SPACE SCIENCES

The presence of clathrates in comet 67P/Churyumov-Gerasimenko

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Adrienn Luspay-Kuti,[1]* Olivier Mousis,[2] Myrtha Hässig,[1,3] Stephen A. Fuselier,[1,4] Jonathan I. Lunine,[5] Bernard Marty,[6] Kathleen E. Mandt,[1,4] Peter Wurz,[3,7] Martin Rubin[3]

Cometary nuclei are considered to most closely reflect the composition of the building blocks of our solar system. As such, comets carry important information about the prevalent conditions in the solar nebula before and after planet formation. Recent measurements of the time variation of major and minor volatile species in the coma of the Jupiter family comet 67P/Churyumov-Gerasimenko (67P) by the ROSINA (Rosetta Orbiter Spectrometer for Ion and Neutral Analysis) instrument onboard Rosetta provide insight into the possible origin of this comet. The observed outgassing pattern indicates that the nucleus of 67P contains crystalline ice, clathrates, and other ices. The observed outgassing is not consistent with gas release from an amorphous ice phase with trapped volatile gases. If the building blocks of 67P were formed from crystalline ices and clathrates, then 67P would have agglomerated from ices that were condensed and altered in the protosolar nebula closer to the Sun instead of more pristine ices originating from the interstellar medium or the outskirts of the disc, where amorphous ice may dominate.

INTRODUCTION

Although there is no doubt that cometary nuclei are, to a large extent, composed of H_2O ice, it is the structure and phase of this H_2O ice that provide insight into the place of origin, formation temperature, and evolution of icy agglomerates in the protosolar nebula (PSN). Whether cometary H_2O ice originated directly from the interstellar medium (ISM) or was derived from the PSN has been a topic of active debate over the past three decades. An origin from the ISM implies formation at larger heliocentric distances, where pristine amorphous H_2O ice could be maintained in the extremely low temperature, nonturbulent protoplanetary disc (*1*–*5*). An origin from the PSN implies formation at smaller heliocentric distances where crystalline ice could form at a temperature of ~150 K in the cooling PSN (*6*, *7*). The phase in which other volatile species are stored in the nucleus strongly depends on the phase of the H_2O ice.

Amorphous H_2O ice very efficiently traps large amounts of volatiles in its highly porous structure [for example, (*8*, *9*)]. The trapped volatiles are then released simultaneously as a result of changes in the ice structure. The major release of trapped gases occurs during the exothermic transition from amorphous to crystalline ice (*8*).

On the other hand, free crystalline H_2O ice could enable various volatile species to be encaged as guest species within clathrate hydrates. In a clathrate, volatile gases are locked inside cage-like structures of crystalline H_2O ice. In the cooling PSN, H_2O will be present in its crystalline structure, with no or very little amorphous H_2O. The fraction of amorphous ice in the PSN would be negligible because condensation of the formerly vaporized H_2O occurs at significantly higher temperatures in the crystalline phase than those needed for the formation of amorphous H_2O ice. By the time the temperature of the PSN was low enough for amorphous H_2O ice formation, most volatile gases themselves either had condensed or were trapped in clathrates. These processes leave no or very little H_2O and other volatile gases available when conditions were right for amorphous ice to form (*2*, *6*, *10*). Lacking in situ measurements of the internal structure and ice phase of cometary nuclei, the composition of the coma and the outgassing pattern of volatile species of major and minor abundance provide the best clues about the ice structure and, as a result, the origin of cometary nuclei.

Recent measurements by the ROSINA/DFMS (Rosetta Orbiter Spectrometer for Ion and Neutral Analysis/Double-Focusing Mass Spectrometer) (*11*) instrument onboard the Rosetta spacecraft showed a strongly heterogeneous coma in the major (*12*) and minor volatile species (*13*) of the Jupiter family comet (JFC) 67P/Churyumov-Gerasimenko (hereinafter 67P). In addition, a strong north-south asymmetry was present in the measured abundances during October 2014 (*14*).

