

## Review



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### Author for correspondence:

I. P. Wright

e-mail: [ian.wright@open.ac.uk](mailto:ian.wright@open.ac.uk)

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# On the attempts to measure water (and other volatiles) directly at the surface of a comet

I. P. Wright, S. Sheridan, G. H. Morgan, S. J. Barber and A. D. Morse

Department of Physical Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK

IPW, 0000-0002-4267-7963

The Ptolemy instrument on the Philae lander (of the Rosetta space mission) was able to make measurements of the major volatiles, water, carbon monoxide and carbon dioxide, directly at the surface of comet 67P/Churyumov–Gerasimenko. We give some background to the mission and highlight those instruments that have already given insights into the notion of water in comets, and which will continue to do so as more results are either acquired or more fully interpreted. On the basis of our results, we show how comets may in fact be heterogeneous over their surface, and how surface measurements can be used in a quest to comprehend the daily cycles of processes that affect the evolution of comets.

This article is part of the themed issue ‘The origin, history and role of water in the evolution of the inner Solar System’.

## 1. Introduction

When considering the notion of ‘water in comets’ this can be from the perspective either that comets represent one aspect/reservoir of the water found within the (inner) Solar System or alternatively that the water represents an integral part of the bodies we know as comets and has had a role to play in their formation and subsequent evolutionary mechanisms. This may seem at first glance like a philosophical issue but it is not. Cosmochemists interested in the broad-scale features of the Solar System as a whole will use the anticipated chemical compositions of comets (*sensu lato*), as well as those derived from asteroids/meteorites, to provide inputs

to models constructed to explain, for instance, the chemical composition of the Earth. By contrast, the (currently) ongoing Rosetta mission to 67P/Churyumov-Gerasimenko has given us an unprecedented opportunity to study the nature of an individual comet. And not merely a snapshot as such, but a chance to observe how a small icy body temporarily transforms into a comet as it approaches the Sun, and then reverts to its non-active state as it moves away again. In this case, the ‘water in comets’ is but one facet in the development of the cometary phenomenon.

There are a number of papers in this themed issue that consider the significance (or otherwise) of comets in terms of the overall distribution of chemical elements within the inner Solar System (see, for instance, [1]). Herein we consider the challenge of trying to understand the nature of comets themselves and how the study of water (directly) aids that cause.

Although it was widely believed that water was a key component of comets, and was likely to be instrumental in the production of comae, it was not until 1986 that water was actually detected [2]. At this time, the working hypothesis of what a cometary nucleus would look like was based on the pioneering study by Whipple [3], who made and interpreted ground-based observations of comet Encke. He proposed that the nucleus was an ‘icy conglomerate’ composed of dust particles embedded in ices. The dust itself was assumed to be similar to meteoritic (chondritic) material, while the ice component was considered to be dominated by water, with other volatiles such as methane and ammonia. It was also envisaged that organics were present. Colloquially, the overall idea became known as the ‘dirty snowball’ of cometary nuclei. In a sense the close-up images of Halley obtained by Giotto [4] confirmed the ‘icy conglomerate’ model but there was a fundamental surprise—the surface was very dark, with an albedo of less than 4% (in fact, history records that this had been predicted just prior to the encounter with Halley; see [5]). The spacecraft found hardly any evidence for bright patches of ice at the surface of Halley. This seemed to suggest that water (ice) was perhaps not as prevalent in comets as once thought. As such, the idea that cometary nuclei were like ‘dirty snowballs’ went a long way out of favour. Indeed, the thinking switched to ‘icy dirtballs’ instead.

That comets include water as a major constituent is clearly established. But the relationships between the water found in different comets (to each other), or between comets and other bodies of the Solar System, require the extra dimension of isotopic measurements to understand the genealogy. It was thus inevitable that an appropriate measurement from Rosetta was eagerly anticipated. Ultimately, the result of hydrogen isotope measurements (made by the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA); see [6]) was something of a surprise. This suggested that the D/H ratio of 67P was a factor of approximately three times that of the terrestrial value, which seemed to confound a previously emerging view that Jupiter-family comets (like 67P) should have the Earth-like values. In fact, for a number of reasons, it is beginning to look like there is no obvious difference between the D/H values of water in Jupiter-family comets and other Oort cloud comets. Rather, comets, in general, appear to have D/H values that span a range of one to three times the terrestrial value, with the exact value being a reflection of the distance from the Sun that the comet condensed [7]. The relevance for studies of the origins of the inner planets is that, as things stand, the elevated D/H ratios in comets mean that they could constitute only a relatively minor proportion of the water on these bodies, including the Earth [8–10].

