Modeling CO, CO$_2$, and H$_2$O Ice Abundances in the Envelopes of Young Stellar Objects in the Magellanic Clouds

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Abstract

Massive young stellar objects (MYSOs) in the Magellanic Clouds show infrared absorption features corresponding to significant abundances of CO, CO$_2$, and H$_2$O ice along the line of sight, with the relative abundances of these ices differing between the Magellanic Clouds and the Milky Way. CO ice is not detected toward sources in the Small Magellanic Cloud, and upper limits put its relative abundance well below sources in the Large Magellanic Cloud and the Milky Way. We use our gas-grain chemical code MAGICKAL, with multiple grain sizes and grain temperatures, and further expand it with a treatment for increased interstellar radiation field intensity to model the elevated dust temperatures observed in the MCs. We also adjust the elemental abundances used in the chemical models, guided by observations of H II regions in these metal-poor satellite galaxies. With a grid of models, we are able to reproduce the relative ice fractions observed in MC MYSOs, indicating that metal depletion and elevated grain temperature are important drivers of the MYSO envelope ice composition. Magellanic Cloud elemental abundances have a subgalactic C/O ratio, increasing H$_2$O ice abundances relative to the other ices; elevated grain temperatures favor CO$_2$ production over H$_2$O and CO. The observed shortfall in CO in the Small Magellanic Cloud can be explained by a combination of reduced carbon abundance and increased grain temperatures. The models indicate that a large variation in radiation field strength is required to match the range of observed LMC abundances. CH$_3$OH abundance is found to be enhanced in low-metallicity models, providing seed material for complex organic molecule formation in the Magellanic Clouds.

Key words: astrochemistry – ISM: abundances – ISM: molecules – Magellanic Clouds

1. Introduction

Much of our understanding about the details of star formation comes from investigations of stars and the interstellar medium (ISM) in the galaxy, yet the peak of star formation occurred in the past at lower metallicity (Madau & Dickinson 2014). The Magellanic Clouds, local dwarf satellites of the Milky Way (MW), provide an astronomical laboratory to study the process of star formation in a metal-poor environment. Comparison studies between sites of star formation in the Magellanic Clouds and the MW can illuminate the metallicity dependence of local physical processes via observational tracers such as molecular emission and absorption features. Knowledge of multiple molecular abundances can begin to separate effects of metallicity from local physical parameters, e.g., the radiation environment and the dust temperature.

Mid-infrared spectral observations of embedded young stellar objects (YSOs) in the MW have found a wealth of solid-state features, showing high column densities of ices such as H$_2$O, CO, CO$_2$, and CH$_3$OH (Gerakines et al. 1999; Gibb et al. 2004). H$_2$O is the most abundant ice, with a typical column density of order $10^{-4}$ with respect to total hydrogen; CO$_2$ is next, at an average value of CO$_2$/H$_2$O $\approx 0.2$ (Boogert & Ehrenfreund 2004). CO and CH$_3$OH ices follow at lower abundance, though with nearly an order of magnitude of variation between lines of sight. These ices are found in the dense, cold envelopes surrounding the luminous central source, and they hold information on the collapse history of the progenitor dense molecular cloud via, e.g., the polar-to-apolar ratio of the CO and CO$_2$ ice features (Gibb et al. 2000). They are processed to some extent by the internal radiation source, yet a complete explanation for the variation in observed galactic YSO ice abundances is not in hand. Local environment likely plays a role, with changes in the nearby interstellar radiation field (ISRF) or the cosmic-ray ionization rate affecting gas and grain-surface chemistry. Additionally, variations in the underlying elemental abundances of the collapsing cloud will influence the general chemistry and total ice column density.