Here, we use these recent coma measurements by ROSINA/DFMS over the September to October 2014 time period (*12*–*14*) to infer the structure of the icy agglomerates from which 67P was assembled. In particular, we restrict our analysis to data obtained when the poorly illuminated, winter southern hemisphere of the comet was in the view of Rosetta. The mid-to-high southern latitude scans revealed an interesting feature in the coma signal over two narrow sub-spacecraft longitude regions (*12*, *13*). Over these narrow southern hemisphere longitude regions, the signals of CO_2, CO, and C_2H_6 clearly deviated from the overall H_2O signal, showing maxima at times of deep H_2O minima (figs. S1 to S3). This telling feature was not present over the well-illuminated northern hemisphere, which was experiencing summer at the time. The higher temperatures experienced by the northern hemisphere make it difficult to reliably infer whether minor species are being released from different ice phases. The observed outgassing over the northern hemisphere with substantial H_2O ice sublimation due to the higher temperatures would be consistent with gas release from either amorphous ice or clathrates, or both. Once the temperature is high enough for H_2O sublimation, as was the case in the northern hemisphere during the period of observation, differences in outgassing due to gas release from amorphous ice, clathrate structures, and nucleus heterogeneity cannot be clearly distinguished. In contrast, temporal variations in the outgassing

[1]Department of Space Research, Southwest Research Institute, 6220 Culebra Road, San Antonio, TX 78238, USA. [2]Aix Marseille Université, CNRS, LAM (Laboratoire d'Astrophysique de Marseille), UMR 7326, 13388 Marseille, France. [3]Physikalisches Institut, University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland. [4]Department of Physics and Astronomy, University of Texas at San Antonio, 1 UTSA Circle, San Antonio, TX 78249, USA. [5]Cornell Center for Astrophysics and Planetary Science, Space Sciences Building Cornell University, Ithaca, NY 14853, USA. [6]CRPG-CNRS, Nancy-Université, 15 rue Notre Dame des Pauvres, 54501 Vandoeuvre-lès-Nancy, France. [7]Center for Space and Habitability, University of Bern, CH-3012 Bern, Switzerland.
*Corresponding author. E-mail: aluspaykuti@swri.edu

of volatiles from the southern (winter) hemisphere are well resolved and distinguishable from each other. At these lower temperatures, volatile outgassing is expected to be different based on the phase of H_2O ice in the nucleus. Hence, the clearly distinguishable outgassing features in the southern hemisphere coma provide insight into the structure and history of 67P's nucleus.

RESULTS

Of the five species studied, CH_4 was the only volatile species whose signal showed no apparent correlation with either CO_2 or H_2O (figs. S1 to S3) over the southern hemisphere scans (*13*). This outgassing behavior provides important clues about the nucleus of 67P. Coma heterogeneity was attributed to heterogeneity in the nucleus (*13*), including possible variations in surface properties (*14*, *15*). These previous results clearly imply the presence of some kind of heterogeneity related to the properties of the nucleus, though the observed time variation of all volatile species would be difficult to explain solely with such variation. A heterogeneous nucleus and/or surface properties would certainly affect the composition of the coma, though it is unclear what surface properties would be able to affect CH_4 differently from the other species. The distinct time variation displayed by CH_4 also strongly suggests that it does not sublimate from a segregated nonpolar ice phase, as proposed for CO, CO_2, and C_2H_6 (*13*).

We are also able to exclude gas release from amorphous H_2O ice based on the available measurements. As has been shown in multiple laboratory experiments, large amounts of volatile gases are released in the phase transition from amorphous H_2O ice to the cubic phase of crystalline H_2O between 135 and 155 K [for example, (*8*)]. This transition is followed by the transition of cubic crystalline to hexagonal crystalline ice between 160 and 175 K [for example, (*16*)]. In these stages, the trapped volatile gases are released simultaneously and independently of their own volatility, with the exception of H_2O. The simultaneous release that would occur with amorphous ice does not agree with the ROSINA/DFMS observations, in which not all minor volatile species were released together from the southern hemisphere nucleus (*13*). For instance, no HCN and CH_3OH outgassing was observed at times of CO_2, CO, and C_2H_6 outgassing maxima over the southern hemisphere during these measurements. The outgassing pattern of CH_4 that is distinct from other major and minor volatile species is also inconsistent with gas release from amorphous ice as currently understood from laboratory studies.