The noble gas (isotopic) compositions of 67P have the potential to offer further constraints on the role of comets in the development of the surface layers of planets like the Earth. These are difficult measurements to make and are, in fact, still being acquired. Initial results from argon are given in Balsiger *et al.* [11] and confirm the fact that comets like 67P were not a significant contributor to water on Earth. However, it may transpire that isotope ratios can be used to constrain the relative inputs of noble gases to the different surface reservoirs on the planet (e.g. the atmosphere as distinct from the hydrosphere). This is important because it gives insights into the significance of comets in delivering species *other than water* to the surface of the early Earth. In this regard, carbon-bearing components are of considerable importance. This includes organic compounds, of course, but also more abundant components such as CH<sub>4</sub>, CO, CO<sub>2</sub>, etc.

## 2. Space missions to comets

The start of close-up investigations of comets began in 1985 when the International Sun–Earth Explorer-3 (ISEE-3) mission was repurposed to become the International Cometary Explorer (ICE), which flew through the tail of 21P/Giacobini–Zinner at a closest approach of 7862 km. This was swiftly followed by the ‘Halley armada’ in 1986, which investigated the famous comet 1P. A total of five spacecraft were involved in this venture including Vegas 1 and 2, Sakigake, Suisei and the European Space Agency mission Giotto, which made a fast flyby of the nucleus at very close range (605 km). Giotto was subsequently reconfigured for an extended mission that took it up close to 26P/Grigg–Skjellerup in 1992. Deep Space 1, which was launched in 1998, was originally destined for 107P/Wilson–Harrington, but problems during cruise forced an alternative plan that took it (successfully) to a flyby of 19P/Borrelly in 2001. The first spacecraft to collect cometary materials (coma dust and organics, from 81P/Wild) and return them to Earth was Stardust, launched in 1999. This craft was also implicated in the Deep Impact campaign, which saw a projectile directed at the surface of comet 9P/Tempel 1 in 2005 (with the subsequent impact plume being observed by the Deep Impact spacecraft itself), followed by a flyby in 2011 of Stardust (known by now as Stardust NExT) to observe the crater that had been formed on the comet’s surface. An overview of the achievements of (most of) these missions can be found in, for instance, Kuppers *et al.* [12].

## 3. The Rosetta space mission

Although it is difficult to track down well-documented evidence of the dates and all of the personnel involved with the development of the Rosetta mission, it seems to have been something that was being discussed within the community in about 1984–1985 (i.e. *before* the Halley encounters). It was originally conceived as a cometary nucleus sample-return mission [13]. However, practical reality coupled with some changes in support from the relevant space agencies ultimately gave rise to the present mission. A complete overview of this can be found in [14] and some of the challenges posed by a launcher failure that preceded Rosetta are described in [15]. In principle, Rosetta is a two-part spacecraft consisting of the main ‘orbiter’ craft and a 100 kg ‘lander’ known as Philae [16]. Originally three lander concepts were considered, which were whittled down to two (‘Champollion’, designed to conduct scientific investigations immediately after landing and have only a limited lifetime, and ‘RoLand’, which, being covered with solar panels, was intended to operate over a much longer period). The two concepts were finally combined into the one lander that was configured so as to offer both types of investigation, i.e. a short-term campaign (the ‘First Science Sequence’, operating intensively over a few days) and a longer-term endeavour (‘Long-Term Science’, which would have had punctuated operations, as batteries needed recharging, but which could have lasted for several weeks). Undoubtedly, the landing was an enormous success, despite the non-nominal landing preventing execution of all of the intended experiments. An overview of the scientific achievements of the on-comet operations can be found in Bibring *et al.* [17], while a summary of some of the first results from the instruments on board the main spacecraft are in Taylor *et al.* [18]. A flavour of the operational aspects of the mission, with its 10 year voyage, four planetary swing-bys, deep-space hibernation, etc., can be gained from Accomazzo *et al.* [19].

## 4. Relevant instruments on the Rosetta orbiter

There are a number of instruments on the main Rosetta spacecraft that have a bearing on the issue of water in comets. There are, of course, the cameras that are continuing to give us an unprecedented insight of what a cometary nucleus looks like at close range. The Optical, Spectroscopic, and Infrared Remote Imaging System (OSIRIS) camera has found evidence of ‘metre-sized’ patches of water ice at the surface of 67P [20]. Then there are the spectroscopic instruments Visual IR Thermal Imaging Spectrometer (VIRTIS) [21] and Alice [22],

which are providing information in the visual-infrared and far-ultraviolet, respectively. Direct measurements of the nucleus of 67P by VIRTIS have afforded information on the diurnal cycling of water ice through the surface layers [23] and are beginning to constrain the locations of exposed water ice [24]. Feldman *et al.* [25], using Alice, have demonstrated how the H I and O I emissions observed in the coma are likely to be the result of photoelectron impact dissociation of H<sub>2</sub>O. Along with measurements of C I emissions, it should ultimately be possible to determine column abundances of H<sub>2</sub>O/CO<sub>2</sub>, which will allow cross-calibration with data from the microwave instrument (Microwave Instrument for the Rosetta Orbiter (MIRO)) [26], which is producing detailed maps of the distribution of water within the coma [27].

