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# Low CO/CO<sub>2</sub> ratios of comet 67P measured at the Abydos landing site by the *Ptolemy* mass spectrometer

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## ABSTRACT

Comets are generally considered to contain the best-preserved material from the beginning of our planetary system, although the mechanism of their formation and subsequent evolution are still poorly understood. Here we report the direct in situ measurement of H<sub>2</sub>O, CO, and CO<sub>2</sub> by the *Ptolemy* mass spectrometer onboard the Philae lander, part of the European Space Agency's Rosetta mission, at the Abydos site of the Jupiter-family comet 67P/Churyumov-Gerasimenko. A CO/CO<sub>2</sub> ratio of around  $0.07 \pm 0.04$  is found at the surface of the comet, a value substantially lower than the one measured by ROSINA in the coma. Such a major difference is a potential indication of heterogeneity of the nucleus and not of changes in the CO/CO<sub>2</sub> ratio of the coma with radial distance.

**Key words.** comets: general – comets: individual: 67P/Churyumov-Gerasimenko – space vehicles – space vehicles: instruments

## 1. Introduction

An understanding of the heterogeneity of comets leads to insights into the formation conditions and processes occurring in the protosolar nebula (PSN). Analysis of the 81P/Wild 2 samples by the Stardust mission has evidenced that radial mixing played a major role in the accretion of comets (Brownlee et al. 2006). This suggests that the initial composition of comets could then be heterogeneous since they may have formed from materials that condensed over a wide range of heliocentric distances in the PSN. In contrast, the great range of D/H ratios of individual comets suggests that radial mixing was not so efficient (Kavelaars et al. 2011; Ceccarelli et al. 2014; Altwegg et al. 2015), with each comet forming in a distinct localized region of the PSN. Investigation into the formation conditions and evolution of comets is further complicated by their subsequent alteration due to surface temperature variations engendered by diurnal, seasonal, and orbital evolutions. Even without direct measurement of a comet's surface composition, remote-sensing observations suggest that these bodies most likely evolved heterogeneously, regardless of their initial state (Fougere et al. 2013; Combi et al. 2014). The measurements performed by the ROSINA instrument onboard Rosetta over the 17 August–22 September 2014 time period also suggest that the coma of comet 67P/Churyumov-Gerasimenko (67P) is highly heterogeneous both in space and time (Hässig et al. 2015). Whilst a connection with the possible heterogeneity of the nucleus of 67P appears likely, this has not yet been demonstrated.

The Philae lander made its initial touchdown at Agilkia on 12 November 15:34:04 UTC. The *Ptolemy* instrument had planned to measure the isotopic composition of solid samples drilled from the subsurface at the Agilkia landing site (Bockelée-Morvan et al. 2015). However, following the one and a half hour bounce and non-nominal landing at the final landing site, Abydos, there was insufficient energy within the lander

battery to deliver a drilled solid sample to *Ptolemy*. Nevertheless, the *Ptolemy* mass spectrometer is connected to the outside of the lander via a vent pipe, which enabled measurements of the local gas environment. In this report, we present the in situ measurement of H<sub>2</sub>O, CO, and CO<sub>2</sub> by the *Ptolemy* mass spectrometer onboard the Philae lander at the Abydos site of 67P. The CO/CO<sub>2</sub> ratio inferred at the surface of the comet is found to be substantially lower than the average value measured by the ROSINA instrument in the coma. This determination potentially indicates heterogeneity of the nucleus.