Observations of massive YSOs (MYSOs) in the nearby Magellanic Clouds show a marked difference in ice abundances with respect to galactic counterparts (van Loon et al. 2005; Shimonishi et al. 2008, 2010, 2016a; Oliveira et al. 2009, 2011, 2013). Shimonishi et al. (2010) and Oliveira et al. (2011) have detected H$_2$O, CO, and CO$_2$ ice in massive YSOs in the Large Magellanic Cloud (LMC); they found bulk compositional differences in LMC sources compared to their galactic counterparts, shown in elevated CO$_2$ ice or depleted H$_2$O ice, with an average value for CO$_2$/H$_2$O of 0.32. Oliveira et al. (2011, 2013) found only an upper limit for CO ice in all Small Magellanic Cloud (SMC) sources studied, with abundances (with respect to their H$_2$O columns) a factor of 3–10 lower than their galactic counterparts. Oliveira et al. (2011) and Shimonishi et al. (2016a) provided additional near-infrared spectra of a sample of LMC MYSOs, with detections or upper limits for CH$_3$OH ice toward all sources studied.

In addition to ice abundance variations, the properties of gas and dust in the Magellanic Clouds also differ from their galactic counterparts. A significant fraction of molecular gas in galaxies like the metal-poor Magellanic Clouds reside in a CO-dark phase, where an extended photodissociation region keeps all atoms but hydrogen in atomic form (Madden et al. 2012, 2016; Roman-Duval et al. 2014). LMC dust temperatures are elevated; Bernard et al. (2008) used Spitzer...
Space Telescope data to find a globally averaged value of 21.4 K, or 23 K in the 30 Dor region. They also performed spectral energy distribution (SED) fitting with a variable ISRF, finding that increasing ISRF strength by a factor of ∼2.1 best fits average LMC observations. Galametz et al. (2013) analyzed data from Spitzer, Herschel, and the Large Apex Bolometer Camera to better model the submillimeter component of the dust SED. Their best-fit dust temperature for the N158-N159-N160 region of the LMC is 27 K.

Dust temperatures in the SMC have been measured toward H II regions and YSOs. Toward N27, a bright H II region in the SMC bar, Caldwell (1997) finds dust temperatures of 33–40 K, while Heikilä et al. (1999) find a similar range of 35–40 K. Van Loon et al. (2010) use observations of YSOs in the Magellanic Clouds to find dust temperatures of 37–51 K in the SMC versus 32–44 K in the LMC. Chiar et al. (1998) find dust and ice temperatures in galactic YSO counterparts to be generally less than 30 K, with some measurements of 23–25 K.

We lack detailed measurements on the ISRF of the Magellanic Clouds; apart from the ISRF fitting of Bernard et al. (2008) in the LMC, Vangioni-Flam et al. (1997) and Pradhan et al. (2011) provide evidence for a factor of 4–10 increase in the UV and far-UV field strength in the SMC when compared to the solar neighborhood.

Chemical models by Garrod & Pauly (2011) found that dust temperatures can strongly affect the abundances of key grain-surface molecules. Above dust temperatures of ∼12 K, grain-surface diffusion of CO becomes rapid, and the reaction CO + OH → CO2 + H efficiently produces CO2. The authors also presented a gas-grain model with free-fall collapse, which reproduced the threshold visual extinctions for detection of H2O, CO2, and CO ice. In this work, we will utilize a similar approach for an investigation of ice abundances toward YSOs in the low-metallicity environments of the LMC and SMC.

Past work by Acharyya & Herbst (2015, 2016) showed that for chemical models with reduced elemental abundances, reproducing observed CO2/H2O ice abundance ratios toward Magellanic Cloud YSOs requires models with AV = 10 and warm dust temperatures, either 20 K ≲ Td ≲ 25 K or 35 K ≲ Td ≲ 45 K. These works produce CO2 via mobile CO in CO + OH; below 20 K, immobile CO causes CO2/H2O to drop below 0.01. They used static cloud models, keeping AV and density fixed while running an array of models across a range of dust temperatures. They did not include the mechanism introduced by Garrod & Pauly (2011) for CO2 production, whereby surface O + H → OH can proceed atop a CO ice surface, and the energy of OH formation overcomes the modest activation energy barrier of the CO + OH → CO2 + H reaction.