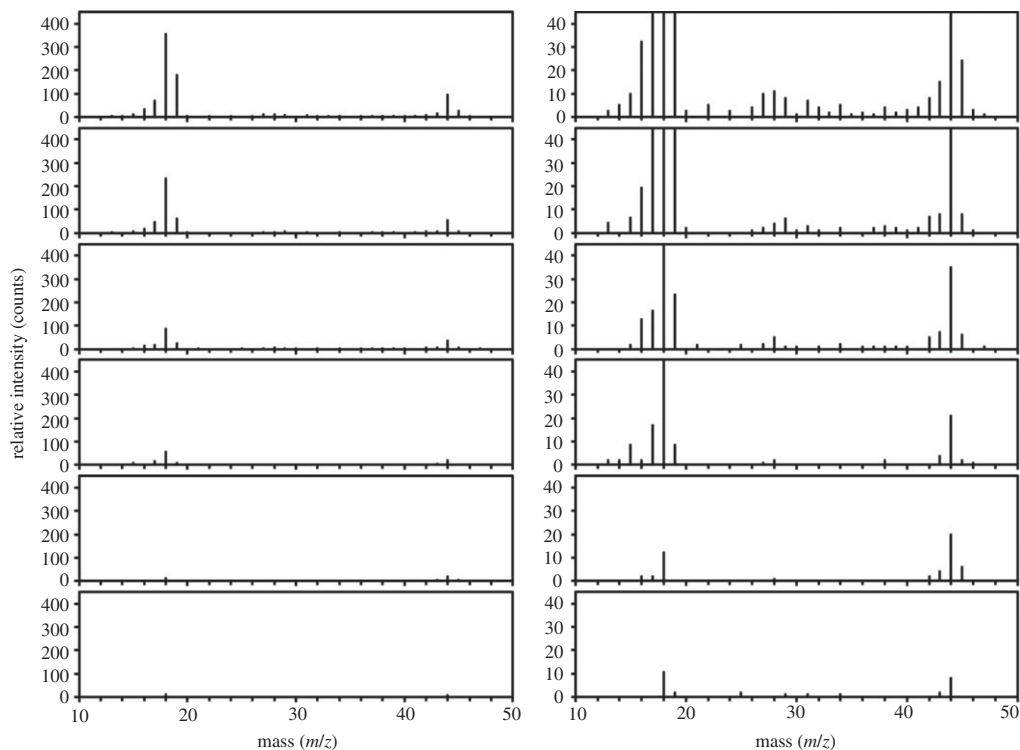
There are two instruments on Rosetta that are making direct measurements of coma materials—these are the COmetary Secondary Ion Mass Analyzer (COSIMA) [28] and ROSINA [29]. The former is a dust collection device that is both imaging the particles and analysing their chemical composition using secondary ion mass spectrometry. Kruger *et al.* [30] outline how the flight spare instrument is being used in the laboratory to analyse calibration materials such as carbonaceous chondrites, and preliminary measurements from space indicate that elemental ratios are compatible with such entities. Since carbonaceous chondrites have long been known to contain high concentrations of ‘water’ (see, for instance, [31])—in hydrated minerals, or as H associated with organic compounds—it is likely that future results from COSIMA will contribute to a description of how water is distributed within cometary nuclei.

## 5. Relevant instruments on the Rosetta lander (Philae)

The two instruments of most relevance for the study of water at the surface of 67P are the COmetary SAMpling and Composition experiment (COSAC) and Ptolemy. Both instruments are technically gas chromatograph–mass spectrometers, but differ in their objectives (and ultimately their design and configuration). Briefly, the COSAC instrument [32] is dedicated to the analysis of high molecular weight organic compounds and includes gas chromatograph columns that distinguish between different chiral species. Ptolemy, on the other hand [33], was intended to make measurements of isotope ratios of light elements such as hydrogen, carbon, nitrogen and oxygen, as well as noble gases (which meant that its mass range extended only as far as about 140). While the two instruments were expecting to get solid samples of the surface using a drilling system known as Sampling, Drilling and Distribution (SD2), they both also had the capability to make measurements by ‘sniffing’ (in which ambient gases flow into the instruments through the ‘vent’ pipes that allow each of them to attain a high vacuum). Given that COSAC and Ptolemy included mass spectrometers (time-of-flight and ion trap, respectively), both were capable of making qualitative/analytical mass spectral measurements (i.e. irrespective of their specific design goals). Obviously, the ultimate non-nominal landing of Philae meant that many of their capabilities could not be used to the full. It also meant that some of the results that were obtained required a greater level of interpretation than may otherwise have been anticipated.

