June are shown in Fig. 2, along with contextual images acquired with the 375 nm filter. All images are oriented such that the direction to the Sun is upward. In each frame, the entire field of view of the WAC is shown, which sides corresponds to 16 and 46 km projected at the nucleus, respectively. In each image a circular feature can be seen on the right side of the nucleus (saturated pixels are masked black in our image processing). These 'ghosts' are caused by internal reflections from optical elements and are always placed on the detector at the same place with respect to the nucleus. A smaller, weaker artifact can be seen in the same direction directly next to the nucleus. Three remnant pinholes can clearly be seen in the OH images.

All continuum images show multiple bright, collimated jets on the sunward side of the nucleus. In the top row, the March data, those jets are not present in any of the continuum-subtracted gas images. At all epochs we see a plume-like morphology perpendicular to the sunward direction. This feature is seen in the OI and CN filter, but not in the OH, NH, and NH_2 filters, where the observed morphology is less pronounced and enhanced towards the Sun (Fig. 2).

The continuum subtracted NH_2 images have poor SNR and show a broad distribution with little structure. For the data acquired in June and July, while assuming the same reddening of 18% per 100 nm (Sec. 3.1.2), the jets are over-subtracted in the OI data and cannot be entirely removed from most of the other filters. We believe this to be a consequence of our approach to the continuum subtraction (i.e. assuming a constant color throughout the inner coma). For each of the images in Fig. 2, the color scale of the look up table was adjusted to best emphasize the morphology. It is clear that while the morphology in the OH and NH images remains isotropic and diffuse, the cone in the [OI] and CN images becomes much fainter and less defined over time.

Radial surface brightness profiles were extracted from a 21-pixel wide box between the left limb of the nucleus and the edge of the frame. We extracted surface brightnesses in both the horizontal and vertical (sunward) direction, starting at the nucleus (orientation as in Fig. 2). The 1-sigma uncertainty was estimated from the standard deviation within the 21-pixel wide box. The resulting continuum subtracted profiles are shown in Fig. 3. The first two epochs show the best SNR. The surface brightness decreased by a factor of 5-10 after February, resulting in visible poorer SNR. For the observations in April, May, and June, data within 1 km from the surface seems unreliable, with the exception of CN. NH₂ is consistently very noisy (as the plots have a logarithmic scale, negative values are not shown), and it was probably not detected in the June and July 2015. On all six epochs, there is a clear difference between the shape of the profiles of OH and NH, which show a 1/r drop-off with distance, and the [OI] and CN profiles, which are flat within the first ~8 km from the surface. In January and March, the OH profiles in the sunward direction are very



FIG 2. Left to right: shape model image for reference, continuum subtracted images acquired with the OH, NH, NH₂, OI, and CN filters, and a long-exposure UV375 filter image for comparison. In the orientation used here, the Sun is always toward the top, and the main reflection ghost can be seen to the right of the nucleus. All images are the entire field of view of the WAC (11.4 x 12.1 degrees). The color scale is different for every filter, but is kept constant throughout all epochs within each filter.

similar to those in the perpendicular direction. After that, the emission on the sunward side of the coma is much stronger (factor 2) than that in the direction orthogonal to the cometsun line. This asymmetry is also present in the NH profiles, albeit less pronounced. In the OI and CN profiles, the emission is somewhat stronger in the orthogonal direction because the plumes visible in Fig. 2 extend to both extraction directions. On the two epochs where we have a good NH2 detection, January and March, its profiles are very flat and very different from the NH profile.



5. EMISSION PROCESSES

There are numerous inconsistencies in our results if we assume standard cometary physics. First, column densities and production rates derived from OSIRIS images are much higher than those measured by other instruments on board *Rosetta* (MIRO, VIRTIS, and ROSINA/COPS; Bieler et al. 2015a; Bockelée-Morvan, D. et al., 2015; Fougere et al., 2016;). Assuming photodissociation of H_2O as the main source of formation and prompt emission by atomic oxygen, and photodissociation and subsequent fluorescent excitation of OH, CN, and NH emission, we derived column densities and calculated global production rates using standard Haser model (Fig. 4, Tables 5 and 6).

There are currently no contemporaneous measurements available of the abundance of CN and NH. Abundances of NH_3 and HCN were 0.06% and 0.09% with respect to water, measured by *Rosetta's* ROSINA instrument at 3.1 AU on the sunward side of the comet (Le Roy et al. 2015). Fink (2009) measured NH_2 and CN abundances of 0.19% and 0.15% from



the ground at 1.35 AU from the Sun post-perihelion during the 1995 apparition. To calculate the expected surface brightness levels, we assumed abundances of 0.1% for HCN and NH_3 , and water production rates from Fougere et al. (2016). As shown in Fig. 4a, water production rates derived from the OH observations using the standard Haser model are initially more then a factor 300 larger then expected. Production rates derived from CN and

DATE	0I ¹	OH ²	CN ³	NH ⁴				
	(photons/molecule/s)							
1/24/2015	9.95E-8	7.13E-5	0.010	1.89E-3				
3/12/2015	1.35E-7	9.21E-5	0.014	2.56E-3				
4/14/2015	1.72E-7	1.18E-4	0.018	3.29E-3				
5/12/2015	2.20E-7	1.61E-4	0.023	4.20E-3				
6/3/2015	2.85E-7	1.95E-4	0.029	5.09E-3				
7/3/2015	3.59E-7	1.43E-4	0.041	6.68E-3				

Table 4 – Photon production efficiencies based on photodissociation rates (OI) and fluorescence models (OH, CN, NH) in units of photons/molecule.

References: 1) Bhardwaj & Raghuram 2012; 2) Schleicher 2010; 3) Schleicher & A'Hearn 1988; Kawakita & Watanabe 2002; 4) Kim et al. 1989.