## 2. Method

The *Ptolemy* instrument on the Philae lander is designed to measure the chemical and isotopic composition of the near-surface coma and the body of 67P (Wright et al. 2007). The analyzer at the heart of the instrument is an ion trap mass spectrometer (March 2000) with a unit mass resolution and an  $m/z$  range of 10 to 150 Da. Ions within the ion trap cavity can be stored by an RF field applied to the ring electrode. The ion trap is operated in a mass-selective mode where ions below a threshold voltage are ejected along the  $z$ -axis of the trap. Neutral molecules within the ion trap cavity are ionized for 1 ms by an electron beam produced by a nano-tip field effect device (FED) operated with an extraction voltage of about 70 eV, while an RF storage voltage on the electrodes traps ions within the cavity. The FED is a low-power, 100 mW electron source with low-background signal. Following ionization, the FED is switched off and the ions are stored within the cavity for an additional 1 ms. The RF voltage is then ramped so that ions of increasing mass become unstable and are ejected from the ion trap to be detected by the ion detector operated in an ion-counting mode. Scans are repeated to build up a mass spectrum with a maximum of 1024 data bins per mass spectrum. A software-programmable scan function is

used to control the voltages on the ion trap electrodes, ionization source, and ion detector as well as the data collection parameters.

In mass spectrometers, molecular species fragment within the ionization source in a predictable fashion. For example, pure carbon dioxide, in addition to the base peak at  $m/z$  44 ( $\text{CO}_2^+$ ), has a fragment ion produced at  $m/z$  28 ( $\text{CO}^+$ ) at a ratio 10/1 (NIST 2005). Here we estimate an uncertainty in this ratio of  $\pm 20\%$  that is due to unconstrained factors such as gas composition and ionization energy, which is based on our experience of operating many different mass spectrometers. A further complicating factor with ion trap mass spectra when compared with the (NIST 2005) fragmentation patterns is the occurrence of ion molecule reactions involving the ambient water, for instance,  $\text{CO}_2^+ + \text{H}_2\text{O} \Rightarrow \text{CO}_2\text{H}^+ + \text{OH}$ , resulting in ions with a mass 1 unit heavier than the main molecular mass. The degree of protonation depends on several factors, including water concentration and ion storage time. Experiments with the *Ptolemy* qualification model (as well as thermodynamic considerations; March & Todd 2005) show that this reaction readily occurs for  $\text{H}_2\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{CO}^+$ , and  $\text{N}_2^+$  to produce their protonated counterparts. Two scan functions were used; the first had an RF storage voltage to store  $m/z$  13 and above, followed by a ramp rate of  $19\,500 \text{ Da s}^{-1}$  to  $m/z$  89 with 13 data bins per mass unit and 300 scans per mass spectrum. The second function was designed to exclude trapping of water ions and have a higher mass range at the expense of data resolution; it had an RF storage voltage to store  $m/z$  25 and above, followed by a ramp rate of  $19\,000 \text{ Da s}^{-1}$  to  $m/z$  136 with nine data bins per mass unit and 230 scans per mass spectrum. The mass spectrometer has a sensitivity of about one ion count per  $10^6$  molecules of argon  $\text{cm}^{-3}$ , determined by in-flight calibration made during the comet approach phase of the mission. The dark current is lower than a single ion per mass spectrum.

### 3. Results

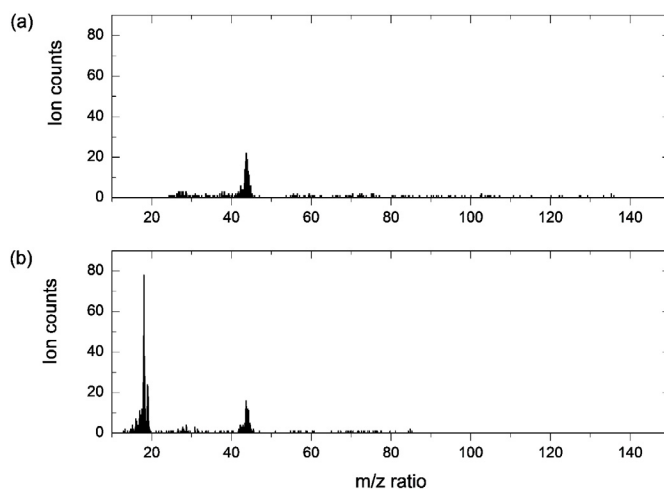
*Ptolemy* observations of the local gas environment were made about 20 min after the initial touchdown at Agilkia (Ag) and a further six times at Abydos (Ab1-Ab6) over a period of 45 h. The observations are summarized in Table 1. Each observation was collected over a period of 1 min. and consisted of six mass spectra each with a measurement time of 2 s; half of the mass spectra with the  $m/z$  range 13 to 89 and the other half with the  $m/z$  range 25 to 136. This is the same procedure as was used during the Rosetta flyby of Lutetia (Andrews et al. 2012) and while approaching the comet and hence enables direct comparison between background, comet coma, and measurements made on the surface.