The presence of clathrates would explain the observed time variation of CH_4 over the southern hemisphere (figs. S1 to S3). Stability curves of CH_4 and C_2H_6 single-guest clathrates, as well as CH_4, C_2H_6, and CO_2 condensation curves, are shown in Fig. 1 as a function of the total PSN gas pressure. In the cooling nebula, CH_4 clathrate forms at temperatures 20 to 30 K higher than the CH_4 condensate (Fig. 1). Figure 1 shows equilibrium curves with gas-phase mole fractions relative to H_2 in the PSN, derived specifically from the measured cometary gas/H_2O ratios of 67P's southern hemisphere (*17*). Note that the abundances of volatiles measured by ROSINA/DFMS in the coma of 67P do not necessarily represent bulk abundances in the nucleus. Thus, several ratios were tested based on other available measurements for known comets. Indeed, CH_4 clathrates will preferentially form instead of condensed CH_4 ice in every case for gas-phase CH_4 mole fractions varied within the range of known comets. Thus, if CH_4 were present as clathrate in the nucleus of 67P, then CH_4 outgassing from the nucleus would occur when the ambient pressure drops below the equilibrium pressure of the CH_4 clathrate at a given temperature. In a cometary environment, the largest contribution to the total pressure within the nucleus comes from H_2O, unlike in the PSN, where the total pressure is mainly given by H_2. To represent clathrate decomposition in the nucleus of 67P, we calculated the equilibrium curves of volatile species as a function of total pressure (Fig. 2). For this calculation, the gas-phase mole fractions relative to H_2O were taken directly from ROSINA/DFMS measurements derived for the southern hemisphere (*14*). We see from these curves that the decomposition of CH_4 clathrate begins at temperatures significantly lower than those needed for the sublimation of the host H_2O cages (Fig. 2). Thus, if CH_4 is present as a clathrate structure in the nucleus of 67P, it is not required for the outgassing pattern of CH_4 to follow that of H_2O or CO_2.

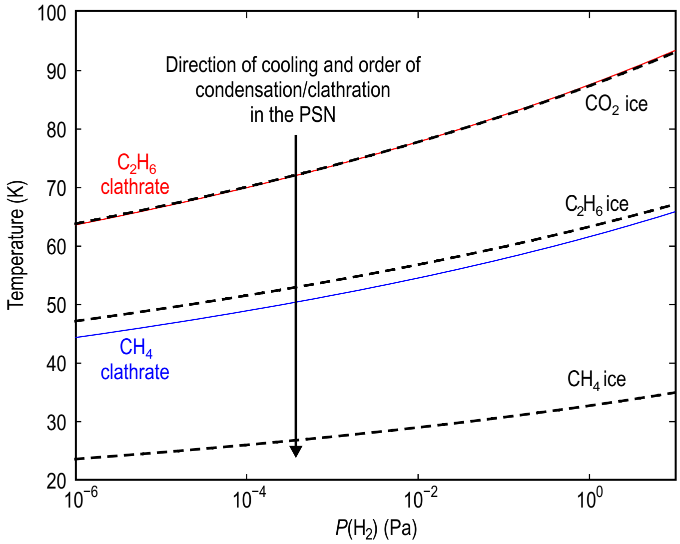

Fig. 1. Equilibrium curves of clathrates and condensation in the PSN. Equilibrium curves of C_2H_6 (red) and CH_4 (blue) clathrates are shown with respect to the equilibrium curves of C_2H_6, CH_4, and CO_2 ices (black dashed lines) as a function of total nebular pressure. The arrow indicates the direction of cooling in the PSN. Above the clathrate stability/condensation curve, a volatile species exists in the gas phase. Below the clathrate stability/condensation curve, a volatile species may form clathrates or pure condensates. The gas-phase mole fractions relative to H_2 were derived from the cometary X/H_2O ratios (*14*) and solar system elemental abundances of O and H (*40*, *41*).

The curves in Fig. 2 are in agreement with the ROSINA/DFMS measurements that show poor correlations of CH_4 with CO_2 and H_2O (R^2 of 0.18 and 0.57, respectively) [figs. S1 to S3 (*13*)]. However, the same ROSINA/DFMS observations show that C_2H_6 follows closely and correlates very well with CO_2 in the southern hemisphere (R^2 of 0.77), unlike CH_4 (*13*). At the same time, Fig. 1 suggests that C_2H_6 also preferentially forms clathrates instead of a pure condensate in the cooling PSN. We conclude that both CH_4 and C_2H_6 are present as clathrates in the nucleus of 67P. In contrast with CH_4, the strong correlation between C_2H_6 and CO_2 is caused by the fact that the dissociation temperature of the C_2H_6 clathrate is coincidentally close to the sublimation temperature of CO_2 ice. There is strong correlation between C_2H_6 and CO_2, as shown by their overlapping equilibrium curves in