## 6. Measurements of water at the surface of 67P

With regard to volatiles, the best set of results obtained from the surface of 67P come from the series of Ptolemy measurements made after the Philae lander came to rest at Abydos. In terms of operations, after it became apparent that the original ‘first science sequence’ would have to be reconfigured, Ptolemy was commanded to make so-called ‘sniffing’ measurements, firstly in ‘safe-mode’ blocks roughly 2 h apart (four separate measurements) and then two further experiments made to coincide with other activities (Multi-Purpose Sensors for Surface and Sub-Surface Science (MUPUS) hammering and SD2 drilling, respectively). The details of instrument operations during these procedures are given in [34]. Note that the COSAC instrument also made relevant measurements at Abydos and in the future it is intended to try and cross-calibrate these with the outputs from Ptolemy (as yet the COSAC data are not published). There is no *a priori* reason that the two sets of results should convey the same information. Certainly, as

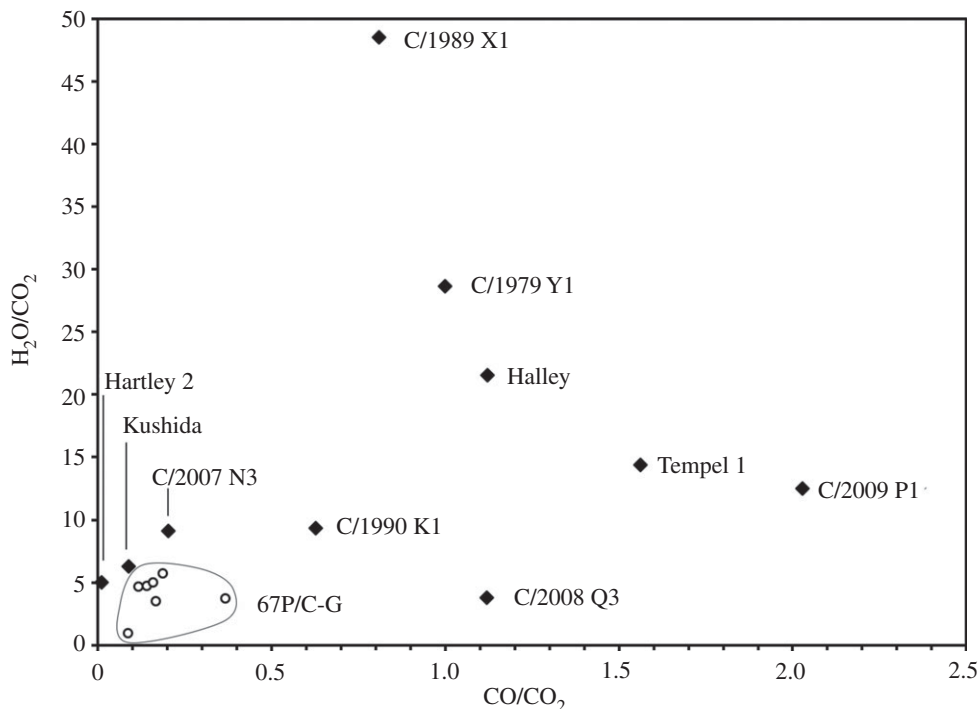


**Figure 1.** Plots of mass spectra taken by Ptolemy at the Abydos landing site. Each plot shows on the  $x$ -axis the mass of the species measured (or, more correctly, the mass/charge ratio, i.e.  $m/z$ ) versus the relative intensity of the signal at each mass ( $y$ -axis). Successive plots from top to bottom were taken at progressively longer intervals after Philae came to rest at Abydos. The plots on the left and right in each case are the same, but with a 10-fold difference in the intensity scale. What can be observed here is that even by the end of the monitoring period there are still peaks at  $m/z$  18 ( $\text{H}_2\text{O}^+$ ) and 44 ( $\text{CO}_2^+$ ), the measured number of counts being way above anything expected as a background.

far as measurements at Agilkia are concerned, Ptolemy recorded an  $\text{H}_2\text{O}/\text{CO}_2$  ratio [35] that is equivalent to those measured at Abydos; by contrast, the COSAC data from Agilkia have been interpreted as showing the presence of water but not  $\text{CO}_2$  [36]. One of the reasons that the instruments may record different information is that the vent pipes through which the analyses were made in both cases are diametrically opposed (COSAC protruding through the bottom of Philae, Ptolemy from the top surface).

The six sets of data acquired at Abydos by Ptolemy are shown in figure 1. Each subplot shows relative intensity in instrument counts versus mass (as mass/charge ratio, i.e.  $m/z$ ). The data in these so-called ‘stick plots’ are binned in such a way that ions only appear at discrete masses (differing by 1 a.m.u.). There is more information about the processes used to derive these in [37]. For each stack of plots shown in figure 1, time after arrival at Abydos increases from top to bottom. So, just looking at the left-hand stack, it can be seen that the peaks all decay with time after the lander came to rest (the range of relative intensities displayed is the same in each plot, and set so that all of the peaks appear on-scale). The right-hand stack shows the same data but with the intensity scale set to 10%. In this format, for the first four experiments there are peaks that go off-scale. But what these plots show is that, although we only consider those peaks that are ascribable to  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{CO}$ , there are clearly additional species present. Further work will be needed to assess the exact nature of these.