We collate observations of MYSOs for which H2O, CO, CO2, and CH3OH detections or upper limits are available, excluding CH3OH for SMC sources (toward which no measurements of CH3OH have yet been achieved). Table 1 lists the total sample we will use for model comparison. Figure 1 shows the observations from Table 1 in a ternary H2O:CO2:CO ice diagram. The ternary plot describes the relative abundances of this three-component ice system. Importantly, we also consider methanol (CH3OH) ice, a key component for galactic YSOs and now detected toward some LMC MYSOs. To include this fourth component on a ternary diagram, we include a second point for those sources with methanol detections or upper limits; these points show the

| Source | H2O | CO | CO2 | CH3OH |
|-------|-----|----|-----|-------|
| MW    |     |    |     |       |
| Mon R2 IRS 2 (a), (c) | 77.1% | 5.8 | 13.0 | 4.1 |
| RAGF89 (a), (d) | 62.7 | 12.6 | 22.7 | 2.0 |
| RAGF2136 (a), (c), (d) | 76.5 | 4.5 | 13.1 | 5.9 |
| RAGF7009 (a), (d), (e) | 59.0 | 9.5 | 13.0 | 18.5 |
| W33 A (a), (c), (d) | 74.2 | 5.4 | 8.6 | 11.8 |
| NGC 7538 IRS1 (a), (e) | 73.3 | 6.0 | 17.0 | <3.7 |
| NGC 7538 IRS9 (a), (c), (d) | 66.5 | 12.4 | 16.9 | 4.2 |
| W3 IRS 5 (a), (d), (e) | 83.7 | 2.4 | 10.5 | <3.4 |
| LMC   |     |    |     |       |
| ST1 (b) | 69.0 | 11.4 | 16.4 | <3.3 |
| ST2 (b) | 77.2 | <2.1 | 15.7 | <5.0 |
| ST3 (b) | 73.8 | 3.2 | 21.7 | <1.3 |
| ST4 (b) | 67.5 | 4.6 | 24.4 | <3.5 |
| ST5 (b) | 72.2 | 3.4 | 20.3 | <4.1 |
| ST6 (b) | 60.8 | <14.7 | 21.1 | 3.4 |
| ST7 (b) | 60.8 | 3.3 | 32.9 | <2.9 |
| ST10 (b) | 67.2 | 10.7 | 19.6 | 2.5 |
| ST14 (b) | 73.9 | 8.7 | 11.8 | <5.6 |
| ST16 (b) | 76.9 | <7.8 | 10.6 | <4.7 |
| SMC   |     |    |     |       |
| IRAS 04340–7326 (f) | 88.3 | <1.3 | 10.4 | ... |
| S3MC 00540–7321 (f) | 85.4 | <0.8 | 13.8 | ... |
| S3MC 00541–7319 (f) | 80.0 | <0.6 | 19.4 | ... |
| IRAS 01042–7215 (f) | 94.6 | <2.6 | 2.8 | ... |

Note. The abundance of each species is shown relative to the sum of the four column densities, in percent.

References. (a) Gibb et al. 2004; (b) Shimonishi et al. 2016a; (c) Brooke et al. 1999; (d) Boogert et al. 2008; (e) Dartois et al. 1999; (f) Oliveira et al. 2013.

Figure 1. Relative abundances of the four major ices in MYSOs in the Milky Way (black), LMC (red), and SMC (blue). SMC sources have only upper limits on CO and no information on CH3OH; SMC points show the composition at the upper limit value with a line drawn to zero CO abundance. For LMC and Milky Way sources, the vertical tick shows the H2O:CO:CO2 composition, while the circles show the composition including CH3OH ice as H2O:(CO + CH3OH):CO2. For LMC sources with only an upper limit on CO, lines have been drawn to zero CO abundance, while sources with an upper limit on CH3OH ice have an open circle. (Ternary figure style from Harper et al. 2015).
fractional abundance of H$_2$O:CO$_2$:CO + CH$_3$OH. This pairing choice of (CO + CH$_3$OH) is chemically motivated, as CH$_3$OH is primarily formed from the successive hydrogenation of CO on grain surfaces (Watanabe & Kouchi 2002; Watanabe et al. 2003, 2004; Cuppen et al. 2009; Fuchs et al. 2009). The figure shows a transition in composition, with some blending between some LMC and galactic sources.