NH surface brightnesses are also large by factors of 1000. This changes dramatically when we assume a more realistic velocity (eq. A2) in the inner coma, see Fig. 4b. Derived production rates for H_2O derived from OH are now about one order of magnitude too large, those of NH and CN parents by about two orders of magnitude. For OH and CN, the July results are consistent with expected production rates. NH emission remains about a factor of 10 too high.

Second, with the WAC we expect to observe two water photolysis products, OH and OI. Using the standard Haser model, water production rates derived from OH seem consistently larger than those derived from [OI], by a factor of 6 in January and by a factor of 30 in July. This situation is not resolved by our appended coma model because both there is no change in the relative column densities of OH and OI if both are assumed to come from H_2O .

Third, all production rates drop significantly between March and June, 2015. This variation is much larger than the diurnal variation of the total water production (\sim 25%; Gulkis et al. 2015) and not consistent with the observed trend of increasing production rates with decreasing heliocentric distance.

Fourth, the luminosity profiles are at odds with the observed morphology. Surface brightness profiles of parent species usually decrease with $\sim 1/r$ close to the nucleus, whereas those of fragment species have shallower slopes (c.f. Combi et al. 2004). The OSIRIS surface brightness profiles (Fig. 3) however are flat for [OI] and CN, for which the morphology suggests a prompt excitation process. In contrast, the morphology seen in the OH and NH filters – a symmetric distribution around the nucleus – is typical for a fragment species that gets a significant vectorial kick upon photodissociation of a parent species. The morphology of emission in the OI and CN images resembles the projection of a cone of gas and indicates a parent dissociation process that produces these fragments directly into an excited state.

We therefore conclude that by adjusting our models to better describe the physical processes in the inner coma we can explain some of the observations, but that the differences between our observations and model results indicate that photodissociation and fluorescence are not the dominant processes resulting in the OH, [OI], CN, and NH emission observed in the inner coma. Instead, the fragments might be fragments from

Table 5 – Surface brightness measured at 1 km above the surface in the horizontal direction (orthogonal to sunward direction). Column densities and production rates are derived assuming photo processes and are only given to show the discrepancy between observations and expected production rates (Sec. 5).

		Log column densities (molec./m ²)							
Date	ΟΙ	OH	CN	NH	NH ₂	OI	OH	CN	NH
1/24/2015	11.5 ± 0.2	1.5 ± 0.2	11.4±0.2	1.4 ± 0.2	5.3±0.3	21.7	17.6	16.5	16.2
3/12/2015	12.1±1.0	11.0±1.3	16.5±0.2	7.4±0.5	4.8±1.4	21.6	18.4	16.5	16.8
4/14/2015	1.3±0.8	2.7±0.2	2.0±0.1	1.1±0.8	0±1	20.5	17.6	15.4	15.9
5/12/2015	2.4±0.9	2.7 ± 0.4	3.7±0.2	2.0±0.5	0.9±1	20.6	17.5	15.6	16.0
6/03/2015	1.6±1.0	3.8±0.2	2.0±0.3	1.7 ± 0.5	0.8±0.8	20.1	17.6	15.2	15.8
7/03/2015	3.1±1.6	6.4±0.3	4.4±0.3	2.7±0.3	1.1±2	20.5	17.9	15.4	15.9

Table 6 – Production rates derived assuming photo processes and are only given to show the discrepancy between observations and expected production rates (Sec. 5). Results are shown for a standard Haser model, for an enhanced model that includes acceleration (incl. OI^a), and for a model that includes quenching and transport of OI (OI^b) The production rates are all for the assumed parents of the observed fragments, the label indicates from what fragment they were derived (i.e. OI for H₂O, OH for H₂O, CN for HCN, and NH for NH₃).

	Standard Haser				Enhanced model				
	Log prod. rates (molec./s)				Log prod. rates (molec./s)				
Date	ΟΙ	OH	CN	NH	OIa	OIb	OH	CN	NH
1/24/2015	28.0	28.8	26.8	27.1	27.7	29.6	27.4	25.4	25.7
3/12/2015	27.9	29.5	26.7	27.6	27.6	29.9	28.1	25.3	26.3
4/14/2015	27.9	28.7	25.6	26.6	26.6	29.0	27.4	24.2	25.3
5/12/2015	27.1	28.5	25.7	26.4	26.7	29.2	27.2	24.3	25.4
6/03/2015	26.8	28.5	25.3	26.5	26.5	29.0	27.2	23.9	25.2
7/03/2015	27.0	28.8	25.5	26.5	26.7	29.1	27.5	24.1	25.2



different parent species and/or formed by other processes. We will discuss this in further detail below.

5.1 Water fragments: OH and OI

As concluded above, the emission from [OI] and OH cannot be explained by photodissociation of H₂O, followed by prompt emission of [OI] or by fluorescence of OH. The surface brightness profile of OH suggests its emission might be the product of a process that produces OH directly in the $A^2\Sigma^+$ state. However, the difference between the [OI] and OH morphology indicates that at least part of the emission of the two fragments is not related.

From the morphology of the [OI] emission we concluded that it is the product of a process that directly produces atomic oxygen in an excited state. Like H_2O , photodissociation of CO_2 and CO produces OI in the ¹D and ¹S states, resulting in [OI] emission at 630 nm. Abundances of CO_2 and CO vary greatly between the summer and



winter hemispheres. Here we assume that the sunlit side dominates the total gas production rate; there, abundance ratios from the 'summer hemisphere' apply, which are $H_2O: CO_2: CO = 100: 2.7: 2.5$ (Le Roy et al. 2015). Assuming CO_2 and CO formation rates into OI ¹D and ¹S from (Bhardwaj & Raghuram 2012), photodissociation of CO_2 and CO contributes 10% and <1% to the [OI] 630 nm emission compared to H_2O (100%).