In principle, ionized water should occur at  $m/z$  18, 17 and 16 ( $\text{H}_2\text{O}^+$ ,  $\text{OH}^+$  and  $\text{O}^+$ ), carbon dioxide at  $m/z$  44, 28 and 16 ( $\text{CO}_2^+$ ,  $\text{CO}^+$  and  $\text{O}^+$ ) and carbon monoxide at  $m/z$  28 and 16 ( $\text{CO}^+$  and  $\text{O}^+$ ). But within a mass spectrometer there are many possibilities for a species of interest

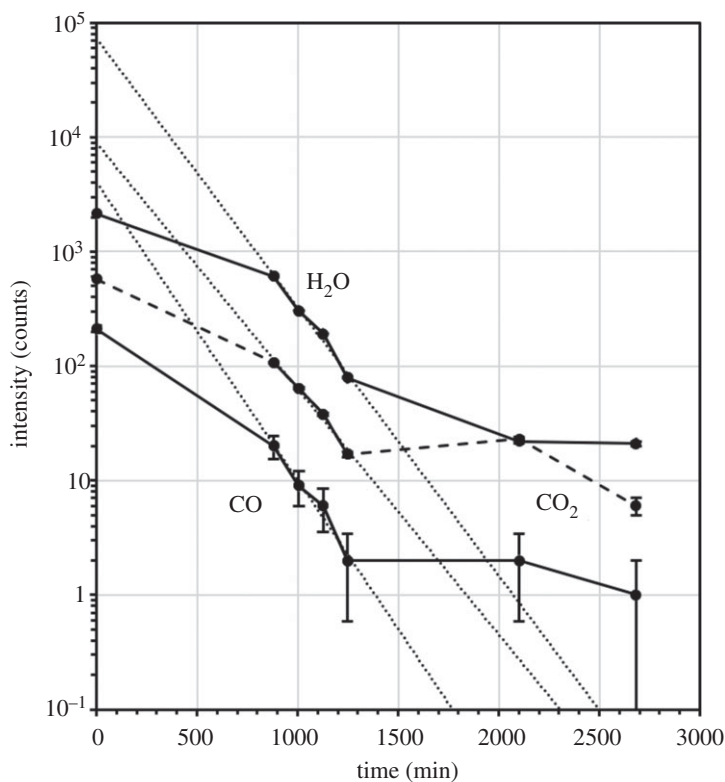


**Figure 2.** Plot of  $\text{H}_2\text{O}/\text{CO}_2$  ratios of comets versus  $\text{CO}/\text{CO}_2$  (data taken from [38]). There are a number of additional measurements that have yielded  $\text{H}_2\text{O}/\text{CO}_2$  ratios (spanning a range of 3.5–14.5) but no accompanying  $\text{CO}/\text{CO}_2$ . Filled diamonds are spectroscopic measurements made by remote, telescopic means. The circles represent the equivalent ratios measured at the nucleus of 67P by Ptolemy (data from [34]); note that there are, in fact, seven points plotted—two of the Abydos points plot on top of each other, while the point that shows the highest  $\text{CO}/\text{CO}_2$  ratio is that measured at Agilkia). The far more extensive datasets acquired by ROSINA are not included since these are influenced by specific regional-scale processes (which are, in turn, the result of daily and seasonal effects) and are complicated by the orientation of the spacecraft with respect to the nucleus at the time the measurements were made. Notwithstanding this, on the basis of data taken from the coma at about 3.5 AU from the Sun,  $\text{H}_2\text{O}/\text{CO}_2$  is typically in the range 5–10 with  $\text{CO}/\text{CO}_2$  of 1–3 [39]. In extreme cases,  $\text{H}_2\text{O}/\text{CO}_2$  drops to about 0.01.

to appear at a different mass peak from that which is expected (i.e. not including differences due to the presence of isotopes). The main problem for consideration here is what we loosely refer to as ‘protonation’; by this is meant a peak appearing at 1 a.m.u. higher than the expected mass ( $M + 1$  instead of  $M$ ). This can be the result of protonation itself (addition to a neutral ion of  $\text{H}^+$ ), but may also result from other processes (proton abstraction from neutral water by an ionized molecule, charge transfer, chemical ionization, and so on). The end result is the same; the volatiles of interest occur (partially) at  $M + 1$  peaks, e.g.  $\text{H}_3\text{O}^+$  at  $m/z$  19 and  $\text{CO}_2\text{H}^+$  at  $m/z$  45. Such effects are dependent upon both the exact mixture of components in the mass spectrometer and the overall pressure. Taking the example of water, the  $m/z$  18/19 ratios shown in figure 1 can be seen to change from 2 to 6 as time progresses and the peak intensities decline. Collectively, these results reflect the drop in pressure of the gases being measured with time at Abydos. We return to this below.

