POSSIBILITY OF CONDENSATION OF GLYCINE NEAR THE SURFACE OF COMET 67P/CHURYUMOV-GERASIMENKO

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ABSTRACT

The cometary materials are thought to be the reservoir of primitive materials in the solar system. The recent detection of glycine and CH$_3$NH$_2$ by the ROSINA mass spectrometer in the coma of 67P/Churyumov-Gerasimenko suggests that amino acids and their precursors have been formed in such an early evolutionary phase of the Solar System. We use our chemical modeling for low-mass star-forming regions to investigate if we can explain observed “Glycine/CH$_3$NH$_2$” ratio. As a result, the predicted molecular ratio of “CH$_3$NH$_2$/Glycine” during star-formation is less than $10^{-2}$, while the ROSINA measurement has shown this value to be unity. With the hypothesis that glycine is condensed in the cometary surface during the numerous passages of perihelion after the formation of the Solar System, we develop the numerical model to discuss this condensation process. Our modeling results suggest that glycine is highly likely condensed in the cometary surface due to its high binding energy, and “Glycine/CH$_3$NH$_2$” ratio will be highly enhanced if the outbursts eject the materials condensed on cometary surface.

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1. INTRODUCTION

Since the pioneering suggestion by Oró (1961), the possibility of external delivery of organic materials by comet or meteorites has been discussed by many researchers as the supplier of organic materials to the early Earth. Ehrenfreund et al. (2002) strengthened the importance of cometary materials for the sources of organic materials compared to other possible sources on the Earth, such as UV photolysis or the electron discharging in the ancient atmosphere. If this is the case, an attempt to understand the origins of life must necessarily begin with detailed studies of the formation and evolution of complex organic molecules, products of a complex chemistry that most likely starts in molecular clouds and continues within the protoplanetary disk, where the comets and asteroids would have been formed. The detections of various kinds of organic materials in the Murchison meteorites, such as sugars and amino acids (Cooper et al. 2001; Engel & Nagy 1982), support this theory.

In addition to the meteorites, a variety of molecules were observed towards the coma of comets thanks to the progress of the technique of radio or infrared observations. The simple molecules, such as H$_2$O, CO, CH$_4$ and CH$_3$OH, have been detected by infrared and radio observation (Mumma & Charnley 2011). The comet C/1995 O1 (Hale-Bopp) and C/1996 B2 (Hyakutake) provided us with the extensive information of the molecular inventory of comets (Bockelée-Morvan et al. 2004; Mumma & Charnley 2011). The historically close approach of C/1996 B2 (Hyakutake), ∼0.1 AU to the Earth, led to a major progress in our knowledge of cometary composition with detections of CH$_3$CN (Dutrey et al. 1996), HNC, HNCO (Lis et al. 1997), and OCS (Woodney et al. 1997) in radio wave observation, and CH$_4$, C$_2$H$_6$ (Mumma et al. 1996), and C$_2$H$_2$ (Brooke et al. 1996) in the infrared observation. The first detections of SO, SO$_2$, HC$_3$N, NH$_2$CHO, HCOOH, and HCOOCH$_3$ were reported by Bockelée-Morvan et al. (2000) toward the extremely bright comet C/1995 O1 (Hale-Bopp). It is also understood that some parental species, which ejects from cometary nucleus directly, are destroyed into daughter radical species through photo dissociation in the coma. For instance, Fink et al. (1991) discussed that NH$_3$ would be a parent species of NH and NH$_2$. The CN radical can form from HCN (Woodney et al. 2002; Fray et al. 2005). The dust samples of comet 81P/Wild 2, which was gathered by Stardust spacecraft and brought to Earth, strongly promoted our knowledge. Sandford et al. (2006) analyzed these samples and reported the existence of polycyclic aromatic hydrocarbon, amides, and nitriles. In addition, methylamine and ethylamine were detected after acid-hydrolysis.

Observations and models about the chemical composition of cometary materials is believed to be the heritage of the chemistry in parental cloud of the Solar System. The chemical compositions in protoplanetary disk and star-forming regions have been improved. The high sensitivity observation of ALMA achieved the detections of complex organic molecules CH$_3$CN (Öberg et al. 2015; Loomis et al. 2018; Bergner et al. 2018) and CH$_3$OH (Walsh et al. 2016). In addition, more complex molecules such as glycolaldehyde (HCOCH$_2$OH) (Jørgensen et al. 2012), methyl isocyanate (CH$_3$NCO) (Martin-Domenech et al. 2017), and CH$_3$Cl (Fayolle et al. 2017) were reported towards low-mass star-forming regions, where observations are much easier compared to protoplanetary disks due to high beam-averaged column densities of molecules. Theoretical studies claimed the agreement of molecular abundance ratios between in the cometary coma and the star-forming regions. For instance, Walsh et al. (2014) performed the chemical modeling study for protoplanetary disk and compared the chemical composition with those of comets. Biver et al. (2015) compared the cometary composition with the warm cores and found good agreement. Their results clearly suggest the link between the chemistry of comet and that of protosolar nebula. However, the comparison of chemistry between cometary coma and star-forming regions and protoplanetary disks has been discussed only for simple species. This was due to the difficulty of the observation of complex organic molecules due to their low abundances and large partition functions that decrease their detectability. Especially glycine (NH$_2$CH$_2$COOH), the simplest and the only non-chiral member out of 20 standard amino acids, has gathered attention of astronomers, however, none of the observations were successful toward star-forming regions (e.g., Ceccarelli et al. 2000). Although Kuan et al. (2003) claimed the first detections of glycine towards high-mass star-forming regions, their detections were refuted by Snyder et al. (2005). The studies of glycine chemistry is the holy grail for the modern astrochemistry.