The ROSINA instrument reported unexpectedly high abundances of O_2 , with an average of $O_2/H_2O = 3.7 \pm 1.5$ %, with local abundances as high as 10% (Bieler et al. 2015b). The distribution of O_2 in the coma suggested it is released by the nucleus and that its release is correlated to the outflow of water. Because the photodissociation of O_2 into OI ¹D is very efficient and at these abundances (Huebner et al. 1992), it can contribute as much as an additional 25 – 60% to the [OI] 630 nm emission from H₂O. Thus while the photodissociation of CO_2 , CO, and O_2 molecules combined may produce as much [OI] emission as the photodissociation of H₂O, it cannot explain the factors of 20 – 40 of flux excess observed between January and March, nor can it explain the OH observations.

We then considered several processes that might produce the high observed surface brightness of both OH and [OI] directly from H_2O , including dissociative recombination of H_2O^+ , electron excitation of OI, and sputtering of water ice (c.f. Bhardwaj & Raghuram 2012) but none of those have reaction rates that exceed that of photo processes. Feldman et al. (2015) concluded that electron impact dissociation of H_2O vapor produced HI and OI



emission observed by *Rosetta*/Alice in the Far-UV. Electron impact dissociation produces OI in the ¹D and ¹S states, and OH in the $A^2\Sigma^+$ state. Those reactions typically have appearance thresholds between 10-20 eV, suggesting that they are driven by the large population of suprathermal electrons observed in by *Rosetta*'s Ion and Electron Sensor (IES; Clark et al. 2015). While electrons with energies of 100 eV and larger were observed, the distribution falls off steeply >30 eV. At these impact energies, the cross section for electron impact production of OH ($A^2\Sigma^+$) is 7 x 10⁻²² m² (Avakyan & al 1998) and that of OI ($^{1}S^{+1}D$) is 6 x 10⁻²³ m² (Bhardwaj & Raghuram 2012).

To test whether electron impact dissociation can explain the observed surface brightness we added electron impact processes to our model (Appendix A). In brief, we assumed a spherically outgassing nucleus with water production rates from the empirical trend reported by Fougere et al. (2016), and relative abundances of 3% for CO and CO₂, 0.1% for HCN and NH₃. For the electrons, we assumed a radial distribution that decreased with the inverse of the distance to the nucleus based on measurements by the *Rosetta*



Plasma Consortium's (RPC) Langmuir- and Mutual Impedance Probes. For the electron density, we used measurements with the Electron and Ion Sensor (IES) (Broiles et al. in press) which we assumed to increase linearly with the production rate and quadratically with the decrease in heliocentric distance. In addition, we included the effects of quenching of the OI ¹D state by collisions with H_2O molecules as well as the effect of transport as the OI atom moves out of the field of view before it can decay to the ground state.

The results of the model are shown in Fig. 5. We find that at 1 km from the surface, electron impact dissociation of H_2O can produce up to a factor of 10 more [OI] 630 nm emission than the photodissociation of H_2O into excited OI ¹D, and at least two orders of magnitude more OH emission than the photodissociation of H_2O and subsequent fluorescent excitation of OH by sun light. However, the morphology and surface brightness profiles seen in the OI and OH filters is very different, which is surprising when we assumed they are both the product of electron impact dissociation of H_2O . In the OI images there is a clear plume visible to the left, which is entirely absent in OH images. If the main emission in the plume originated from electron impact dissociation of H_2O , it should also be present in OH emission. If electron impact dissociation drives the emission of [OI] and OH in the coma, then the atomic oxygen emission in the plume is probably produced from a molecule other than H_2O .

We are not aware of experimental cross sections for the production of OI (¹D), but based on theoretical cross sections, Bhardwaj & Raghuram (2012) suggest that reaction rates for producing OI (¹D) from CO₂ are as much as 40 times larger than reaction rates producing OI (¹D) from H₂O. The reaction rates for the production of excited oxygen atoms from CO are much lower than those of H₂O. Assuming these electron impact dissociation cross sections, a CO_2/H_2O abundance of 3% would imply that 60% of the observed [OI] emission comes from CO₂. This large contribution by electron impact dissociation of CO₂ explains the differences between both the morphology and surface brightness profiles of the [OI] and OH emission. The plume is visible in [OI] but not in OH. Its [OI] surface brightness at the core is ~2x that at similar distances in the ambient coma, suggesting a local enhancement of the CO₂ abundance.

We do not expect our model to provide a fully realistic description of the inner coma. Predicted OH surface brightnesses are higher than observed, and quenching and transport may remove as much as factor 100 from the detectable [OI] surface brightness (Fig. 5a and Fig. 5c). In particular, the asymmetric outgassing of 67P will affect the impact of these processes. However, our results do confirm that electron impact dissociation can indeed explain the emission observed in OSIRIS' OI and OH filters from January through April 2015.

5.2 Ammonia fragments: NH and NH₂

The photodissociation of NH₃ results in the production of NH₂ (96%) and NH (~3%); most of the NH is thus normally a granddaughter product of NH₃ (Huebner et al. 1992). Electron impact dissociation of NH₃ has been relatively well studied and cross sections for the production of NH₂ (\tilde{A} ²A₁) and NH ($A^{3}\Pi_{1}$) at 100 eV are both ~2-3 x 10⁻²² m² (Müller & Schulz 1992), i.e. three times smaller than the production of excited hydroxyl (Table A1). To our knowledge, a detailed study of the excitation of NH₂ through this process is not available, leaving the relative intensities of the NH₂ bands that contaminate several filters an open question (Sec. 3.1.1). Surprisingly, the surface brightness profiles of NH₂ and NH are very different (Fig. 3), which is inconsistent if the emission from both fragments is produced by electron impact dissociation of NH₃. We used our model to evaluate the surface brightness expected from different emission processes. In all observations, the profile of NH resembles that of OH, suggesting that the same physical process causes the emission. The profile of NH₂ resembles that of OI and CN in January and March, and was probably not detected after that.