In order to derive measurements of the  $\text{H}_2\text{O}/\text{CO}_2$  and  $\text{CO}/\text{CO}_2$  ratios it is necessary to sum relevant peaks (as described in [34]). Taking this approach, we can then include the relevant data on a plot of  $\text{H}_2\text{O}/\text{CO}_2$  versus  $\text{CO}/\text{CO}_2$ . This is shown in figure 2, which compares data obtained at the surface of 67P with spectroscopic measurements of comets (comae) made over a number of years. It is immediately apparent that 67P has a relatively low water content (compared with  $\text{CO}_2$  at least), consistent with results made by ROSINA around the same time [39]. At this time the comet was at 3 AU, beyond the snowline and relatively inactive, so it is probable that the

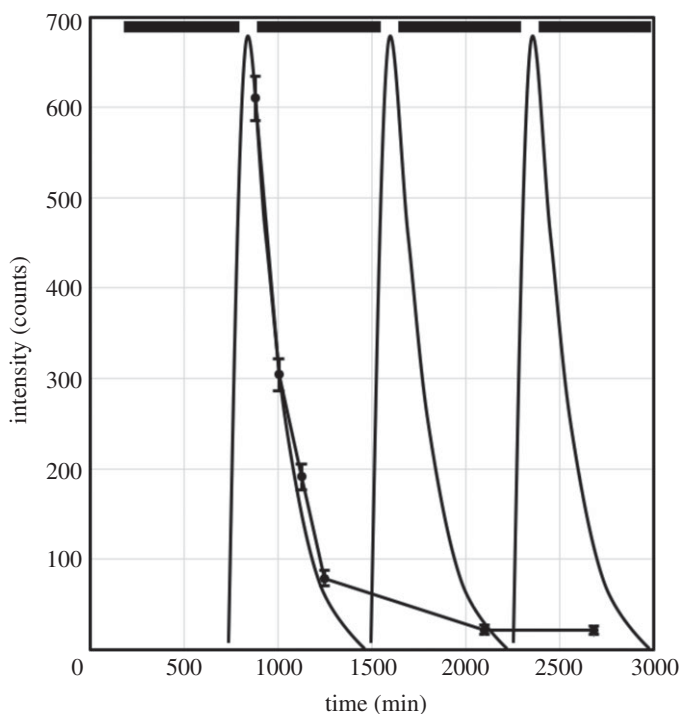




**Figure 3.** Plot of the intensities of mass spectral peaks due to H<sub>2</sub>O, CO<sub>2</sub> and CO showing how these varied with time after the arrival of Philae at the surface of 67P. The first data point in each case is from the experiments conducted at Agilkia; the remainder are from the long-term monitoring campaign at Abydos. Best-fit lines through data collected between 881 and 1248 min (four consecutive points in each case) are shown as the dotted lines. Note that the species labelled as CO<sub>2</sub> and CO are not corrected for the effects of cracking of CO<sub>2</sub><sup>+</sup> (*m/z* 44) to CO<sup>+</sup> (*m/z* 28). This has not been done herein because the exact details of corrections like this are not yet certain and will require further work. However, it is a fact that without correction the values recorded for CO are upper limits. Error bars are 1 s.d. (i.e. the noise associated with ion counting).

low H<sub>2</sub>O/CO<sub>2</sub> ratio is a consequence of low activity—this will be resolved as Rosetta continues to follow the comet through Perihelion and beyond. As noted previously [34] there is a low CO/CO<sub>2</sub> ratio at Abydos; in fact, since the data are not corrected for the effects of cracking of CO<sub>2</sub>, this means that the values are upper limits since the measured CO<sup>+</sup> signal is not entirely from ionized CO (i.e. some is from CO<sup>+</sup> that is cracked from CO<sub>2</sub><sup>+</sup> within the mass spectrometer). Corrections are not applied for this because the magnitude of the effects are uncertain and require further laboratory calibrations (see electronic supplementary material, notes). Notwithstanding this issue, looked at another way, the Abydos landing area of 67P seems to be relatively depleted in H<sub>2</sub>O and CO.