Recently, the observation and the theoretical studies of interstellar glycine and its precursor has been promoted. The observations of possible precursors of glycine, CH$_3$NH$_2$ and CH$_2$NH, have been performed and their detections were reported towards high-mass star-forming regions (Suzuki et al. 2018a; Ohishi et al. 2017). The chemical network simulation of interstellar glycine was also developed (Garrod 2013; Suzuki et al. 2018b). The amino acids are also major target for the missions of comets. Elsila et al. (2009) claimed the detection of glycine in the Stardust sample with its carbon isotopic ratio ∆C$^{13} = +29 ± 6$, suggesting the extraterrestrial origin. The latest paradigm shift of our knowledge was brought by the detailed analysis of comet 67P/Churyumov-Gerasimenko (hereafter 67P) by
Rosetta mission, enabling us the direct measurement of chemical composition. Altwegg et al. (2017) reported a great variety of CH-, CHN-, CHS-, CHO2- and CHNO- bearing saturated and unsaturated species. This mission confirmed not only all chemical species ever known at that time (Roy et al. 2015), but also new detections of complex species (e.g., CH3NCO, CH3COCH3, C2H5CHO, and CH3CONH2) through the direct analysis of ROSINA (Rosetta Orbiter Spectrometer for Ion and Neutral Analysis) mass spectrometer (Goesmann et al. 2015). In addition, the volatile glycine and its precursor, CH3NH2, were detected in the coma of comet 67P by the ROSINA mass spectrometer (Altwegg et al. 2016), excluding the possibility of terrestrial contamination which was a concern for the result of Stardust mission. These progresses enable us to discuss the difference of molecular ratio of glycine and its precursors in the different stages of the chemical evolution. In Section 2, we will theoretically evaluate the possibility that glycine and CH3NH2 are inherited from the parental molecular cloud, by comparing their molecular ratio towards 67P using a chemical modeling of low-mass star formation. In Section 3, we describe the details about Simplified Cometary Condensation Model (SCCM) to discuss how chemical composition can change from the star-forming regions inside of cometary bodies. Then, in Section 4 we will discuss the possibility of condensation of glycine with our very simple evaporation model, and suggest the possibility that the observed ratio of “CH3NH2/glycine” might be significantly increased due to the effect of condensation with SCCM model. We will summarize our work in Section 5.

2. THREE-PHASE CHEMICAL MODEL OF GLYCINE IN LOW-MASS STARS

As Biver et al. (2015) claimed the similarity of chemistry between the cometary coma and hot corino, it is interesting to compare cometary glycine with the chemical modeling for low-mass star-forming regions. We have used the latest chemical code NAUTILUS (Ruaud et al. 2016) to theoretically predict the chemical composition of icy mantle of grains. NAUTILUS allows us to compute the time evolution of chemical abundances for a given set of physical and chemical parameters. It simulates the chemistry in three phases i.e. gas-phase, grain surface and grain bulk. It also considers various possible exchanges among the different phases via adsorption of gas phase species on to grain surfaces, the thermal and non-thermal desorption of species from grain surface into the gas phase and the surface-bulk and bulk-surface exchange of species. Our gas-grain chemical network of glycine is based on the latest theoretical and experimental formation/destruction mechanisms described in detail in Suzuki et al. (2018b). This full gas-grain chemical network is available on request to taiki.suzuki@nao.ac.jp and liton.majumdar@jpl.nasa.gov. To simulate the physical conditions in low mass star-forming regions, we have used the slow warm-up model of Garrod (2013) to assume the physical evolution of low-mass star-forming regions where the cold collapse phase starts from the number density of molecular hydrogen of 3×10^3 to 1×10^7 cm^{-3} with the temperature warming-up from from 8 to 400 K. The timescale of warm-up phase, which corresponds to the heating time-scale of the surrounding material of newly born star, is 1.43×10^6 years.

During the low-mass star-formation, complex molecules are built on grain in the gravitational collapsing phase. The thermal evaporation of complex organic molecules are negligible in this phase due to the very low the gas temperature of almost 10 K. The frozen species on grains are liberated during the warm up phase, triggered by the birth of the star. The maximum temperature of 400 K is corresponding to the inner part hot core and hot corino, where the complex organic molecules are detected. Then, along with the accretion of the gas, which will lead to the formation of proto-planetary disks and comets inside, gas phase species would accrete on grains again. Considering that gas phase species would be incorporated into grains again, we summed the molecular abundances in the gas phase, on the grain surface, and in the grain mantle for the comparison with 67P. In Figure 1 (a), we show the time dependence of the sum of the abundances of these three phases with the time of zero being the beginning of the warm-up phase. With these values, we plotted the abundance ratios, “glycine/H2O” and “glycine/CH3NH2”, in Figure 1 (b). How is it likely that glycine and CH3NH2 are heritage of a parental cloud of our Solar System by comparing the report by ROSETTA mission? The maximum values for “glycine/H2O” and “glycine/CH3NH2” ratios are ∼10^{-5} and ∼10^{-3}, respectively. Altwegg et al. (2016) reported the relatively wide values for “glycine/H2O”, ranging from zero to 0.0025, while it was unity for “glycine/CH3NH2” ratio.

3. SIMPLIFIED COMETARY CONDENSATION MODEL (SCCM)

3.1. Background of This Model

It is widely accepted that cometary chemical composition is the inheritance of those of parental nebula of our Solar System. The combination of previous observations and theoretical studies supported this idea (Walsh et al. 2014). However, it is also suggested that the chemical composition on the cometary surface would be altered due to thermal
processing. Capaccini et al. (2015) reported very low albedo on the surface of 67P, conflicting the understanding that water is the most abundant component on the interstellar grain mantle. They suggested that there is a condensation process of refractory organic materials of the cometary surface by observing the spectra of infrared emission from the comet. The alteration of chemical component on the cometary surface is also supported by a report of the Deep Impact mission (Mumma et al. 2005). They reported the significant increase of a volatile species, C$_2$H$_6$, after impact to comet 9P/Tempel 1, indicating the loss of volatile species on the cometary surface.