Using the single-point free-fall collapse model detailed by Garrod & Pauly (2011) and Pauly & Garrod (2016), we investigate parameters responsible for the chemical variation among MYSOs in the galaxy, LMC, and SMC. We take the elemental abundances and dust temperatures to be the parameters of interest for the model study. We describe our model methods and parameterization in Section 2. Results of the model grid are shown in Section 3. Discussion of the results and additional parameters of interest are presented in Section 4. Section 5 concludes the study with some thoughts on future work.

2. Methods

We use the gas-grain chemical code MAGICKAL and its associated chemical network, first presented by Garrod (2013) and updated by Pauly & Garrod (2016) to include a grain-size distribution consisting of five grains. The model features 475 gas-phase species and 200 grain-surface species with a network of roughly 9000 reactions and processes. Grain-surface species are tracked in two separate phases, surface and mantle; the surface species participate in desorption, reaction, and diffusion across grain sites, while the ice mantle is treated as a separate phase that is coupled to the surface. Bulk diffusion in the mantle ice is treated explicitly, allowing reactions within the mantle, as well as exchange between surface and mantle components; however, for the low temperatures involved in this work we treat the mantle phase as inert except for the transfer of surface material into the bulk, as the mantle grows. The model uses the modified-rate approach detailed in Garrod (2008) (method “C”) to account for possible stochastic effects in the surface chemistry. The chemical network also includes photodissociation and photoionization processes, with photons sourced from either the ambient field or the cosmic-ray-induced UV field.

2.1. Physical Model

The updated MAGICKAL code utilizes a grain-size distribution. Following Pauly & Garrod (2016), we adopt the power-law fit to the size distribution of silicate grains in the ISM provided by Mathis et al. (1977), which follows the relationship $dn/da = Ca^{-3.5}$. Upper and lower limits to the distribution adopted in the model, as well as the power-law constant, are given in Table 2. The upper limit from Mathis et al. (1977) is loosely constrained by extinction curve measurements, while the lower limit is a practical modeling constraint imposed by stochastic single-photon heating of very small dust grains (Cuppen et al. 2006). At sizes smaller than roughly ~0.02 $\mu$m, grains experience single-photon heating to temperatures sufficient to evaporate surface species at timescales shorter than accretion rates; therefore, they are not expected to contribute significantly to ice-mantle formation. The power-law constant is taken from Draine & Lee (1984), though it is scaled down to match the original gas-to-dust ratio; this is required owing to our shift in $a_{\text{min}}$ and $a_{\text{max}}$ from the values given by Mathis et al. (1977).

We assume a spherical shape for grains, with the cross-sectional area as $\sigma = \pi a^2$. We discretize the grain-size distribution into five bins, equally spaced in log($\sigma$). For each bin, $i$, the mean cross-sectional area of grains in the bin, $\langle \sigma_i \rangle$, is calculated via the power law. This $\sigma$ and its associated radius are used as representative values for all grains in that bin.

The power-law exponent from Mathis et al. (1977) concentrates cross-sectional area in grains with the smallest radius, which are more numerous, whereas dust mass and volume are concentrated in the largest, least populous grains. Small grains will drive the bulk surface chemistry owing to concentrated accretion cross section.

2.2. Collapse Method

We use free-fall collapse to simulate the density of the YSO envelope, using the methods presented by Garrod & Pauly (2011), following Spitzer (1978) and Brown et al. (1988). The density increases following

$$\frac{dn}{dt} = \left( \frac{n_i}{n_j} \right)^{1/3} \left\{ 24\pi G m_H n_i \left[ \left( \frac{n_i}{n_j} \right)^{1/3} - 1 \right] \right\}^{1/2},$$

with $n_i$ the initial density, $G$ the gravitational constant, and $m_H$ the mass of a hydrogen atom. Initial and final densities and visual extinctions are given in Table 2, where the final visual extinction is not a parameter but is determined from the other three parameters via the relation $A_V = A_{V,0}(n_{H,0}/n_{H,1})^{2/3}$.