The mass spectra collected at Abydos for each type of mass spectrum were summed and the results are shown in Fig. 1. The mass spectra have two clear groups of peaks, which are apparent at around  $m/z$  18 and around  $m/z$  44, with the third most intense group at around  $m/z$  28. This relatively simple mass spectrum is interpreted (using fragmentation patterns of simple molecules (NIST library) and the effects of protonation) as water around  $m/z$  18,  $\text{CO}_2$  around  $m/z$  44, and a combination of CO,  $\text{N}_2$ , and  $\text{CO}_2$  fragment around  $m/z$  28, with a small amount of organics contributing to other peaks. The degree of protonation in the mass range where the two types of mass spectra overlap is similar, indicating that the protonation is an ion molecule reaction between the stored ions and neutral water molecules rather than between neutral molecules with stored  $\text{OH}^+$ . The low intensity at  $m/z$  14 indicates that most of the  $m/z$  28 peak can be attributed to  $\text{CO}^+$  rather than  $\text{N}_2^+$  since nitrogen spectra have a fragment at

**Table 1.** Summary of *Ptolemy* sniff operations at the surface of 67P at the Agilkia and Abydos landing sites.

Obs.	Date and time (UTC)	Temp. ( $^{\circ}\text{C}$ )	Comments
Ag	12-Nov. 15:54	0	20 min. after touchdown
Ab1	13-Nov. 06:35	0	0:30 h, day
Ab2	08:37	-2	2:30 h, day
Ab3	10:39	-2	4:30 h, night
Ab4	12:41	-4	6:30 h, night
Ab5	14-Nov. 02:54	-17	8:00 h, night
Ab6	12:36	-23	5:30 h, night

**Notes.** The temperature is measured inside the instrument from house-keeping data, which have a resolution of  $2^{\circ}\text{C}$ . The approximate time after comet noon for Ab1-6 is indicated in the comments, night is from about 4:00 h to 9:00 h.



**Fig. 1.** Summed mass spectra a)  $m/z$  25 to 136 and b)  $m/z$  13 to 89 of the coma at the Abydos landing site. The spectra were acquired at six discrete times over a period of 45 h. The main peaks are at  $m/z$  18 and 44 with a smaller peak at  $m/z$  28.

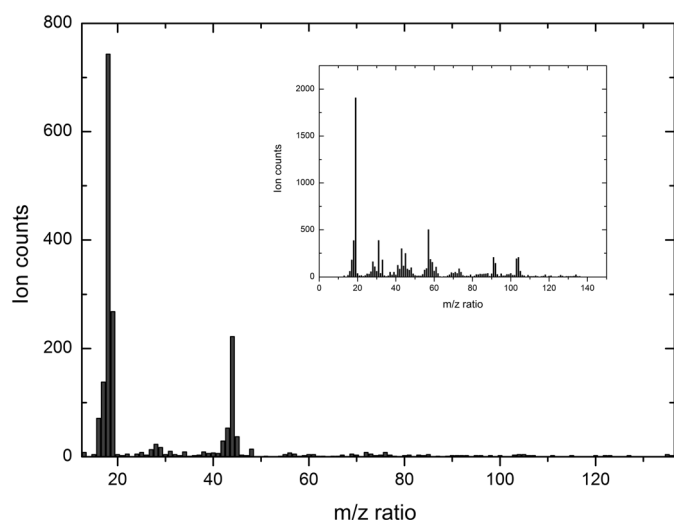
$m/z$  14 typically 0.14 relative intensity to  $m/z$  28 (NIST 2005). This is further supported by the low  $\text{N}_2/\text{CO}$  ratio of  $5.7 \times 10^{-3}$  measured in the coma directly by ROSINA (Rubin et al. 2015).