The outburst, which is defined as the increase of luminosity on the cometary surface, is the potential process to release the condensed material from the cometary surface to the coma. Rosetta observed 34 outbursts within three months surrounding its perihelion passage, suggesting this event is ubiquitous at least for 67P (Vincent et al. 2016). Several mechanisms for outburst has been suggested such as crystallization of amorphous ice, enrichment of volatile inside the comet, and receding fractured cliffs (e.g., Agarwal et al. 2017; Vincent et al. 2016). Altwegg et al. (2016) suggested the correlation of glycine abundance with the dust density, giving the possibility that glycine is not directly evaporated from the core of comet but evaporated from small grains, ejected by outburst. This scenario also agrees with the high evaporation temperature for glycine of more than 300 K, measured by temperature programmed desorption (TPD) experiment by Tzvetkov et al. (2004). The surface temperature of 67P would be less than 200 K, considering the brightness temperature observed in Gulkis et al. (2015). While the cometary surface cannot reach such high temperature between two and three AU, where glycine was observed, such small grains can be efficiently heated by solar flux (Altwegg et al. 2016).

Taking into these facts, condensation process can affect the cometary molecular abundances of less volatile species. In the following section, we develop Simplified Cometary Condensation Model (SCCM) to see how the condensation process is important. The molecular percentages of H$_2$O, CH$_3$NH$_2$, and glycine reported in the Rosetta mission provides us with the essential benchmark of SCCM.

### 3.2. Calculation Method of SCCM

Since comets would have been formed through the collisions of the small icy materials in the protoplanetary disk, we assume that the comet has rubble pile structure. The assumption of rubble pile structure is supported by observation of cometary surface. For instance, Murdoch et al. (2015) reported that the size distribution of particles found in asteroid is ranging from a few to hundreds meters. The rubble pile structure would transmit heat to keep the same temperature in a single ice body. Our layer structure is depicted as Figure 2. The typical size for one ice body is assumed to be the thickness of the layer. Since the size of ice is uncertain, it is regarded as the free parameter in our calculation. We assume 100 layers in our calculation.

In SCCM model, we calculate the temperature of the nth layer at the time t, $T[n, t]$, in the following procedure. First, we calculate the surface temperature as a function of time, $T[n=1, t]$. We simulate the orbit of 67P with the orbit parameters of 67P. Then, we assume the radiative equilibrium between the irradiation from the Sun and the blackbody radiation of the comet. The obtained temperature is in good agreement with that of Guilbert-Lepoutre et al. (2016) for the surface. For simplicity, we calculate the surface temperature only from zero comet year to 0.5 comet year and assume periodic time variation after 0.5 comet year. For the depth dependence, we used the temperature of 260, 240, 190, and 120 K at the depths of 0, 10, 50, and 200 cm, respectively, at the perihelion ($t=0$), following the calculation of Guilbert-Lepoutre et al. (2016). The peak temperature of other depth, $T[n, t=0]$, were linearly interpolated. Following Guilbert-Lepoutre et al. (2016), we assume that the temperatures are almost the same for all layers at the comet year of 0.5, $T[n, t=0.5] = 120$ K, when the comet is the most distant from the Sun. Then, for the depth of less than 200 cm, we calculate the temperature of the nth layer at the time t as

$$T[n, t] = T[n=1, t] \times f[n, t],$$

where $f[n, t] = 2 \times (1 - q[n]) \times t + q[n]$ and $q[n] = T[n, t=0]/T[n=1, t=0]$. We set the temperature of 120 K as the lower temperature limit. For the temperature of the layers deeper than 200 cm, we assume the temperature of 120 and 30 K at the depth of 200 and 1000 cm, respectively, and use linear interpolation at other depths. The time variation of the temperature is neglected for the layers deeper than 200 cm. We note that there is no temperature gradient inside of the single layer for all layers.

The obtained temperature distribution is shown in Figures 3 (a) and (b). The timescale of our SCCM model is presented by “comet years”, where one comet year is 6.57 years, corresponding to one orbital period of the comet 67P. Figure 3 (a) shows the time dependency of the temperature distribution inside the comets, while Figure 3 (b)
Condensation of Cometary Glycine

represents the vertical temperature distribution at the different depth from the surface at the different distance from the Sun.

Once the temperature is obtained, we calculate the evaporation rate from cometary surface with the equation (2) of Hasegawa et al. (1992), which is frequently used in chemical modeling for the star-forming regions.

\[ t[n, j, t]_{\text{evaporation}} = v_0^{-1} \exp(E[j]/k_B T[n, t]), \quad (2) \]

The inverse of evaporation timescale is the evaporation rate \( k[n, j, t] \) (i.e., \( k[n, j, t] = t[n, j, t]^{-1}_{\text{evaporation}} \)). \( E[j] \) is the binding energy, which is determined by the strength of interaction of species \( j \) with water ice, \( n_s \) is the surface density of the site (1.5\times10^{15} \text{ cm}^{-2}), \( m \) is the mass of the molecules, \( k_B \) is the Boltzmann constant. Since the evaporation rate of species \( j \) at \( n^{th} \) layer and \( t \) comet year, \( k[n, j, t] \) is proportional to \( \exp(-E[j]/k_B T[n, t]) \), the binding energy and the temperature are essential parameters to determine the evaporation rate. We assumed that all molecules can evaporate from the surface without being trapped inside. While the molecules in the deeper layer have to move to upper layers one by one through this usual evaporation process (equation (5)), they can escape directly from the comet from any layer via a direct evaporation process as described below (equation (6)). The binding energies for \( \text{H}_2\text{O}, \text{CH}_3\text{NH}_2 \), and glycine are 5700, 6500, and 13000 K, respectively, based on the theoretical prediction developed by Wakelam et al. (2017) and temperature programmed desorption (TPD) experiment by Tzvetkov et al. (2004).