Assuming an abundance of 0.1% with respect to H₂O, we included electron impact excitation and fluorescent emission in our model. Photodissociation of NH3 into NH2 and NH cannot explain the emission for any of the observations (Fig. 4b), nor does electron impact dissociation (Fig. 5c), which both fall about a factor 100 short. Upon further investigation, the only plausible explanation for the NH filter observations appears to be emission from the OH⁺ ($A^{3}\Pi - X^{3}\Sigma^{-}$ 0-0) band. Electron impact dissociation on H₂O can indeed produce excited hydroxyl ions with a cross section of 8 x 10⁻²⁴ m² at 100 eV (Müller et al.1993), or about 100 times smaller than that for the production of OH ($A^{2}\Sigma^{-}$). The emission cross sections for neutral and ionized OH both depend strongly on the electron impact energy and the ratio between the surface brightnesses in the NH and OH filters will therefore depends strongly on the electron temperature in the coma.

5.3 CN

The morphology of the CN emission resembles that of [OI] at all six epochs, and like the water group fragments, its surface brightness is higher than expected from photo processes, by as much as a factor of at least 200 (Fig. 4b). Prompt excitation of CN following photodissociation of HCN is not a very efficient emission mechanism (Fray et al. 2005; Bockelée-Morvan & Crovisier 1985), and our model indeed suggests that photodissociation of HCN and subsequent fluorescent excitation of CN would produce at least 50 times more light than prompt excitation of CN following the photodissociation of HCN. Following the discussion on the production of [OI] and OH emission, we then evaluated if electron impact dissociation of HCN into the CN ($B^2\Sigma$) state can drive the production of excited CN. Qualitative results confirm that this reaction channel is important in electron impact dissociation of HCN (Nishiyama et al. 1979), but cross sections are not available in the literature. Assuming cross sections and abundances similar to NH₃ reactions for HCN, we would expect surface brightnesses comparable to NH in January (Fig 5c), i.e. around 10⁻⁸ $W/m^2/sr$ at 1 km from the surface. Interestingly, owing to the large fluorescence efficiency of CN, emission levels from the photodissociation of HCN followed by fluorescent excitation of CN likely produces an order of magnitude more light than electron impact dissociation of HCN. Dissociative electron impact excitation of HCN cannot explain our observations.

This suggests that the light observed in the CN filter in January is produced by another species. According to Ajello et al. (1971) about 5% of the light emitted following ionizing electron impact excitation of CO₂ falls within the CN filter's passband. This also explains the similarity in morphology between the OI and CN filter images. At an impact energy of 30 eV, the emission cross section for the entire CO_2^+ ($\tilde{A}^2\Pi - X^3\Sigma^-$) band is 4 x 10⁻²¹ m^2 , thus resulting in an emission cross section of 2 x $10^{-22} m^2$, about 4x smaller than that of dissociative electron impact excitation of H₂O into OH*, and about 10x smaller than the production of OI ¹D from the dissociative electron impact excitation of CO₂. We note that while the [OI] emission is strongly affected by quenching and transport effect but that the $CO_{2^{+}}$ emission is not, which may explain why [OI] surface brightnesses are comparable to those measured in the CN filter (Table 5). The expected CO_{2^+} surface brightness can be estimated from the CO₂-to-[OI] profile in Fig. 5a and will be of order 10^{-5} W/m²/sr, or about 100 times that of fluorescent emission from CN. Photodissociation of a parent molecule and subsequent fluorescent excitation of fragment CN can explain the observed surface brightness levels after May 2015, but the persistent plume morphology suggests that the observed emission may be a product of both CN fluorescence emission and CO₂⁺ emission from electron impact.

6. TRENDS WITH PERIHELION DISTANCE

The production rates shown in Fig. 4 suggest three different epochs: increasing emission before March 2015 following the heliocentric trend observed by MIRO, then a sharp decrease between mid-March and June, 2015, followed by an increase after June 2015. The drop in coma emission is more than an order of magnitude and is seen in the OI, OH, CN, NH, and NH₂ filters. Over the course of our observations, the morphology of the emission in the different filters does not change noticeably (Fig. 2). After May, the OH and CN emission



levels are at the level expected from photoprocesses alone (Fig 4). If the electron density evolved with our scaling law (linear with the gas production and inverse quadratically with the heliocentric distance), we would expect 1000 times more OH emission than was observed (Fig. 5d). Similarly, the predicted [OI] emission from dissociative electron impact of H_2O and CO_2 would produce 10x more emission than was observed in July. However, production rates derived from [OI] and NH surface brightnesses assuming photodissociation still require unrealistically high production rates (Fig. 4), and the morphology in the CN filter still resembles that seen in the OI filter, suggesting that collisions with electrons still play a role in the emission observed after May 2015. We propose that the drop between March and June 2015 was thus caused by a change in the number or temperature of projectile electrons available, and that this affects the emission in the different filter in different ways depending on the energy dependence of the relevant electron impact dissociation processes.

To explain the decrease of emission, we first consider the production of electrons. The *Rosetta*/RPC observations in February, 2015 indicate that the main source of electrons within 256 km of the nucleus is the neutral gas in the coma (Edberg et al. 2015). The far and extreme ultraviolet (FUV/EUV) solar flux determines the photoionization rates of H_2O and other molecules in the coma, and thus also controls the number of electrons available. Inspection of daily averaged solar UV spectra acquired with Extreme Ultraviolet Variability Experiment on board the Solar Dynamics Observatory (SDO/EVE; Woods et al. 2012). We



integrated the irradiance spectra over the range 30 – 100 nm¹, the wavelengths that are most efficient in producing electrons by ionizing water (Huebner et al. 1992; Budzien et al. 1994). The results are shown in Fig. 6a. Over the course of our observations, the UV irradiance decreased gradually, and it varied by 10% at time scales of 1 or 2 weeks. Comparing the production rates and UV irradiances in Fig. 6a suggests there is no clear correlation between the short-term solar variations. In this period the comet approached the Sun from 2.5 AU to 1.3 AU, an effect much larger than the weekly UV variations.