For each observation the three mass spectra from each scan type were summed to give two mass spectra, one with  $m/z$  13 to 89, with approximately 13 bins per mass unit, and the other with  $m/z$  25 to 136 with approximately 9 bins per mass unit. Ions were assigned to their corresponding mass in the 7 and 11 central bins around each mass unit. The final mass spectrum for each observation was obtained by summing ions where the mass spectra overlapped ( $m/z$  25 to 89) and using the ratio of the overlapped range to calculate the ion intensity for the missing range of each mass spectrum. This enables comparison with the results of other instruments, which usually measure CO and  $\text{CO}_2$  ratios with respect to water. Since CO and  $\text{CO}_2$  both occur in the overlapping range of both the mass spectra, the ratio of  $\text{CO}/\text{CO}_2$  is not affected by this procedure. Figure 2 shows the results of this processing on the combined mass spectrum for all the Abydos observations (for comparison the mass spectrum for Agilkia is shown in the inset of Fig. 2). The results along with ion counts of the masses of interest for water CO,  $\text{N}_2$ , and  $\text{CO}_2$  are shown in Table 2. The data have not been corrected for ionization efficiency because the electron ionization energy is modified by the RF field and is not well constrained. Typically, water, nitrogen,

**Table 2.** Ion counts for each type of mass spectrum at each observation during the Philae first-science sequence.

Obs.	Mass spectrum	Mass range				Selected ion masses							
		13–24	25–89	90–132	TIC	<i>m/z</i> 16	<i>m/z</i> 17	<i>m/z</i> 18	<i>m/z</i> 19	<i>m/z</i> 28	<i>m/z</i> 29	<i>m/z</i> 44	<i>m/z</i> 45
Ag	MS1	1326	2098	546	3970	29	90	193	954	90	47	45	312
	MS2	919	1452	380	2751	20	62	134	660	40	34	40	178
	combined	2245	3550	926	6721	49	152	327	1614	130	81	85	490
Ab1	MS1	265	115	12	392	13	27	146	72	5	4	41	9
	MS2	361	157	13	531	18	37	199	98	6	5	49	8
	combined	626	272	25	923	31	64	345	170	11	9	90	17
Ab2	MS1	167	62	5	234	10	16	109	29	2	3	31	0
	MS2	143	73	5	221	8	14	93	25	2	2	28	5
	combined	310	135	10	455	18	30	202	54	4	5	59	5
Ab3	MS1	78	52	2	132	7	10	47	13	5	1	19	2
	MS2	115	35	2	152	10	15	70	19	0	0	14	3
	combined	193	87	4	284	17	25	117	32	5	1	33	5
Ab4	MS1	39	16	2	57	1	8	24	4	1	0	10	1
	MS2	44	14	2	60	1	9	27	5	1	0	5	1
	combined	83	30	4	117	2	17	51	9	2	0	15	2
Ab5	MS1	7	12	0	19	0	0	6	1	0	1	4	2
	MS2	14	6	0	20	0	0	12	2	0	0	0	0
	combined	21	18	0	39	0	0	18	3	0	1	4	2
Ab6	MS1	6	19	3	28	1	1	4	0	1	1	11	2
	MS2	7	16	3	26	1	5	5	5	0	0	6	4
	combined	13	35	6	54	2	6	9	5	1	1	17	6
Bkg	MS1	48	22	1	71	1	8	38	1	3	0	2	2
	MS2	33	15	1	49	1	5	26	1	2	0	2	1
	combined	81	37	2	120	2	13	64	2	5	0	4	3

**Notes.** Mass spectra are from *m/z* 13–89 for MS1 and *m/z* 25–132 for MS2. Ion counts for the missing mass ranges (*m/z* 90–132 for MS1 and *m/z* 13–24 for MS2) are calculated as explained in the text; these extrapolated values are shaded. The resulting total ion count (TIC), i.e., the number of ions in each mass spectrum, is also listed.