In SCCM modeling, we define the porosity as

\[ P[n, t] = \frac{M_{\text{Max}} - M_{\text{Real}}[n,t]}{M_{\text{Max}}}, \quad (4) \]

where \( M_{\text{Real}}[n,t] = \sum_j M_{\text{Real}}[n,j,t] \) represent the sum of the actual amount of materials of all species \( j \) at \( n^{th} \) layer and \( t \) comet year, while \( M_{\text{Max}} \) denotes maximum amount of materials in a certain layer. From this definition, it is apparent that the term \( M_{\text{Real}}[n,t] = (1 - P[n,t]) \times M_{\text{Max}} \) denotes the actual amount of material in a layer. Although \( M_{\text{Max}} \) seems to be a parameter for the SCCM result, we will show that SCCM modeling result is independent of \( M_{\text{Max}} \) value with the below equations later. The porosity of \( n^{th} \) layer, \( "P[n]" \) is assigned to be zero for each layer at the beginning, and their evolution is calculated in each time step with the evaporation rate of species. Here we introduce the percentage of certain species \( "j" \) in \( n^{th} \) layer at the time \( t \), \( r[n, j, t] \), defined as \( r[n, j, t] = M_{\text{Real}}[n,j,t]/M_{\text{Real}}[n,t] \). The sum of the percentages of all molecules, here \( \text{H}_2\text{O}, \text{CH}_3\text{NH}_2 \) and glycine, \( \sum_j r[j,n,t] \) should always be unity. The initial molecular abundances were uniformly assigned to each layer.

With the term of \( M_{\text{Real}}[n,j,t] = M_{\text{Real}}[n,j] \times r[n,j,t] = (1 - P[n,t]) \times M_{\text{Max}} \times r[n,j,t] \), the evaporated amount of species \( j \) from the first layer \((n = 1)\) during the time step \( \Delta t \) is given by

\[ \frac{\Delta M_{\text{evap}}[1,j,t]}{\Delta t} = k[1,j,t] \times M_{\text{Real}}[1,j,t]. \quad (5) \]

Since the porosity \( P[1,t] \) represent the percentage of cavity, \( (1 - P[1,t]) \times M_{\text{Max}} \) represent the actual amount of material in the \( 1^{st} \) layer. The amount of material transfered from \( n + 1^{th} \) layer to \( n^{th} \) layer during the time step \( \Delta t \) is calculated as

\[ \frac{\Delta M_{\text{evap}}[n + 1,j,t]}{\Delta t} = P[n,t] \times k[n + 1,j,t] \times M_{\text{Real}}[n + 1,j,t] \quad (n \geq 1). \quad (6) \]

Although the default time step \( \Delta t \) is 1000 second, the time step is halved when (1) the evaporation rate of at least one species \( j \), \( \Delta t \times k[n,j,t] \), is less than 1, and (2) the molecular ratio of species \( j, r[n,j,t] \), is more than 1%. The first criteria will enable us to perform accurate calculation of volatile species, especially \( \text{H}_2\text{O} \) When \( \Delta t \times k[n,j,t] \) exceed 1 and \( r[n,j,t] \) is less than 1%, the term of \( \Delta t \times k[n,j,t] = 1 \), corresponding to the situation that all material is transfered to the upper layer during \( \Delta t \). Similar to the equation for the evaporation process from the first layer, \( k[n + 1,j,t] \times M_{\text{Real}}[n + 1,j,t] \) denotes the total amount of thermal evaporation for species \( j \). However, this equation represents the blocking of material transfer to the upper layer by multiplying the porosity of upper layer, \( P[n,t] \) (Figure 2).

In addition, we assume that a part of \( \Delta M_{\text{evap}}[n + 1,j,t] \) can evaporate directly from any layer if there is enough porosity in upper layer (Figure 2). The amount of direct evaporation for species \( j \) from \( n^{th} \) layer is presented as

\[ \Delta M_{\text{direct}}[n + 1,j,t] = (\prod_{k=n}^{k=n+1} P[k,t]) \times \Delta M_{\text{evap}}[n + 1,j,t]. \quad (7) \]
By multiplying the term of \( \prod_{k=n}^n P[k, t] \), this equation permits to evaporate materials directly from the inner layer when the porosities of the upper layers are high enough.

Through the evaporation processes (5) to (7), the amount of lost material from the layer can be given. Then, the differentiation of porosity and molecular percentages as the result of above processes can be calculated. The differentiation of material amount during the time step \( \Delta t \) can be calculated as

\[
\Delta M_{\text{Real}}[n, j, t] = -\Delta t \times (\Delta M_{\text{evap}}[n, j, t] / \Delta t - \Delta M_{\text{evap}}[n + 1, j, t] / \Delta t + \Delta M_{\text{direct}}[n, j, t] / \Delta t).
\]

Then, the actual amount of material changes during the time step \( \Delta t \) is presented as

\[
M_{\text{Real}}[n, j, t + \Delta t] = M_{\text{Real}}[n, j, t] + \Delta M_{\text{Real}}[n, j, t].
\]

Then, recalling the definition of the porosity, new porosity is calculated as

\[
P[n, t + \Delta t] = \frac{M_{\text{Max}} - \sum_j M_{\text{Real}}[n, j, t + \Delta t]}{M_{\text{Max}}}. \tag{10}
\]

Since \( M_{\text{Real}}[n, j, t] = (1 - P[n, t]) \times r[n, j, t] \times M_{\text{Max}} \), this equation is independent of \( M_{\text{Max}} \). The time evolution of molecular percentages is calculated as

\[
r[n, j, t + \Delta t] = \frac{M_{\text{Real}}[n, j, t + \Delta t]}{M_{\text{Real}}[n, j, t]} = M_{\text{Real}}[n, j, t] + \Delta M_{\text{Real}}[n, j, t] / (1 - P[n, t + \Delta t]) \times M_{\text{Max}}. \tag{11}
\]

