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$_2$O ice, it is the structure and phase of this H$_2$O ice that provide insight into the place of origin, formation temperature, and evolution of icy agglomerates in the protosolar nebula (PSN). Whether cometary H$_2$O 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$_2$O 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$_2$O ice.

Amorphous H$_2$O 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$_2$O 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$_2$O ice. In the cooling PSN, H$_2$O will be present in its crystalline structure, with no or very little amorphous H$_2$O. The fraction of amorphous ice in the PSN would be negligible because condensation of the formerly vaporized H$_2$O occurs at significantly higher temperatures in the crystalline phase than those needed for the formation of amorphous H$_2$O ice. By the time the temperature of the PSN was low enough for amorphous H$_2$O ice formation, most volatile gases themselves either had condensed or were trapped in clathrates. These processes leave no or very little H$_2$O 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$_2$H$_6$ clearly deviated from the overall H$_2$O signal, showing maxima at times of deep H$_2$O 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 made 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$_2$O 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$_2$O 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...
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$_2$O 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$_2$O (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$_2$H$_6$ (13).

We are also able to exclude gas release from amorphous H$_2$O 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$_2$O ice to the cubic phase of crystalline H$_2$O 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$_2$O. 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$_3$OH outgassing was observed at times of CO$_2$, CO, and C$_2$H$_6$ 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$_2$H$_6$, single-guest clathrates, as well as CH$_4$, C$_2$H$_6$, 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$_2$O were taken directly from ROSINA/DFMS observations, in which not all minor volatile species were released together from the southern hemisphere (13). For instance, no HCN and CH$_3$OH outgassing was observed at times of CO$_2$, CO, and C$_2$H$_6$ 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.

**Fig. 1. Equilibrium curves of clathrates and condensation in the PSN.** Equilibrium curves of C$_2$H$_6$ (red) and CH$_4$ (blue) clathrates are shown with respect to the equilibrium curves of C$_2$H$_6$, 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$_2$O ratios (14) and solar system elemental abundances of O and H (40, 41).
uring that abundances in the coma do not necessarily represent bulk
depend on the measured abundance ratios in the coma of 67P, consid-
Mole fractions of each species shown are directly taken from ROSINA/DFMS
and sublimation of pure ices occur at temperatures above the equilibrium
crystallization of amorphous ice, as was proposed for the distant out-
perihelion outbursts (28).

Figs. 1 and 2. Outgassing as a result of decomposition of CH₄ and C₂H₆
clathrates is in full agreement with the time variation of the volatile spe-
cies 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, consid-
ering that abundances in the coma do not necessarily represent bulk
abundances in the nucleus. Varying the abundances of CH₄, C₂H₆, and CO₂ within the range of other known comets results in the same
ordering of species as shown in Figs. 1 and 2. C₂H₆ and CH₄ clathrates always form before their pure condensates, that is, at temperatures
about 20 K higher. In addition, C₂H₆ clathrates form at about the same
time (within <1 K) as CO₂ ice (fig. S4). In addition, the equilib-
rium pressure curves of the JFCs (67P and Hartley 2) have very si-
ilar 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 con-
strained reliably, our results provide a strong argument for the presence
of CH₄ and C₂H₆ 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 out-
bursts 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 crystal-
lization of H₂O ice was likely not responsible for its 2007 post-perihelion
megaburst (26). Recently, the exothermic phase transition of amor-
phous to crystalline H₂O 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 H₂O ice is not the only process ca-
pable of producing outbursts and pits. Pressure pulses resulting in out-
bursts 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 thermody-
namic 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 H₂O ice, even if the original ice phase of 67P was
amorphous H₂O. 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 crys-
talline H₂O 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 for-
mation 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, includ-
ing 67P, formed out of clathrates. Yet, our results, along with other re-
cent efforts supporting the presence of N₂, 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 H₂O 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 amor-
phous 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 ac-
creted from clathrate-rich planetesimals originating from Saturn’s feed-
ing zone (3). Dynamical model results suggest that both JFCs and
Oort cloud comets may have formed in the same environment ex-
tending 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 crys-
talline 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 con-
strained (38), was located beyond the present asteroid belt in the PSN.
This would suggest that comets formed from at least two distinct res-
ervoirs: a crystalline H₂O reservoir located inside the disc and an
amorphous H₂O ice reservoir located outside the disc (5). Future di-
rect 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.

Fig. 2. Equilibrium curves of clathrates and pure condensates in the
cometary environment. The equilibrium curves are shown here as a
function of total H₂O 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).
MATERIALS AND METHODS

Calculation of pure condensate and clathrate equilibrium curves

Condensation curves of CH4, C2H6, and CO2 were calculated based on Fray and Schmitt (39). The fitting expression used is lnPcond = A0 + Σm=1 Am/Tm. Fitting parameters Ai for CH4, C2H6, and CO2 are summarized in table S2. The condensation curve of H2O vapor was calculated via the following equations (39)

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

\[
\eta \left( \frac{T}{T_t} \right) = \sum_{i=0}^{3} \epsilon_i \left( \frac{T}{T_t} \right)^i
\]

P_t and T_t are the triple point pressure and temperature of H2O, respectively, and parameters \( \epsilon_i \) 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/H2 ratios in the PSN were determined using the X/H2O ratios measured for 67P, multiplied by the estimated H2O/H2 abundance in the solar system (40). The composition of the protosolar disk and the formation conditions for comets. Space Sci. Rev. 197, 151–190 (2015).

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