Figure 3 shows the time-dependent variation in abundances of the species under investigation. Plotted here are the six results obtained at Abydos (i.e. those already discussed) along with a measurement made just after touchdown at Agilkia. The time axis is, therefore, graduated in minutes after (first touchdown). The plot shows some rather obvious features, most notably that the first four Abydos points (sniffing measurements at 2 h intervals), in all cases, show an exponential decay in measured H<sub>2</sub>O, CO<sub>2</sub> and CO. Best-fit lines through these points are included in the plot; the significance of these is unquestionable. Clearly, beyond a certain point the decays level off, presumably to some kind of background level of outgassing. Typical instrument background as measured during the Lutetia flyby [40] and operations near the comet prior to



**Figure 4.** The  $\text{H}_2\text{O}$  data acquired at Abydos plotted in linear format as intensity versus time (the data are the same as those in figure 3). The broken line at the top of the plot shows the times when Philae was illuminated (white) and in darkness (black). Superimposed on the first four points is a freeform shape meant to represent a putative spike of outgassing, as might be envisaged to accompany the daily period of illumination. The profile is assumed to show a sharp, rapid development of outgassing, followed by an exponential decay in intensity as the local site cools during the night. This is certainly consistent with the measured data (i.e. the filled dots joined by a line). The outgassing profile is then reproduced to coincide with the two further cycles of day–night experienced at Abydos. Note that the Agilkia data are not included to avoid confusion. Error bars are 1 s.d. (i.e. the noise associated with ion counting).

landing were 100, 4, 10 for  $\text{H}_2\text{O}$ , CO and  $\text{CO}_2$ , respectively (see the electronic supplementary material, notes, for a more detailed discussion).

The question arises as to whether the data from Abydos have any connection with the results from Agilkia. At face value it would appear not to be the case on account of the obvious deviation from the decay lines. However, we consider this further. During the touchdown at Agilkia it is apparent that dust/volatiles were disturbed from the nucleus during the brief encounter of the lander with the surface and that these materials were transported into the instrument (through its vent pipe). Now, if we consider that nothing extra was added at Abydos then it could be argued that the drop in peak heights from the Agilkia data to the (first) points at Abydos represents some kind of decay process (e.g. in the outgassing of materials trapped in the vent pipe). If so, we might expect a continued downward trend with slopes equivalent to those defined by the first two points in each case. Clearly this does not happen. The alternative perspective is that, based on the decays experienced at Abydos, the peak heights at Agilkia should have been much higher than those measured (i.e. the intercepts of the decay lines at  $t = 0$  in figure 3). Again, this is not the case. As such, it would seem that the gases analysed at Abydos represent a separate injection of materials. Furthermore, the measured signals then decayed (down to a baseline level over the course of about 6 h). There are two possible interpretations here; either there was a single instantaneous injection of gas, with the subsequent decay representing the long-term removal of this from the instrument, or that local outgassing at the surface of 67P at Abydos declined over a period of a few hours. The former possibility seems unlikely but will be explored in a future study



by comparing Ptolemy and COSAC data. Herein, we consider either that the arrival of Philae at Abydos effectively coincided with the tail end of a local outgassing event (i.e. that was already taking place) or that the spacecraft itself was responsible for initiating the outgassing. In the latter case, the decline in outgassing was then a reflection that things returned to normal over the course of a few hours (to the sort of background levels that were eventually recorded).

Considering the  $\text{H}_2\text{O}/\text{CO}_2$  and  $\text{CO}/\text{CO}_2$  ratios measured at the surface, the data in figure 3 show that after arriving at Abydos they may have changed in a systematic way. If we just consider the slopes of the best-fit lines,  $\text{H}_2\text{O}/\text{CO}_2$  and  $\text{CO}/\text{CO}_2$  both decline with time. The ratios defined by the measured points themselves can be seen in figure 2 as the uppermost points in the 67P/C-G field. Although this has the capacity to look like the same trend as that observed with the linear fits this is not actually the case because the  $\text{H}_2\text{O}/\text{CO}_2$  and  $\text{CO}/\text{CO}_2$  ratios calculated from the discrete points do not vary monotonically with time (a result, presumably, from the influence of uncertainties and errors in the data; an assessment of these was given in [34]). Returning to the linear fits, and taking consideration of the relative volatilities of the species under investigation ( $\text{CO} > \text{CO}_2 > \text{H}_2\text{O}$ ), we might have expected that a process that resulted in a lowering of the  $\text{CO}/\text{CO}_2$  ratio would also cause a decline in  $\text{CO}_2/\text{H}_2\text{O}$  (i.e. a rise in  $\text{H}_2\text{O}/\text{CO}_2$ ). Obviously, this is at odds with what is actually observed. Now, in detail, the data displayed in figure 3 are not corrected for the effects of the cracking of  $\text{CO}_2^+$  to  $\text{CO}^+$ . Any attempt to introduce a correction for this will make the decay line due to CO steeper than shown, and, correspondingly, the  $\text{CO}_2$  will be less steep. In other words, the overall decline in  $\text{CO}/\text{CO}_2$  would become greater than it was while that for  $\text{H}_2\text{O}/\text{CO}_2$  would become less pronounced. This actually has the effect of increasing the disparity of what is observed versus that expected from volatility considerations. Thus, it would appear that the  $\text{H}_2\text{O}/\text{CO}_2$  and  $\text{CO}/\text{CO}_2$  ratios at Abydos did indeed change over the course of a few hours as overall outgassing declined. Furthermore, these changes were influenced by a process other than temperature.