Finally, we consider the merging of layers when the porosity gets larger than 0.7 after above calculations. This value of 0.7 is determined considering the observed porosity of 67P (Pätzold et al. 2016). In addition, the sum of the actual amount of layers, \( M_{\text{Real(before)}}[n, t] + M_{\text{Real(before)}}[n + 1, t] \), must be smaller than \( M_{\text{Max}} \) before the merging process so that the amount of new layer do not exceed the limitation after merging. Then, using the definition of porosity, the merging process is considered when \( P[n, t] + P[n + 1, t] > 1 \) is achieved. With these restrictions, new molecular ratios and the porosity for the \( n \)th layer can be calculated from the definition of porosity. We fix \( M_{\text{Max}} \) during merging but the real material contained in the merged layer is regarded as the sum of the original two layers.

\[
P_{\text{new}}[n, t] = \frac{M_{\text{Max}} - (M_{\text{Real(before)}}[n, t] + M_{\text{Real(before)}}[n + 1, t])}{M_{\text{Max}}} = (P_{\text{before}}[n, t] + P_{\text{before}}[n + 1, t]) - 1. \tag{12}
\]

Then, new molecular percentages can be calculated with this new porosity considering the amount of materials exchanged between layers through thermal evaporation:

\[
r_{\text{new}}[n, j, t] = \frac{(1 - P_{\text{before}}[n, t])r[n, j, t] + (1 - P_{\text{before}}[n + 1, t])r[n + 1, j, t]}{1 - P_{\text{new}}[n, t]}. \tag{13}
\]

After the merging process, we reassign the layer number to compensate the merged layer. In this process, the old \( n + 2 \)th layer is regarded as new \( n + 1 \)th layer by applying \( r_{\text{new}}[n + 1, j, t] = r_{\text{before}}[n + 2, j, t] \) and \( P_{\text{new}}[n + 1, t] = P_{\text{before}}[n + 2, t] \). The conservation of amount of material is kept with above equations.

Although the photodissociation process may destroy the molecules, we do not include it in the SCCM modeling. This simplification would be justified by the experimental result that high energy particle can penetrate only thousands of nanometers (Barnett et al. 2012). Such a scale is negligible compared to the spatial scale of SCCM. Finally, the timescale is also important factor to develop the SCCM modeling since the longer timescale to be processed by the heat of the Sun will make it easy to condense less volatile species. For 67P, its history of orbital evolution due to the gravitational interactions between giant planets was calculated by Ip et al. (2016). They suggested that the perihelion of comet 67P has suddenly changed in 1959 from 2.7 to 1.3 AU. Their calculation implied the similar perihelion of 67P during about 600 years about 300 years ago. Therefore, this comet would have experienced the strong heat processing by the Solar Flux for several hundred years. To simulate such a long thermal processing timescale, we calculated the time evolution of the porosity and the molecular percentages during 100 comet years.

4. SCCM RESULTS

4.1. The Simulation Results
We performed SCCM modeling under the eight different sets of chemical percentages, the sizes of layer, and the initial porosity. These parameters are summarized in Table 1. The included species are only H$_2$O, CH$_3$NH$_2$ and glycine in default, while the importance of the other species will be discussed by Sets 7 and 8. First of all, we focus on the result of Set 1 as the most standard one in our sets. In this case, we employed the initial glycine percentage of $10^{-3}$ %, the layer thickness of 10 cm, and the initial porosity of zero. The dependencies of the parameters will be discussed in the following section.

In Set 1, the averaged porosities in 0-40, 40-80, and 80-120 cm from the surface get to $\sim$0.7 within 35 comet years (see Figure 4). The time evolution of the porosity can be explained by the exchanging of species through the thermal evaporation. While H$_2$O is the most dominant among three species, it is lost easily by the thermal evaporation leading to the high porosity. We can see that H$_2$O, presented by a green line in Figure 5, is quickly lost from the surface within one comet year, increasing the porosity. As a result, the merging processes of layers lead the condensation of less volatile species, glycine, as shown by a blue line in Figure 5. The evaporation of glycine is so slow compared to H$_2$O, that the porosity of the 0-40 cm position (the first-fourth layer) only gradually increases once the glycine abundance ratio gets to almost 100 % in the layer. When the porosity of the first layer get larger than 0.7 at $\sim$ 55 comet years, the first and the second layers merge with the beneath layer comet years to suddenly decrease the porosity. The time evolution of the averaged porosity and the averaged chemical compositions can also been recognized at 40-80, 80-120, 120-160, 160-200 cm positions (the averages of fifth-eighth, ninth-twelve th, thirteenth-sixteenth, and seventeenth-twenty th layer, respectively). In these beneath layers, the lower temperatures makes it take more time to loss H$_2$O and complete the condensation than surface. The averaged porosity at 160-200 cm position (the seventeenth-twenty th layer) still changes even after 100 comet years, suggesting that the evaporation of H$_2$O and merging with the beneath layers are still going on. The condensation process of CH$_3$NH$_2$ can also seen at 160-200 cm position from the surface, while H$_2$O is still dominant there.

### 4.2. Parameter Dependency

In Sets 2 and 3, we increased and decreased the initial percentage of glycine by a factor of 10 compared to Set 1, respectively. The layer thickness and the initial porosity are fixed to be 10 cm and zero, respectively. As a result, we clearly confirmed the acceleration and slow down of the evolution of porosity in these Sets. This is because higher abundance of glycine makes the timescale of condensation process to be short, contributing to stabilization of the time evolution of the porosity. While Figure 6 shows that condensation of glycine complete within 10 comet years even at 80-120 cm position from the surface, Figure 7 suggests that the most dominant species is still H$_2$O after 100 comet years at 120-160 cm position (the thirteenth-sixteenth layer) from the surface.