With increasing gas production rates, the optical depth of the inner coma increases and fewer photoelectrons are produced. To investigate the optical depth of the coma, we calculated H₂O column densities using a Haser distribution (Appendix A), and assumed water production rates from the empirical formula by Fougere et al. (2016; Fig. 4). The dominant photons for ionization have wavelengths between 30 – 85 nm (Huebner et al. 1992; Budzien et al. 1994). At these wavelengths, H₂O has photo-absorption cross sections of $1.0 \times 10^{-21} \text{ m}^2$ and $1.6 \times 10^{-21} \text{ m}^2$, respectively (Phillips et al. 1977). The results are shown in Fig. 6b. The relevant region here is between 1 and 10 km from the surface. In January, only 1 to 10% of photons were lost within this region. This increased to 10 to 64% in July.

¹ We used SDO/EVE level 3 version 5 data acquired with the MEGS-B instrument, available online at http://lasp.colorado.edu/eve/data_access/evewebdata/products/level3/

The electron production thus likely decreased in the region seen by OSIRIS, but not enough to explain the observed drop in emission.

Along with the gas production rates, dust production rates also increased significantly over the course of our observations. Based on *Cassini* observations, it has been suggested that nano-grain charging could result in significant electron depletion (Vigren et al. 2015; Nilsson, et al. 2015b). Reaction rates for attachment of electrons to grains are very low for suprathermal electrons and would mostly affect electrons with much lower energies than those responsible for the electron impact dissociation (>10 eV). We do not expect electron-dust interactions to affect the observed emission.

The most likely explanation of the decrease in emission from the inner coma is a significant decrease in the electron temperature, which reduces reaction rates. At energies of a few eV, when temperatures fall below the appearance thresholds of the dissociative reactions, the excitation of H_2O molecules becomes an effective cooling process (Cravens & Korosmezey 1986). Electrons gain energy by photo-ionization processes, comet-solar wind interactions (Clark et al. 2015), and lose energy through collisional processes, for example (Wegmann et al. 1999):

$$H_2 0 + hv \to H_2 0^+ + e \ [+12.3 \ eV]$$

$$H_2 0 + e \to H_2 + O(\ ^1D) + e \ [-12.3 \ eV]$$

$$H_2 0 + e \to OH + H + e \ [-5.1 \ eV]$$
[6]

The *Giotto* probe observed maximum ion density 12000 km from the nucleus of 1P/Halley (Häberli et al. 1995). This was attributed to a steep increase of the electron temperature with distance to the nucleus, in turn caused by decreased cooling through collisions between electrons and neutrals.

In the period January – July 2015, the neutral gas density increased much faster ($\sim r_h^{-4.2}$) than the increase of solar radiation ($\sim r_h^{-2}$), which should lead to a decrease in the electron temperature. The electron impact dissociation processes that produce the emission observed with OSIRIS all have relatively high appearance energies (Avakyan et al. 1998). Cooling of the electrons below those energies could lead to an abrupt decrease in the emission.

Lastly, the observed decrease in the emission might be related to changes in the interaction between comet and solar wind. Solar wind electrons have higher temperatures than photo-electrons and its interaction with the coma may heat electrons (Häberli et al. 1996; Clark et al. 2015). Initially, the solar wind could penetrate deep into the coma (Nillson et al. 2015a,b). With increasing production rate plasma boundaries separated the solar wind from the cometary gas (Rubin et al. 2015). By the end of February 2015, the RPC/Ion Composition Analyzer measured that the proton energy spectrum started to change, indicative of an increasing interaction between comet and solar wind.

SUMMARY AND CONCLUSION

This study uses data from *Rosetta*'s OSIRIS camera system and presents observations of the inner coma of 67P/Churyumov-Gerasimenko acquired with narrow band filters centered on the emission features of OH, OI, CN, NH, and NH₂. The observations explore a new regime in cometary science: the inner coma of a low-activity comet at large heliocentric

distances, and the *Rosetta* mission allows us to study how this environment changed over time. We developed an extensive image reduction procedure and applied this to observations acquired between January and July, 2015, when the comet's distance to the Sun decreased from 2.5 to 1.3 AU.

The observations in all filters at all epochs indicated surface brightnesses that are one or more orders of magnitude higher than can be explained by photodissociation. Instead, the emission is likely the result of dissociative electron impact excitation, and/or different species. The OH emission can be attributed to electron dissociative excitation of H₂O, and the observed intensities are generally consistent with neutral column densities and electron densities observed by other instruments on board *Rosetta*. We attribute most of the [OI] 630 nm emission in the inner coma to electron impact dissociative excitation of CO₂, which has a much larger cross section than H₂O. The emission detected in the NH filter is likely the result of electron dissociative excitation that produces OH⁺ ions from H₂O molecules directly in an excited state. The surface brightness levels observed in the CN filter and the similarity between the morphology observed in the CN and [OI] filters suggests that the emission is the product of both electron impact dissociative excitation produced CO_2^+ ions and of fluorescent emission by CN radicals. Follow-up studies of the correlation between the emission seen in CN vs. [OI], and OH vs. NH might provide very interesting windows on the different reaction channels from impact on the same species.

The intensity of the emission in the inner coma decreased between March and June, despite increasing gas production rates as the comet approached the Sun. The most likely explanation is that because the gas production rates increased much faster than the ionizing solar radiation, collisions between electrons and neutral water molecules lowered electron temperatures in the inner coma below the activation threshold of the dissociative impact excitation reactions. The increase of optical depth and deflection of the solar wind may have further contributed to the electron cooling.