The  $\text{H}_2\text{O}/\text{CO}_2$  ratios at Abydos appear to change from about 6 to 5 during the course of the first few hours, with the background outgassing at a value somewhere between 1 and 3. By contrast, the ratio at Agilkia was calculated as about 3.75 [34]. The equivalent data for  $\text{CO}/\text{CO}_2$  are 0.37 at Agilkia, varying at Abydos from 0.2 at arrival to a background value of something like 0.1. So, it seems like different values were recorded at the two locations. This could be explained by heterogeneity in the nucleus, but could also just be the result of chance circumstances accompanying the interaction of Philae with the surface at the different sites. In order to pursue this, it is important to take into consideration as many relevant factors as possible. So, for instance, it would appear that the surface at Agilkia was covered by a layer of dust, perhaps 20 cm thick. By contrast, Abydos tends to look like something that is more 'rocky' in appearance, and is perhaps far more consolidated. Then there are conditions of illumination to consider; figure 3 includes the relevant information. Thus, it can be seen that (as planned) Philae arrived at Agilkia in the daytime. In other words, the surface of 67P was in full illumination when the first measurements were made. The arrival at Abydos was about 2 h later, after which time the site went into darkness (for several hours). The first sniffing measurement was made after the lander once again came into full illumination; subsequent measurements were then made at what might be thought of as dusk, followed by two that were progressively deeper into the night. Clearly, therefore, what could have been observed at Abydos was part of a daily cycle of outgassing that would ordinarily accompany the day–night cycle (i.e. with maximum outgassing in full illumination followed by a decline as the site went into darkness). This is illustrated in figure 4, where it can be seen that the proposed scenario looks plausible. Obviously, if the Long-Term Science campaign of Philae had been successful it would have been possible to verify this hypothesis.

## 7. Conclusion

Herein we have described how the Ptolemy instrument on board the Philae lander was successful in making measurements of water, carbon monoxide and carbon dioxide directly at the surface of a comet. Such a feat has never been attempted before and, as things stand, there are no (selected)

missions that will endeavour to repeat the analyses. We believe that the ratios of the volatiles studied were different at the two landing sites studied (Agilkia and Abydos). This was made possible because Rosetta included a lander capable of sampling the surface at a geographically distinct point; and ultimately, of course, this was done at two separate locations. Although a rather serendipitous aspect of Philae's operation, it is hoped that this will be a major consideration for a future cometary mission. Landing is demonstrably a risky venture but represents the only way of sampling at specific sites. And, in any case, a sample-return mission to a comet necessarily requires getting into contact with the surface in some way.

We have argued that what was observed over time at Abydos could be part of a regular day-night cycle of outgassing (when in illumination) followed by an almost complete shut-down of the process during the cometary night. Such processes represent the beating heart of an object that is both evolving and ageing (dying) because of them. It is vital that we understand such phenomena so that we have a better understanding of what it means to talk about 'comets' in the context of those entities that were brought together 4.5 billion years ago to build the planets.

While cosmochemists strive to understand the workings of the Solar System by reference to broad-brush categories of objects such as 'asteroids' or 'comets', the Rosetta space mission has opened up the possibility of studying one particular object in great detail. This, in turn, will ultimately offer the chance of adding further refinements to the system-wide modelling that is currently in progress. A full understanding of water (and other volatiles) in comets will ultimately require integration of the results obtained at the surface of 67P, along with the long-term monitoring of the nucleus from afar and direct study of the emerging/declining coma. Furthermore, the results of the ostensibly disparate investigations need to be considered alongside each other. In simplistic terms, this means assimilating the results of those investigations dedicated to 'chemistry' with those aimed at 'physics', and factoring in what is apparent from observations. One imagines this is a task that could take 10 years or more.

**Data accessibility.** All data from the Rosetta space mission (including those from Ptolemy) are available in PDS format through the Planetary Science Archive of the European Space Agency; see: [www.cosmos.esa.int/web/psa/rosetta](http://www.cosmos.esa.int/web/psa/rosetta).

**Authors' contributions.** All authors have been involved with Ptolemy since its design and construction and were all active with post-launch operations including commissioning and on-comet science measurements. I.P.W. is the principal investigator of Ptolemy, involved in the overall system design of the instrument, and takes the lead in data interpretation. S.S. takes responsibility for the operation and performance of the vacuum manifold of Ptolemy, and is involved with data interpretation. G.H.M. takes responsibility for the operation and performance of the gas chromatography system on Ptolemy, and is involved with data interpretation. S.J.B. is the overall project manager of Ptolemy, is an expert in the interpretation of mass spectra from ion trap instruments and is involved with data interpretation. A.D.M. is the deputy principal investigator of Ptolemy, takes responsibility for the operation and performance of the mass spectrometer, leads the data archiving and is involved with data interpretation.

**Competing interests.** The authors declare that there are no competing interests.

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