The layer thickness is changed to be 20 cm in Set 4, while the initial glycine percentage and the initial porosity are fixed to be $10^{-3}$ % and zero. From Figures 4, 5, and 8, we confirm the very good agreement in both porosity and molecular ratio with Sets 1 and 4. This similarity suggests that SCCM results do not affected by the layer thickness. We also add Set 5 with its thick layer size of 100 cm as the extreme case, and the fixed glycine percentage and the initial porosity of $10^{-3}$ % and zero Only Set 5 shows dynamic time evolution of averaged porosity at 100-200 cm position (the second layer in Set 5) from the surface (Figures 4). Since the evaporation rate of H$_2$O is almost negligible at 200-300 cm position (the third layer of Set 5) enough amount of H$_2$O is stored in 200-300 cm position of Set 5 (Figure 9). As a result, H$_2$O can be supplied to 0-100 and 100-200 cm position (the first and the second layers in Set 5) through the merging process. The porosity at 100-200 cm position is still changing at 100 comet years due to the effect of low spatial resolution.

We change the porosity from zero to 0.2 in Set 6. The percentage of initial glycine and the layer thickness are fixed to be $10^{-3}$ and 10 cm, respectively. The averaged porosity and the time evolution of the chemical composition in Set 6 (Figures 4 and 10) show good agreement with Set 1. Therefore, the initial porosity, i.e., the condition of ice, does not affect our calculation results.

One of the important simplification in our modeling is that we assumed only three species in the calculation, although actual chemical composition would be the mixture of variety of different molecules. Finally, we consider the effect of other materials on our calculation with Sets 7 and 8. The percentage of the fourth material is $10^{-2}$ % in both Sets 7 and 8, while the binding energies are 13000 and 6500 K, respectively. The higher binding energy of 13000 K is the same with glycine, and Set 7 assumes the existence of less volatile species. The smaller binding energy of 6500 K in Set 8 is the same as that of CH$_3$NH$_2$. Figures 4 shows that the evolution of the porosity is accelerated in Set 7 than Set 1. This is due to higher abundance of less volatile species in Set 7. On the other hand, the evolution of porosity
in Set 8 is similar to Set 1. Figures 11 and 12 show the time evolution of the chemical composition. In Set 7, the large part of glycine is replaced by the newly added material shown in the black line. Since the cometary interior is occupied by not only glycine but also other species, the percentage of glycine is decreased by adding new species. On the other hand, this effect is almost negligible in Set 8, since the other material can quickly evaporate than glycine. Therefore, the percentage of other less volatile species can be the important parameter in SCCM modeling.

5. DISCUSSION

Can this model reproduce the molecular ratio obtained in Rosetta mission? If outbursts eject molecules from the deeper layers to the surface, the integrated molecular abundances from the surface to inner layer, hereafter net abundance, would be the good tool for the comparison. This net abundance of species $j$ is calculated by integrating the net abundance of the layers, as $\Sigma_n(1 - P[n, t]) \times r[n, j, t]$.

The net abundances and their ratios depend on the depth of outburst, which is not determined by observation of Rosetta mission. Since the porosity and the molecular ratios do not change at $\sim 1000$ cm position, we fix the molecular ratios to be the initial values for the deeper positions than 1000 cm. In Figure 13, we plot the net abundance ratios of “glycine/CH$_3$NH$_2$” and “glycine/H$_2$O” with Set 1, assuming the different depth of outburst. The deeper position of outburst will increase CH$_3$NH$_2$ and water compared to glycine, since the condensation of glycine is important only in the surface. These result clearly suggest that the depth of outburst is the essential parameter that change the molecular ratios especially for less volatile species. The result of Rosetta mission, “glycine/CH$_3$NH$_2$” of unity and the upper limit of “glycine/H$_2$O” of 0.0025, can be well explained by assuming the outburst depth of 10000 cm.

To see the parameter dependence of the molecular ratios, the integrated net abundance ratio is shown in Figure 14. The depth of outburst is fixed to be 10000 cm for all sets. Similar to the above discussion, we compensate the layers deeper than 1000 cm for Sets 1, 2, 3, 6, 7, 8, whose layer size is 10 cm, and 2000 cm for Set 4, whose layer size is 20 cm. Since the layer size is 100 cm for Set 5, we can use our simulation result without compensation for this Set. Figure 14 suggests that the “glycine/CH$_3$NH$_2$” ratio is between 0.1 and 1 except for Set 7. Especially, “glycine/CH$_3$NH$_2$” ratio is between 0.1 and 1 even for Sets 2 and 3, where the initial abundance ratio of “glycine/CH$_3$NH$_2$” was $10^{-2}$ and $10^{-4}$, respectively. This result suggests that condensation process can strongly alter the initial molecular abundance ratio for the less volatile species. If molecules are ejected from the outburst, initial molecular ratio achieved in the ISM circumstance would have been lost due to the condensation process. Our SCCM model also achieves the similar “glycine/CH$_3$NH$_2$” ratio under the different thickness of layer (Sets 4 and 5) and different initial porosity (Set 6). Despite the simplified physics in the SCCM model, the condensation process of less volatile molecules would be the secure at least in our different parameters. In addition, our SCCM model can solve the disagreement of “glycine/CH$_3$NH$_2$” ratio between the ISM chemical model and the result of Rosetta mission. If the “glycine/CH$_3$NH$_2$” ratio has increased through the process of perihelion, “glycine/CH$_3$NH$_2$” ratio would have dramatically increased due to the condensation of glycine. According to a result of Set 7, the most important uncertainty is the existence of less volatile species. Such species may be PAH and other very complex organic molecules. The percentage of glycine should further be explored.