**Fig. 2.** Processed mass spectrum of the coma at the Abydos landing site with the mass spectrum acquired at the Agilkia landing site shown in the inset for comparison.

and carbon monoxide have similar ionization efficiency, whereas carbon dioxide is increased by  $\sim 40\%$ . Table 2 summarizes the results collected at Abydos, just after touchdown and instrument background. The ion counts are divided into four groups: “H<sub>2</sub>O” *m/z* 16 to 19, “CO<sub>2</sub>” *m/z* 44 and 45, “CO” *m/z* 28 and 29, and “other” for all the remaining masses. The presence of organics will contribute to a slight overestimate of the water and carbon dioxide groups. The carbon monoxide group is a significant overestimate, as the effects of nitrogen and carbon dioxide have not been removed. The apparent CO/CO<sub>2</sub> ratio at the Abydos

**Table 3.** Ion counts for each of the main compounds made during the Philae first-science sequence.

Obs.	H <sub>2</sub> O	CO	CO <sub>2</sub>	Other	H <sub>2</sub> O/CO <sub>2</sub>	CO/CO <sub>2</sub>
Ag	2142	211	575	3793	$3.7 \pm 0.2$	$0.37 \pm 0.04$
Ab1	610	20	107	186	$5.7 \pm 0.8$	$0.19 \pm 0.06$
Ab2	304	9	64	78	$4.5 \pm 0.9$	$0.14 \pm 0.06$
Ab3	191	6	38	49	$5.0 \pm 1.2$	$0.16 \pm 0.09$
Ab4	79	2	17	19	$4.6 \pm 1.6$	$0.12 \pm 0.11$
Ab5	21	1	6	11	$3.5 \pm 2.2$	$0.17^{+0.23}_{-0.17}$
Ab6	22	2	23	7	$1.0 \pm 0.4$	$0.09 \pm 0.08$
Bkg	81	5	7	37	$11.6 \pm 4.5$	$0.71 \pm 0.58$

**Notes.** Errors in ratios estimated from counting statistics.

site is  $0.16 \pm 0.03$  (calculated from Ab1 to Ab6 of Table 3). This is reduced to  $0.07 \pm 0.04$  when taking the estimated contribution of the fragmentation of CO<sub>2</sub> to the *m/z* 28 peak into account, but assuming no contribution from N<sub>2</sub> or organics (calculated by taking the counts for the three measurements that had higher CO values than the background, i.e., Ab1 to Ab3).

#### 4. Discussion

Several possible sources can be considered for the measured gas: (i) instrument and lander contamination; (ii) volatiles released due to lander interaction with the surface; (iii) a homogeneous coma with low CO/CO<sub>2</sub> ratio; and (iv) coma gas originating from deeper sublimation. Instrument contamination is always a concern for in situ measurements, but the background observations made in orbit at distances farther than 30 km from the comet while still attached to the spacecraft typically had ion counts

of 30, 2, and 4 for water, carbon monoxide, and carbon dioxide, respectively, which is significantly lower than most of the measurements made at Abydos. A more detailed investigation of the spacecraft contamination (Schläppi et al. 2010) showed that the main components of contamination were water followed by carbon monoxide and then carbon dioxide, and that operation of Philae increased the background intensity of water by a factor of 2, while CO and CO<sub>2</sub> only increased marginally. This is reinforced by *Ptolemy* background measurements made during the comet approach (shown as Bkg in Tables 2 and 3).