2.3. Dust Temperatures

We model the evolution of dust temperature as a function of the visual extinction and dust radius, following methods outlined in Garrod & Pauly (2011). We add an additional variable in a model-dependent ISRF. With dust heating from the ISRF equal to cooling from dust radiation, we solve

$$\int_0^\infty Q_{\nu, \text{ISRF}}(A_V) d\nu = \int_0^\infty Q_{\nu, \text{IR}}(T_d) d\nu,$$

with $Q_{\nu, \text{ISRF}}$ the frequency-dependent efficiency of absorption or emission, $J_\nu$ is the radiation field intensity incident on the cloud edge, $D_{\nu}(A_V)$ is the attenuation of the radiation field at a
given frequency for a given $A_V$, and $B_\nu(T_d)$ is the Planck function. We use the assumption from Krügel (2003) for the right-hand side of Equation (1), expressed in cgs units, valid for grains between the small- and large-grain limits, to find

$$
\int_0^\infty Q_\nu J_\nu(D_\nu(A_V))d\nu = 1.47 \times 10^{-6}\alpha T_d^6,
$$

with $a$ as the dust grain radius. We use tabulated data on line-of-sight extinction profiles with $R_V = 5$ from Cardelli et al. (1989) and Mathis (1990) to determine $D_\nu(A_V)$. This approach assumes plane-parallel geometry. The absorption efficiency of dust grains at wavelengths relevant to the ISRF is approximated as $Q_\nu^{abs} \propto a^{-1.5}$, with a maximum $Q$ value of 2.0, a reasonable assumption for carbonaceous grains. Silicate dust has a more complex (and generally weaker) absorption behavior in the 0.1–10 $\mu$m range. Our treatment therefore implicitly considers only carbonaceous grains. Of note, we treat the growth of the ice mantle during model evolution as extra grain material and not explicitly as ice for the value of $Q_\nu^{abs}$.

We approximate the ISRF in various environments by modifying the multicomponent fit from Zucconi et al. (2001) for the MW. The fit includes contributions from three discrete stellar blackbody populations, both hot and cool diffuse dust components, and the cosmic microwave background. To simulate variation in ISRF intensity in the Magellanic Clouds, we scale the stellar components uniformly, from the base factor of 1.0–3.0 in increments of 0.5. The resulting dust temperatures are shown in Figure 2 for a range of dust radii spanning the sizes explored in our models, with the smallest grains having the highest temperature. Note that the largest radius bin is $10^{-0.1}$ $\mu$m and not $10^0$ owing to the discretization of the power law into five sizes in each model. The dashed vertical lines show the extent of $A_V$ covered during the model collapse; the increase in $A_V$ during the collapse process results in a general cooling and a flattening of the temperature distribution with respect to grain size.

The dust temperature tracks in Figure 2 are for grains of constant radius, but it should be noted that the effective grain radius is not constant during the model evolution; as gas species accrete and form an ice mantle, the grain radius grows, increasing in $A_V$ during the collapse. This approach assumes plane-parallel geometry. The absorption efficiency of dust grains at wavelengths relevant to the ISRF is approximated as $Q_\nu^{abs} \propto a^{-1.5}$, with a maximum $Q$ value of 2.0, a reasonable assumption for carbonaceous grains. Silicate dust has a more complex (and generally weaker) absorption behavior in the 0.1–10 $\mu$m range. Our treatment therefore implicitly considers only carbonaceous grains. Of note, we treat the growth of the ice mantle during model evolution as extra grain material and not explicitly as ice for the value of $Q_\nu^{abs}$.

The ISRF factor used to scale the dust heating is also used to scale the photoionization and photodissociation rates in the model, as the stellar component of the ISRF is the primary source of UV photons. Ionization and dissociation via the secondary UV field from cosmic rays are treated separately.