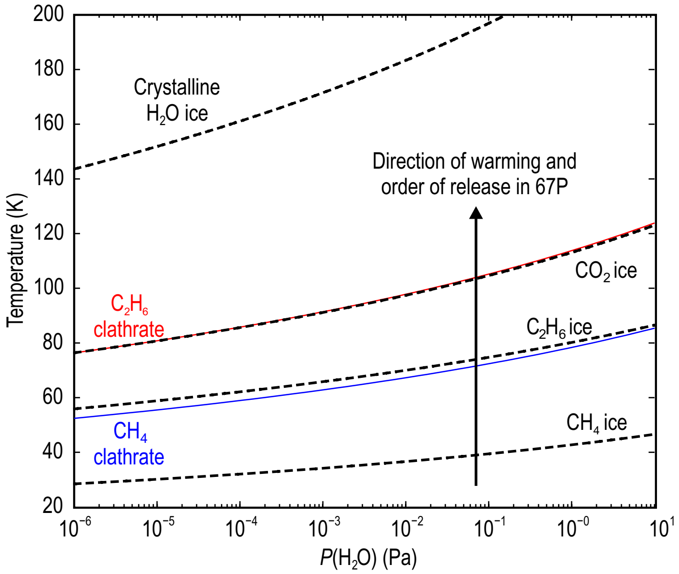

Fig. 2. Equilibrium curves of clathrates and pure condensates in the cometary environment. The equilibrium curves are shown here as a function of total H_2O pressure. Decomposition of the clathrate structures and sublimation of pure ices occur at temperatures above the equilibrium curves, whereas clathrates/pure condensates remain stable below the curves. Mole fractions of each species shown are directly taken from ROSINA/DFMS measurements of the coma of 67P (*14*).

Figs. 1 and 2. Outgassing as a result of decomposition of CH_4 and C_2H_6 clathrates is in full agreement with the time variation of the volatile species in the southern hemisphere coma of 67P measured by ROSINA/DFMS (*13*). At the same time, the implications of our results do not depend on the measured abundance ratios in the coma of 67P, considering that abundances in the coma do not necessarily represent bulk abundances in the nucleus. Varying the abundances of CH_4, C_2H_6, and CO_2 within the range of other known comets results in the same ordering of species as shown in Figs. 1 and 2. C_2H_6 and CH_4 clathrates always form before their pure condensates, that is, at temperatures about 20 K higher. In addition, C_2H_6 clathrates form at about the same time (within <1 K) as CO_2 ice (fig. S4). In addition, the equilibrium pressure curves of the JFCs (67P and Hartley 2) have very similar temperature dependences, as do those of comets Halley and Hale-Bopp, which belong to the Oort cloud (fig. S4). On the basis of our results, clathrate and pure condensate formation temperatures change as a function of the abundance ratio used. Thus, although the specific formation temperature of the nucleus of 67P cannot be constrained reliably, our results provide a strong argument for the presence of CH_4 and C_2H_6 clathrates in the nucleus of 67P.

DISCUSSION

Circumstantial evidence for the existence of amorphous ice in comets was previously given based on the onset of cometary activity at large heliocentric distances [for example, (*18*)], as well as distant and near-perihelion outbursts (*19*). These phenomena could be explained by the crystallization of amorphous ice, as was proposed for the distant outbursts of 1P/Halley (*20*) and Hale-Bopp (*21*–*23*), the perihelion activity of 2060 Chiron (*24*), and the erratic activity of comet Schwassmann-Wachmann (*25*). In the case of comet 17P/Holmes, however, the crystallization of H_2O ice was likely not responsible for its 2007 post-perihelion megaburst (*26*). Recently, the exothermic phase transition of amorphous to crystalline H_2O ice has been proposed as a potential cause for the observed active pits in the nucleus of 67P (*27*). At the same time, crystallization of amorphous H_2O ice is not the only process capable of producing outbursts and pits. Pressure pulses resulting in outbursts could also be caused by clathrate decomposition at depths comparable to the depths of observed pits on time scales shorter than the lifetime of 67P, as has been shown recently (*28*).

The kinetics of clathrate formation at low temperatures are not well known, but the nature of the differences in prevailing thermodynamic conditions (P, T) in the PSN versus the ISM makes it more likely that clathrate will form in the former as opposed to the latter (*5*). Clathrates could also form later in the nucleus in the presence of free crystalline H_2O ice, even if the original ice phase of 67P was amorphous H_2O. If clathrates formed in the nucleus of 67P at a later period after the comet's formation, then clathration would have had to occur on significantly shorter time scales than the formation of crystalline H_2O and clathrate ice grains in the PSN. Unfortunately, the currently loosely constrained kinetics of clathrate formation (*29*) do not allow us to distinguish between a nebular and a postnebular formation of clathrate in 67P.