During the landing of the Huygens probe on Saturn's moon Titan, the methane concentration increased after landing because of the effect of the hot lander in contact with the surface (Niemann et al. 2010). The Philae temperature was about 0 °C, much warmer than the comet surface of around -150 °C (Gulkis et al. 2015; Capaccioni et al. 2015); however, considerable design effort was made to minimize the heat loss (Bibring et al. 2007) to enable the operation of the lander at 3 AU. An estimate of the heat input to the comet surface is around 4 W m<sup>-2</sup> through radiation and less than 10 W m<sup>-2</sup> by direct contact of the lander feet, both considerably lower than the solar irradiance of around 150 W m<sup>-2</sup> at 3 AU. Furthermore, even if the lander induced some limited depletion of the very close subsurface, its top few cm probably have already been depleted in volatiles by previous perihelion passages.

Measurements made by the ROSINA mass spectrometer during August and September 2014 show variable CO/CO<sub>2</sub> ratios, typically ~5 and rarely lower than 1 (Hässig et al. 2015). The larger variations in water concentration were attributed to water sublimation occurring at shallower depths and being more readily affected by surface temperature and topography. By similar reasoning, it might be expected that CO<sub>2</sub> sublimates from a shallower depth than CO and so the CO concentration over the comet would be less variable. One possibility is that CO concentration is lower near the surface and that the CO observed at the orbiting spacecraft contains a secondary component produced through photochemistry on the way to the spacecraft. Dissociation of CO<sub>2</sub> is considered unlikely, however, because the CO/CO<sub>2</sub> ratio would continue to increase farther from the comet, and there should be some correlation between the CO and CO<sub>2</sub> variations of concentrations when Rosetta was orbiting at a constant distance in September, neither of which are observed (Hässig et al. 2015). Alternatively, if CO is formed from another parent molecule, for example, formaldehyde, then this would require a high concentration of the parent molecule at the surface followed by extremely rapid dissociation. No such parent molecule is observed in our mass spectra.

The CO/CO<sub>2</sub> ratio of 0.07 or lower measured at Abydos instead suggests that the nucleus exhibits some compositional heterogeneity. The most likely explanation for this apparent CO impoverishment is that this molecule comes from deeper layers at this location because of its higher volatility compared to CO<sub>2</sub> (Fray & Schmitt 2009), in contrast with other regions of the comet. It is difficult at present to identify the cause of such heterogeneity, based solely on our determination of the CO/CO<sub>2</sub> ratio at Abydos. Some insight may be offered as to whether this heterogeneity is due to the accretion conditions of the comet or to its thermal history by the water D/H measurements planned to be performed by the ROSINA instrument close to the nucleus. A very homogeneous D/H in water would imply that the building blocks of 67P were formed at close distances in the PSN and argue in favor of a homogeneous accretion. Under these circumstances, the comet's heterogeneity would result from its thermal evolution after accretion, as suggested by thermal evolution

models (Marboeuf et al. 2011; De Sanctis et al. 2005; Prialnik et al. 2008). In contrast, the measurement of D/H variations would indicate that the comet's building blocks formed with different compositions at various locations of the PSN (Bonev et al. 2008). Heterogeneity would then have been acquired by the nucleus during both its formation and thermal evolution.

## 5. Summary

Philae landed at the Abydos site on comet 67P where the *Ptolemy* mass spectrometer made six discrete measurements of the coma gas composition over the following 45 h with the main constituents being H<sub>2</sub>O, CO<sub>2</sub>, and CO. An apparent CO/CO<sub>2</sub> ratio of 0.16 ± 0.03 was measured, which is lower than results taken from orbit by ROSINA; this is reduced even further to 0.07 ± 0.04 after taking into account the likely effect of CO<sub>2</sub> fragmentation in the *Ptolemy* mass spectrometer. This low ratio is an indication that the nucleus of comet 67P is heterogeneous, which heterogeneity was acquired either during the comet formation or its subsequent thermal alteration.

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