Our results thus show that the narrowband filters on *Rosetta*/OSIRIS can be used to remotely study the interaction between electrons and the neutral gas in the inner coma. However, the lack of experimental cross sections hampers the interpretation of our results; most urgently needed are those for the production of OI ¹D from CO₂ and H₂O, and of CN from HCN). In addition, we have identified the need for models that combine the physical and chemical processes of cometary gases with plasma characteristics such as electron temperatures.

Impact excitation may matter in different planetary environments through different interaction mechanisms (photo-electrons, solar wind protons and/or electrons). First, since the resulting emission traces the distribution of a parent species, electron impact dissociation could explain the excitation of fragments whenever a steep, radial gradient is seen in the emission morphology of the fragment species, such as in the large-scale jet-like structures around comets (A'Hearn et al. 1986). Second, under conditions similar to that of 67P, dissociative electron impact excitation can lead to significant emission by fragment species. This might lead to detectable emission from Main Belt Comets or even Ceres – or to an overestimate of production rates if only photo-processes are assumed to drive the emission of fragment species.

Comet 67P reached its perihelion on August 13, 2015, at a heliocentric distance of 1.24 AU. The Rosetta spacecraft will continue to orbit its nucleus and study how its coma evolves while the comet moves away from the Sun again.

27

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REFERENCES

- A'Hearn, M.F., Hoban, S., Birch, P. V., et al., 1986. *Nature*, 324, pp.649.
- A'Hearn, M.F., Belton, M. J. S., Delamere, W. A., et al., 2005. Science, 310(5), pp.258.
- A'Hearn, M.F., Belton, M. J. S., Delamere, W. A., et al., 2011. *Science*, 332(6), pp.1396.
- A'Hearn, M.F., Krishna Swamy, K. S., Wellnitz, D. D., and Meier, R., 2015. AJ, 150(1), p.5.
- Atkinson, R., Baulch, D. L., Cox, R. A., et al., 1997. *Journal of Physical and Chemical Reference Data*, 26(6), pp.1329.
- Avakyan, S.V. II'in, R. N., Lavrov, V. M., and Ogurtsov, G.N., 1998. Collision processes and excitation of UV emission from planetary atmospheric gases : a handbook of cross sections. Ed. S.V. Avakyan. (Amsterdam, Netherlands: Gordon and Breach Scientific Publisers).
- Bhardwaj, A. & Raghuram, S., 2012. *ApJ*, 748(1), p.13.
- Bieler, A., Altwegg, K., Balsiger, H., et al., 2015a. Astron. Astroph., 583, p. A7.
- Bieler, A., Altwegg, K., Balsiger, H., et al., 2015b. *Nature*, 526(7575), pp.678.
- Bockelée-Morvan, D. & Crovisier, J., 1985. Astron. Astroph., 151, pp.90.
- Bockelée-Morvan, D., Debout, V., Erard, S., et al., 2015. Astron. Astroph., 583, P. A6.
- Brownlee, D.E., Horz, F., Newburn, R. L. et al., 2004. Science, 304(5), pp.1764–1769.
- Budzien, S.A., Festou, M.C. & Feldman, P.D., 1994. Icarus 107, p164.
- Clark, G., Broiles, T. W., Burch, J. L., et al., 2015. Astronomy and Astrophysics, 583, p.A24.
- Cochran, A.L., 2002. *Icarus*, 157(2), pp.297.
- Cochran, A.L., 2008. Icarus, 198(1), pp.181.
- Combi, M.R., Harris, W.M. & Smyth, W.H., 2004. in Comets II, ed. M. C. Festou, H. U. Keller, & H. A. Weaver (Tucson, AZ: Univ. Arizona Press), p. 523.
- Cravens, T.E. & Korosmezey, A., 1986. PSS, 34, 10, pp. 961.
- Edberg, N.J.T., Eriksson, A. I., Odelstad, E., et al., 2015. GRL, 42(1), pp.4263–4269.
- Farnham, T.L., Schleicher, D.G. & A'Hearn, M.F., 2000. *Icarus*, 147, p.180.
- Feldman, P.D., A'Hearn, M. F., Bertaux, J.-L., et al., 2015. Astron. Astroph., 583, p. A8.
- Fink, U., 2009. Icarus, 201(1), pp.311-334.
- Fougere, N., Altwegg, K., Berthelier, J.-J., et al., 2016. *Astronomy and Astrophysics*, 588, p.A134.
- Fray, N., Benilan, Y., Cottin, H., Gazeau, M.-C., and Crovisier, J., 2005. *PSS*, 53(1), pp.1243–1262.
- Gulkis, S., Allen, M., Von Allmen, P., et al., 2015. Science, 347(6), p.aaa0709.
- Häberli, R.M. et al., 1995. Astron. Astroph., 297, pp.881
- Häberli, R., Altwegg, K., Balsiger, H., and Geiss, J., 1996. *Journal of Geophysical Research*, 101(A7), pp.15579.
- Huebner, W.F., Keady, J.J. & Lyon, S.P., 1992. Astroph. Sp. Sci., 195, p.1.
- Kawakita, H. & Watanabe, J.-I., 2002. Ap.J., 572(2), pp.L177.
- Keller, H.U., Delamere, W. A., Huebner, W. F., et al., 1987. Astron. Astroph., 187, pp.807–823.
- Keller, H.U., Kueppers, M., Fornasier, S., et al., 2007. Sp. Sci. Rev., 128, p.433.
- Keller, H.U., Mottola, S., Skorov, Y., and Jorda, L., 2015. Astron. Astroph., 579, p.L5.
- Kim, S.J., A'Hearn, M.F. & Cochran, W.D., 1989. *Icarus*, 77, p.98.
- Le Roy, Altwegg, K., Balsiger, H., et al., 2015. Astron. Astroph., 583, p. A1.

Magrin, S., La Forgia, F., Da Deppo, V., et al., 2015. *Astron. Astroph.*, 574, p.A123.