Our results do not exclude the existence of amorphous ice in the solar nebula, which may have been quite abundant in the low-temperature, outer regions of the disc [for example, (*4*, *30*)]. In addition, the presence of clathrates in the nucleus of 67P does not prove that comets, including 67P, formed out of clathrates. Yet, our results, along with other recent efforts supporting the presence of N_2, Ar, and CO clathrates in the nucleus of 67P (*31*, *32*), suggest a picture of the origin of 67P that is different from what was envisaged before, where crystalline H_2O ice, pure condensates, and clathrates, rather than amorphous ice, may play a leading role. If clathrates did form in the PSN, then 67P would have agglomerated from ices condensed and altered in the PSN instead of pristine ices from the ISM or the outskirts of the disc, where amorphous ice may dominate (*4*, *5*). This idea is consistent with scenarios arguing that the building blocks of giant planets and satellites were formed in a similar manner in the nebula (*33*, *34*) and that Titan accreted from clathrate-rich planetesimals originating from Saturn's feeding zone (*3*). Dynamical model results suggest that both JFCs and Oort cloud comets may have formed in the same environment extending over heliocentric distances of tens of astronomical units (*35*). If the nucleus of 67P agglomerated from crystalline ices and clathrates, then it likely formed closer to the Sun than previously considered for JFCs (*35*). This also implies that other comets with measured D/H ratios lower than that of 67P (*36*) should have been formed from crystalline ices and clathrates, because they probably formed closer to the Sun than 67P (*37*). In any case, the presence of clathrates in 67P would indicate that the snow line, whose position is still loosely constrained (*38*), was located beyond the present asteroid belt in the PSN. This would suggest that comets formed from at least two distinct reservoirs: a crystalline H_2O reservoir located inside the disc and an amorphous H_2O ice reservoir located outside the disc (*5*). Future direct sampling of ices from other comets will be crucial in locating the boundary between these reservoirs and will better constrain the phase of ice in various comets at the time of their formation.

MATERIALS AND METHODS

Calculation of pure condensate and clathrate equilibrium curves

Condensation curves of CH_4, C_2H_6, and CO_2 were calculated based on Fray and Schmitt (*39*). The fitting expression used is $\ln P_{eq} = A_0 + \sum_{i=1}^{n} A_i/T^i$. Fitting parameters A_i for CH_4, C_2H_6, and CO_2 are summarized in table S2. The condensation curve of H_2O vapor was calculated via the following equations (*39*)

$$\ln\left(\frac{P_{cond}(T)}{P_t}\right) = \frac{3}{2}\ln\left(\frac{T}{T_t}\right) + \left(1 - \frac{T_t}{T}\right)\eta\left(\frac{T}{T_t}\right)$$

$$\eta\left(\frac{T}{T_t}\right) = \sum_{i=0}^{6} e_i\left(\frac{T}{T_t}\right)^i$$

P_t and T_t are the triple point pressure and temperature of H_2O, respectively, and parameters e_i are given in table S3. P_{cond} and P_t are expressed in bar; T and T_t are expressed in kelvin.

The gas-phase X/H_2 ratios in the PSN were determined using the X/H_2O ratios measured for 67P, multiplied by the estimated H_2O/H_2 ratio in the PSN. The H_2O/H_2 ratio was derived from the elemental O and H abundances in the solar system (*40*), assuming that 57% of H_2O was present in the form of H_2O ice (*41*), leaving 43% of the total solar $(O/H_2)_\odot$ to exist in the gas phase. Because $(O/H_2)_\odot = 0.0011$ (*40*), and assuming that O is in the form of H_2O, we derive $H_2O/H_2 = 0.5 \times (O/H_2)_\odot = 2.15 \times 10^{-4}$. Then, the X/H_2 ratio is calculated as the cometary X/H_2O times the calculated H_2O/H_2.

To test the sensitivity of the clathrate and condensate equilibrium curves, the gas-phase X/H_2O was varied within the range of known comets (*14*) and taken relative to H_2 as described above. Varying the gas-phase X/H_2O (hence, the X/H_2) does not change the ordering of the curves as a function of temperature, and the CO_2 condensate and C_2H_6 clathrate curves match each other well for the variety of X/H_2O ranges of known comets. To demonstrate the latter point, equilibrium curves of four selected comets are shown in fig. S4.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/2/4/e1501781/DC1

Fig. S1. Time variation of major and minor volatile species from ROSINA/DFMS on 18 September 2014.

Fig. S2. Time variation of major and minor volatile species from ROSINA/DFMS on 29 September 2014.

Fig. S3. Time variation of major and minor volatile species from ROSINA/DFMS on 11 October 2014.

Fig. S4. Equilibrium curves in the PSN for various known comets.

Table S1. Fitting parameters used in calculating clathrate equilibrium curves of CH_4 and C_2H_6.

Table S2. Fitting coefficients used to calculate condensation curves.

Table S3. Fitting coefficients for the condensation pressure of crystalline H_2O ice.

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