In contrast to the excellent agreement for “glycine/CH$_3$NH$_2$” ratio, some sets showed higher “glycine/H$_2$O” ratio than Rosetta mission. One possibility of this disagreement may have come from the calculation method to evaluate the amount of ejected molecules, in which we simply integrated the net amount of molecules in Figure 14. Since the “glycine/CH$_3$NH$_2$” and “glycine/H$_2$O” ratios were observed at $\sim 3$ AU, not only the outburst but also thermal evaporation would provide H$_2$O to cometary coma while the thermal evaporation is much less effective for CH$_3$NH$_2$ and glycine. In this case, it is possible that the SCCM model underestimate H$_2$O abundance in Figure 14, making “glycine/H$_2$O” ratio much higher.

6. SUMMARY

We found that the chemical modeling for star-forming regions can not explain the high relative abundance of glycine reported by Rosetta mission. We developed SCCM model to see if we can reconcile this discrepancy by considering the evaporation process of molecules from the cometary surface. Our SCCM model suggests that the chemical compounds of less volatile species, such as glycine, may be enhanced dramatically on the cometary surface, while the chemical composition at the age of comet formation is saved at the deep inside of comets. This condensation mechanism enables us to solve the strong discrepancy between the chemical model for low-mass star forming regions. It is also possible that the relative abundances of other less volatile molecules are also enhanced than the initial value, despite the widely accepted idea that chemical composition of cometary material is heritage of the primordial Solar System.
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REFERENCES

Agarwal, J., Corte, V., D., Feldman, P. D., et al, 2017, MNRAS, 469, S606
Altwegg, K., Balsiger, H., Berthelier, J., J., et al, MNRAS, 469, S130 (2017)
Altwegg, K., Balsiger, H., Bar-Nun, A., et al, 2016, Sci, 2, id=e1600285
Barnett, I., L., Lignell, A., & Gudipati, M. S., 2012, ApJ, 747, 13
Bergner, J. B., Guzmán, V., G., Öberg, K., I., Loomis, R., A., & Pegues, J., A&A, 857, 16 (2018)
Biver, N., et al, Science Advances, 1, e1500863 (2015)
Bockelée-Morvan, D., Lis, D., Wink, J., et al, 2000, A&A, 353, 1101
Bockelée-Morvan, D., Crovisier, J., Mumma, M. J., & Weaver, H. A. 2004, in The composition of cometary volatiles, ed. G. W. Kronk (University of Arizona Press), 391
Brooke T.Y., Tokunga A.T., Weaver H.A., et al., 1996, Nat 383, 606
Capaccini, F., Coradini, A., Filacchione, et al, 2015, Sci, 347, ISSUE 6220
Ceccarelli, C., Loinard, L., Castets, A., Faure, A., & Lefloch, B A&A, 362, 1122 (2000)
Cooper, G., Kimmich, N., Belisle, et al, 2001, nature, 414, 879
Dutrey A., Despois D., Bockelée-Morvan D., et al, 1996, IAU Circ., 6364
Elsila, J., Glavin, D., P., & Dworkin, J., P., Meteoritics & Planetary, 2009, Sci, 44, Nr 9, 1323
Engel, M., H., & Nagy, Bartholomew, 1982, nature, 296, 29
Ehrenfreund, P., et al, 2002, Rep. Prog. Phys, 65, 1427
Fayolle, E., C., Öberg, K., I., Jørgensen, J., K., 2017, nature astronomy, 1, 703
Fink, U., Combi, M. R., & Disanti, M. A. 1991, ApJ, 383, 356
Fray, N., Bénilan, Y., Cottin, H., Gazeau, M.-C., & Crovisier, J. 2005, Planet Space Sci., 53, 1243
Garrod, R., T., 2013, ApJ, 765, 60
Goessmann, F., Rosenbauer, H., & Bredehöft, J., H., et al, 2015, Sci, 349, 6247
Guilbert-Lepoutre, A., Rosenberg, E. D., Prihnik, D., & Besse, S., 2016, MNRAS, 462, S146
Gulkis, S., Allen, M., Allmen, P, et al, (2015), Sci, 347, Issue 6220, aaa0709
Hasegawa, T. I., Herbst, E., & Leung, C. M., 1992, ApJS, 82, 167
Ip, W.-H., Lai, I.-L., Lee, J.-C., Cheng, Y.-C., Li, Y., Lin, Z.-Y., & Vincent, J.-B., et al, 2016, A&A, 591, A132
Jørgensen, J. K., Favre, C., Bisschop, S. E., et al, (2012), ApJL, 757, L4
Kuan, Y. J., Charnley, S. B., Huang, H. C., Tseng, W. L., & Kisiel, Z., ApJ, 2003, 593, 848
Loomis, R. A., Cleaves, L. I., Öberg, K. I., et al, A&A, 859, 11 (2018)
Lis D.C., Keene J., Young T.G., et al., 1997, Icarus 130, 355
Ohishi, M., Suzuki, T., Hirota, T., Saito, M., & Kaifu, N, 2017, arXiv:1708.06871
Roy, L., L., Altwegg, K., Balsiger, H., et al, 2015, A&A, 583, A1
Martín-Doménech, R., Rivilla, V., M., Jimenez-Serra, I., 2017, MNRAS 469, 2230
Murdoch, N., Sánchez, P., Schwartz, S. R., & Miyamoto, H., 2015, Space Science Series, edited by P. Michel, F. DeMeo and W. Bottke
Mumma M.J., DiSanti M.A., Dello Russo N., et al., 1996, Sci 272, 1310
Mumma, M. J., DiSanti, M. A., Magee-Sauer, K., Bonev, B. P., Villanueva, G. L., Kawakita, H., et al, 2005, Sci, 310, 270
Mumma, M. J., & Charnley, S. B., 2011, Annu. Rev. A&A 49, 471
Öberg, K. I., Guzman, V. V., Furuya, K., et al, 2015, nature, 520, 198
Oró, P. J., 1961, nature, 4774, 389
Pätzold, M., Andert, T., Hahn, M., et al, 2016, nature, 530, 63
Ruaud, M., Wakelam, V., & Hersant, F., 2016, MNRAS, 459, 3756
Sandford, S. A., Alén, J., Alexander, C. M, O'D., et al, 2006, Sci, 314, 1720
Snyder, L. E., Lovas, F., J., Hollis, J. M., et al, ApJ, 2005, 619, 914
Suzuki, T., Majumdar, L., & Ohishi, M., et al 2018b, ApJ, 863, 51
Suzuki, T., Ohishi, M., Majumdar, L., Saito, M., Tomoya, H., & Wakelam, V., 2018a, ApJS, 237, 3
Tzvetkov, G., Ramsey, M. G., & Netzer, F. P., 2004, Chemical Physics Letters, 397, 392
Vincent, J.-B., A’Hearn, M. F., Lin, Z.-Y., et al, 2016, MNRAS, 462, S184
Wakelam V., Loison, J. C, Mereau, R., & Ruaud, M., 2017, Molecular Astrophysics, 6, 22
Walsh, C., Millar, T. J., Nomura, H, et al., 2014, A&A, 563, A33
Walsh, C., Loomis, R. A., Öberg, K. I., et al, 2016, ApJL, 823, L10
Woodney L.M., McMullin J., A’Hearn M.F., 1997, Planet. Space Scie, 45, 717
Woodney, L., A’Hearn, M., Schleicher, D. G., et al. 2002, Icarus, 157, 193
Table 1. The Parameters for SCCM Modeling