McConkey, J.W., Malone, C. P., Johnson, P. V., et al., 2008. Physics Reports, 466(1), pp.1–103.

Müller, U. & Schulz, G., 1992. J. Chem. Phys, 96(8), p.5924.

Müller, U., Bubel, Th., and Schulz, G., 199#. Z. Phys. D, 25, p.167.

Nilsson, H., Stenberg Wieser, G., Behar, E., et al., 2015a. Science, 347(6220), pp.aaa0571.

Nilsson, H., Stenberg Wieser, G., Behar, E., et al., 2015b. Astron. Astroph., 583, P. A20.

Nishiyama, I., Kondow, T. & Kuchitsu, K., 1979. Chem. Phys. Lett., 62(3), pp.462–465.

Phillips, E., Lee, L.C. & Judge, D.L., 1977. Journal of Quantitative Spectroscopy, 18, pp. 309

Rubin, M., Gombosi, T. I., Hansen, K. C., et al., 2015. *EMP*, 116, p141-157.p14

Schleicher, D.G., 2010. *AJ*, 140, p.973.

Schleicher, D.G. & A'Hearn, M.F., 1988. *ApJ*, 331, p.1058.

Snodgrass et al., 2015, Astron. Astroph., 588, A80.

Soderblom, L. A., Becker, T. L., Bennett, G. et al., 2002. *Science*, 296(5), pp.1087.

Streit, G.E., Howard, C. J., Schmeltekopf, A. L., Davidson, J. A., and Schiff, H. I., 1976. *J. Chem. Phys.*, 65, pp.4761.

Tubiana, C., Guettler, C., Kovacs, G., et al., 2015. Astron. Astroph., 583, p.A46.

Tubiana, C., Böhnhardt, H. & Agarwal, J., 2011. Astron. Astroph. 527, pp. A113.

Veverka, J., Klaasen, K., A'Hearn, M., et al., 2013. *Icarus*, 222(2), pp.424–435.

Vigren, E., Galand, M., Lavvas, P., and Eriksson, A. I., 2015. ApJ, 798, p130.

Weaver, H. A., Feldman, H. A., A'Hear, M. F., et al., 1999. *Icarus*, 141, p.1.

Wegmann, R., Jockers, K. & Bonev, T., 1999. PSS, 47, p.745.

Woods, T.N., Eparvier, F. G., Hock, R., et al., 2012. *Solar Physics*, 275(1), pp.115.

APPENDIX A: EMISSION MODEL

To aid in our interpretation of our results, we have developed a basic coma model, summarized below. A true model would combine a realistic distribution of the neutral gas, the cometary and solar wind plasma, and all relevant chemical and physical reactions, and the complexity of such a model is outside the scope of this paper.

A1. Neutral density model

Total water production rates of 67P were estimated using the empirical relation derived between water production $Q(H_2O)$ and heliocentric distance r_h by Fougere et al. (2016):

$$Q(H_2O) \sim 1.02 \times 10^{28} r_h^{-4.2}$$
 (molecules/s) [A1]

We assumed constant abundances of $CO_2/H_2O = 3\%$, $CO/H_2O = 3\%$, $O_2/H_2O = 3.8\%$, and $HCN/H_2O = 0.1\%$ (LeRoy et al 2015; Fougere et al. 2016; Bieler et al. 2015). For the distribution of fragment species we assumed a standard Haser model (Festou 1981, Combi et al. 2004). The photodissociation rates of the different gases are listed in Table A1, and those were scaled with the heliocentric distance as $1/r_h^2$. We assumed that all gases are accelerated to a bulk velocity v_g within a distance d = 200 km from the center of the nucleus (Combi et al. 2004) using the empirical relation:

$$v_g = 0.85 * r_h^{-1/2} * \left[1 - \exp\left(\frac{-d}{50 \ km}\right) \right] \text{ (km/s)}$$
 [A2]

We assumed the same bulk outflow gas velocity for both parent and fragment species.

A2. Electrons

The electron density in the coma was measured by the Langmuir (LAP) and mutual impedance probes (MIP) on *Rosetta* between 2015, February 4 – 28 (2.3 AU from the Sun; Edberg et al. 2015). For the electron density we assumed that the number density and radial distribution measured by LAP/MIP scaled linearly with the water production rate and the photoionization rate (thus the square of the heliocentric distance):

$$n_e = \frac{Q_{H2O}}{10^{26}} * \frac{10^{14}}{d} * \frac{3}{r_h^2}$$
 (m⁻³) [A3]

where n_e denotes the electron density and d the distance from the comet's surface. Rather than assuming a temperature distribution, we assumed a fixed electron temperature of 30 eV (3.3 x 10⁶ m/s) for electron fluxes and for the cross sections of electron impact reactions. To calculate the emission resulting from dissociative electron impact dissociation, we multiplied the neutral densities in the coma n(d) at a distance d from the nucleus with the local electron density $n_e(d)$, electron velocity v_e , and emission cross section σ or with the reaction rate where applicable (Table A1):

$$S(d) = \frac{n(d) * n_e(d) * v_e * \sigma}{4\pi}$$
 (ph/s/m³) [A4]

This is then integrated over the line of sight (from the position of the spacecraft Δ to infinity) to produce the surface brightnesses $B(\theta)$ as a function of the angle between spacecraft-comet line along the comet-Sun line:

$$B(\theta) = \int_{\Delta}^{\infty} \frac{S(d)}{4\pi} \delta d \quad (ph/s/m^2/sr)$$
 [A5]

The radial distance *d* from the nucleus in any position in the comet-sun-spacecraft plane can be calculated using the cosine rule.