### 2.4. Elemental Abundances

To model the ISM of the metal-poor galaxies, we deplete the heavy elemental abundances in the initial setup of our models. The Magellanic Clouds have bulk metallicity of $Z_{LMC} \sim 0.4Z_\odot$ and $Z_{SMC} \sim 0.2Z_\odot$ (Russell & Dopita 1992). Kurt & Dufour (1998) collated observations of eight LMC and six SMC H II regions with updated atomic transition data to find the mean abundances of carbon, nitrogen, and oxygen. Peimbert (2003) collected a UV–visible spectrum of 30 Doradus in the LMC with the Very Large Telescope; with 269 identified emission lines, they calculate the total abundance of carbon, nitrogen, and oxygen. The results differ slightly if recombination lines are used rather than collisionally excited lines; we have chosen to use the results of the collisional lines. These two studies provide us with ISM compositions to model the metal-depleted environments associated with star formation in the Magellanic Clouds. The abundance values are shown in Table 3; these abundances will be referred to as MW, LMC, and SMC.

**Table 3**

| Element | MW | LMC | SMC |
|---------|----|-----|-----|
| H       | 5.000(−5) | 5.000(−5) | 5.000(−5) |
| H2      | 0.499975  | 0.499975  | 0.499975  |
| O       | 3.200(−4) | 2.140(−4) | 1.047(−4) |
| C+      | 1.400(−4) | 6.310(−5) | 1.585(−5) |
| N       | 7.500(−5) | 1.12(−5)  | 2.820(−6) |
| C/O ratio | 0.438  | 0.295  | 0.151  |

*Note.* The first column represents galactic abundances, taken from Garrod & Pauly (2011). The second column is used as representative values for the LMC, taken from Peimbert (2003). The final column gives the most depleted abundances considered, which are taken from the sample of SMC H II regions in Kurt & Dufour (1998).
Figure 3. Dust temperature (solid lines) and dust radius (dashed lines) vs. time for the five grain sizes in the 12 models. Models with MW abundances are shown in the left column, LMC in the middle column, and SMC in the right column. Dust radius comprises the combined radius of the underlying dust grain plus the ice mantle. The first row has the base ISRF; ISRF increases with decreasing row with values of 2.0, 2.5, and 3.0.
3. Results

We computed a grid of 15 models by multiplying the stellar component of the ISRF with values of {1.0, 1.5, 2.0, 2.5, 3.0} and varying the elemental abundances between initial elemental abundance setups, MW, LMC, and SMC. Figure 3 shows the evolution of the dust temperatures and radii for 12 of the 15 models. The end of collapse is apparent at \( \sim 8 \times 10^5 \) yr, seen in the dust temperature minima; the model is then held at the final collapse density of \( 2 \times 10^6 \text{ cm}^{-3} \) until \( 5 \times 10^6 \) yr. The visual extinction remains constant after the peak density is reached, effectively fixing the dust temperatures; there is a slight decrease during this phase owing to grain mantle growth, but the temperature–radius relation is roughly flat at \( A_V \approx 10 \). At the final visual extinction of 10.6, the dust temperatures are equal for all but the largest grains, which are slightly cooler. Ice-mantle growth primarily occurs at times immediately before and after the peak density is reached, when accretion onto the grains from the gas phase becomes rapid. The cross-sectional area is concentrated in the grains with small radius, causing the accretion rate to be highest for the smallest grains. The radius of this bin increases by up to a factor of three in models with high metal abundances; combined grain and ice radius values are given in Table 4.

Figure 4 shows, for a selection of models, the fractional ice-mantle composition by species, aggregated over all grain populations and plotted against ice layer depth. This ice depth is normalized to the final total ice abundance. Aggregate abundances for a given species are computed by first determining its fractional surface coverage on each grain size. Next, these fractional coverages are weighted by each grain’s relative growth rate with respect to the total grain-surface growth rate. These panels plot this weighted aggregate surface composition against the total ice abundance; the upper axis plots time for comparison. The mantle deposition rate for a given species depends directly on its relative surface population, such that the surface composition is indicative of the newly formed mantle composition at each point in model time. Therefore, these plots can be read as the mantle composition as a function of aggregate “layer.”