| Model | Glycine (%) | Layer Size (cm) | Initial Porosity | other species |
|-------|-------------|-----------------|------------------|---------------|
| Set 1 | 10^{-3}     | 10              | 0                | No            |
| Set 2 | 10^{-2}     | 10              | 0                | No            |
| Set 3 | 10^{-4}     | 10              | 0                | No            |
| Set 4 | 10^{-3}     | 20              | 0                | No            |
| Set 5 | 10^{-3}     | 100             | 0                | No            |
| Set 6 | 10^{-3}     | 10              | 0.2              | No            |
| Set 7 | 10^{-3}     | 10              | 0                | Yes           |
| Set 8 | 10^{-3}     | 10              | 0                | Yes           |

Note—The parameters for SCCM modeling are summarized. The relative abundances of glycine is shown in percentage, and the other material is CH$_3$NH$_2$ (1%) and water (∼99%). We included the other material with its percentage of 0.01% in Sets 7 and 8. The binding energy of this fourth material is assumed to be 13000 and 6500 K in sets 7 and 8, respectively, which correspond to the binding energies of glycine and CH$_3$NH$_2$. 
Figure 1. The results of chemical model under the condition of low-mass star-formation. Considering that gas phase species will finally frozen onto grains in the phase of comet formation, the fractional abundances of glycine (red line), CH$_3$NH$_2$ (blue line), and H$_2$O (green line) were summed through the gas phase, on grain surface, and in the grain mantle. Based on this result, we plotted the time dependence of molecular ratios of “Glycine/CH$_3$NH$_2$ (green line)” and “Glycine/H$_2$O (blue line)”.

(a) Evaporation Process

(1) usual evaporation

(2) direct evaporation

1st layer

2nd layer

3rd layer

4th layer

(b) Merging Process

1st layer $P=0.8$

2nd layer $P=0.4$

3rd layer $P=0.2$

4th layer $P=0.1$

1st layer $P=0.2$

2nd layer $P=0.2$

3rd layer $P=0.1$

Figure 2. Our SCCM model includes two evaporation mechanisms. In addition to the usual evaporation process to transport molecules towards upper layer, we consider the direct evaporation process whose efficiency strongly depends on the porosity of upper layers. When porosity exceeds 0.7, the layer will merge with the beneath layer.
Figure 3. The distribution of temperature inside the comets. (a) The temperature distributions in the different distance from the surface along with the comet years. The time of 0 year is corresponding to the position of perihelion. (b) The vertical temperature distribution of cometary surface in the different distances from the Sun.

Figure 4. The evolution of averaged porosity for the different depths are shown with different colors. The purple, green, blue, and orange lines, respectively, represent the depth of 0 to 40, 40 to 80, 80 to 120, and 120 to 180 cm except for Set 5, where we assumed the layer size of 100 cm. The averaged porosity in Set 5 is shown by the purple, green, and the blue lines to represent the depth of 0 to 100, 100 to 200, and 200 to 300 cm.
**Figure 5.** With Set 1, the time evolution of molecular percentages, for H$_2$O, glycine, and CH$_3$NH$_2$, are shown by green, blue, and red lines, respectively. The horizontal axis represents the time in comet year, with one unit being the one orbital motion around the Sun.

**Figure 6.** The same as Figure 5 but with Set 2.
Figure 7. The same as Figure 5 but with Set 3.

Figure 8. The same as Figure 5 but with Set 4.
Figure 9. The same as Figure 5 but with Set 5.

Figure 10. The same as Figure 5 but with Set 6.
Figure 11. The same as Figure 5 but with Set 7. The abundance of newly added material in Set 7 is shown by a black line.

Figure 12. The same as Figure 5 but with Set 8. The abundance of newly added material in Set 8 is shown by a black line.
Figure 13. With Set 1, the net abundance ratios of “glycine/CH$_3$NH$_2$” and “glycine/H$_2$O” are shown in the green and blue lines, respectively. The outburst depth of 500, 1000, 1000, and 100000 cm are assumed for these four cases.
Figure 14. The net abundance ratios are shown. The depth of outburst is 10000 cm from the surface for all sets. The green line shows “glycine/CH$_3$NH$_2$” while the blue line shows “glycine/H$_2$O”.