A3. OI quenching and transport

The [OI] 630 nm emission is different from the other emission features because it is a forbidden line, and we expect quenching of the OI ¹D state by the reaction OI ¹D + H₂O \rightarrow 2 OH to decrease the [OI] 630 nm emission with increasing production rates. The OI ¹D state has a long lifetime of 101 s (Atkinson et al. 1997). To assess the effect of the deactivation of OI ¹D through collisions with H₂O on the surface brightness profile we combined the Haser model from Sec. A1 and adopted experimental rate coefficients of 2 x 10⁻¹⁹ m³/s/molecule (Streit et al. 1976). To correct for excited OI atoms lost through collisional quenching, we calculate an effective density n'(d) by weighting the neutral gas density function n(d) from equation A3 by a correction factor. Assuming a quenching rate R (Table A1), the distance l(d) an OI atom moving with velocity v_d can travel before colliding is:

$$l(d) = \frac{v_d}{R*n(d)}$$
[A6]

Now the fraction of atoms that can emit and thus is not quenched is given by:

$$n'(d) = n(d) * \left[1 - \exp\left(\frac{-l(d)}{v_d * \tau}\right)\right]$$
 [A7]

where τ is the lifetime of the OI ¹D state (101 s), and n(d) the density of neutral water at a distance d of the surface. The effect of quenching on the surface brightness is shown in Fig. A1. We assumed a fixed distance between comet and spacecraft of 100 km to evaluate the effect of quenching and have added the [OI] emission from all H₂O and CO₂ processes (the dominant contributions to the OI emission, see Fig. 5 in the main text). In January, only the first kilometer is affected by quenching in the inner coma. In July, the inner 3 kilometers are affected, and at 1 km approximately the observed surface brightness is approximately 50% of the emitted light.

In addition, because of the long lifetimes of the ¹D state, only part of the atoms decay to the ground state within the field of view. We account for this with a second correction factor:

$$n''(d) = n'(d) * \left[1 - \exp\left(\frac{-d}{v_d * \tau}\right)\right]$$
 [A8]

The results, again for a fixed spacecraft distance of 100 km, are shown in Figs. 5c and 5d. The effect of the OI ¹D lifetime is dramatic and flattens the surface emission in the first few kilometers around the nucleus.

A4. Optical depth

With increasing gas production rates, the optical depth of the inner coma increases and fewer photoelectrons are produced. To investigate the optical depth of the coma, we calculated H_2O column densities using a Haser distribution (Sec. 3.3), and assumed water production rates from the empirical formula by Fougere et al. (2016; see also Fig. 4a). The dominant photons for ionization have wavelengths between 30 – 85 nm (Huebner et al. 1992; Budzien et al. 1994). At these wavelengths, H_2O has photo-absorption cross sections of 1.0 x 10^{-21} m² and 1.6 x 10^{-21} m², respectively (Phillips et al. 1977). The results are shown

in Fig. 6b. The relevant region here is between 1 and 10 km from the surface. In January, only 1 to 10% of photons were lost within this region. The effects of the increasing optical depth on the neutrals and electrons in the inner coma is not included in the surface brightness model.

Reaction	Product	Cross section or rate	Reference
$H_2O + hv$	any	1.04 x 10 ⁻⁵ s ⁻¹	Combi et al. 2004
$H_2O + hv$	OH + hv	8.5 x 10 ⁻⁴ s ⁻¹	Combi et al. 2004
$H_2O + hv$	OI $({}^{1}S + {}^{1}D)$	8.6 x 10 ⁻⁷ s ⁻¹	Bhardwaj & Raghuram 2012
$CO_2 + hv$	any	2.2 x 10 ⁻⁶ s ⁻¹	Weaver et al. 1999
$CO_2 + hv$	OI (1D)	1.9 x 10 ⁻⁶ s ⁻¹	Bhardwaj & Raghuram 2012
CO + hv	any	3.3 x 10 ⁻⁶ s ⁻¹	Huebner et al. 1992
CO + hv	OI (1D)	9.1 x 10 ⁻⁸ s ⁻¹	Bhardwaj & Raghuram 2012
$O_2 + hv$	any	4.5 x 10 ⁻⁶ s ⁻¹	Huebner et al. 1992
$O_2 + hv$	OI (1D)	4.0 x 10 ⁻⁶ s ⁻¹	Huebner et al. 1992
$NH_3 + hv$	any		
$NH_3 + hv$	NH		
HCN + hv	any	7.5 x 10 ⁻⁵ s ⁻¹	Huebner et al. 1992
HCN + hv	CN	7.5 x 10 ⁻⁵ s ⁻¹	Huebner et al. 1992
HCN + hv	$CN (B^2\Sigma^+)$	4.5 x 10 ⁻⁵ s ⁻¹	Fray et al. 2005
H ₂ O + e-	OH $(A^2\Sigma^+)$	8.5 x 10 ⁻²² m ²	Avakyan et al. 1998
H ₂ O + e-	$OI(^{1}S + ^{1}D)$	9.7 x 10 ⁻¹⁶ m ³ s ⁻¹	Bhardwaj & Raghuram 2012
CO ₂ + e ⁻	$OI(^{1}S + ^{1}D)$	5.3 x 10 ⁻¹⁴ m ³ s ⁻¹	Bhardwaj & Raghuram 2012
CO + e-	$OI(^{1}S + ^{1}D)$	2.9 x 10 ⁻¹⁶ m ³ s ⁻¹	Bhardwaj & Raghuram 2012
0 ₂ + e-	$OI(^{1}S + ^{1}D)$	1 x 10 ⁻¹⁴ m ³ s ⁻¹	Estimated from Avakyan et al. 1998
0 ₂ + e-	X ^{q+}	1.5 x 10 ⁻²⁰ m ²	Straub et al. 1996
NH ₃ + e-	NH (Α ³ Π ₁)	2.8 x 10 ⁻²² m ²	Müller & Schulz 1992
OI ¹ D + H ₂ O	20H	2 x 10 ⁻¹⁶ m ³ /s/molecule	Streit et al. 1976

Table A1. Assumed reaction rates (at $r_h = 1$ AU) and cross sections