\( \text{H}_2\text{O} \) is the dominant ice component in nearly all models as expected, following observations. The collapse is complete by \( \sim 8 \times 10^5 (10^{5.5}) \) yr; for models with 1.0, 1.5, or 2.0 stellar intensity, this causes dust temperatures to drop below an efficiency threshold for producing \( \text{CO}_2 \) from \( \text{CO} \) \(+\text{OH} \), identified by Garrod & Pauly (2011). CO mobility on the grain surface is sufficiently slowed at temperatures below \( \sim 12 \) K; by this point, the fractional abundance of CO grows above that of \( \text{CO}_2 \). Models with 2.5 or 3.0 stellar intensity never drop below this temperature threshold, and as a result high \( \text{CO}_2 \) ice abundances are found throughout those models.

\( \text{CH}_3\text{OH} \) ice is formed via the hydrogenation of surface \( \text{CO} \), which is only present after temperatures drop below the 12 K threshold. For MW models with abundant CO ice, the efficiency of \( \text{CH}_3\text{OH} \) formation appears low, with the abundance ratio of \( \text{CH}_3\text{OH} : \text{CO} \) ranging from 1:2 to 1:5. However, in SMC models with low CO surface abundance, surface \( \text{CH}_3\text{OH} \) can be equal in abundance to CO, and these molecules are similarly abundant throughout those model runs.

The hydrides \( \text{CH}_4 \) and \( \text{NH}_3 \) appear to track closely the elemental abundance of their atomic parent, with some dependence on temperature shown for models with galactic elemental abundances.

The following subsections describe the important reactions producing and destroying each primary ice component; we refer to relative abundance trends seen in Figure 4 or to abundance values at \( 10^5 \) or \( 5 \times 10^5 \) yr, found in Tables 5 and 6.

3.1. \( \text{H}_2\text{O} \) Ice Behavior

\( \text{H}_2\text{O} \) ice formation occurs primarily through the surface hydrogenation of OH, which is in turn formed via O \(+\text{H} \) on the surface. Prior to the completion of collapse, if dust temperatures are greater than \( \sim 13.5 \) K, reaction proceeds primarily through \( \text{OH} \) \(+\text{H} \). At these dust temperatures, desorption of \( \text{H}_2 \) is strongly competitive with the barrier-mediated \( \text{OH} \) \(+\text{H} \). After collapse, the dust is cool enough such that \( \text{H}_2 \) resides on the grain surface for a sufficient time to react and becomes the dominant \( \text{H}_2\text{O} \) formation route.

Figure 4 shows that \( \text{H}_2\text{O} \) is the most abundant ice-mantle component for all models except those with MW elemental abundances at high stellar intensity, 2.5_MW and 3.0_MW. In these models the CO gas abundance is high, and post-collapse dust temperatures are warm enough for CO mobility on the grain surface. These effects combine for CO \(+\text{OH} \) to compete effectively with \( \text{H} \) \(+\text{OH} \) and \( \text{H}_2 \) \(+\text{OH} \), reducing \( \text{H}_2\text{O} \) ice abundance while enhancing \( \text{CO}_2 \). In models with reduced elemental abundances, CO never attains the surface coverage required for \( \text{CO}_2 \) production to reach similar levels. Additionally, the increased C/O ratio in “LMC” and “SMC” chemistries further enhances \( \text{H}_2\text{O} \) dominance over carbon-bearing ice species.

The absolute abundance of \( \text{H}_2\text{O} \) ice (Table 5) does not strictly follow the abundance of oxygen across the different models; because the carbon abundance serves to lock oxygen into CO-structured molecules, the fraction of oxygen found in \( \text{H}_2\text{O} \) is determined in large part by the C/O ratio. As dust temperature increases owing to increased stellar intensity, \( \text{H}_2\text{O} \) ice abundance drops. This is due to increased competition between \( \text{OH} \) \(+\text{CO} \) and \( \text{OH} \) \(+\text{H}_2 \); increasing temperatures

Table 4

| Model | Grain 1 | Grain 2 | Grain 3 | Grain 4 | Grain 5 |
|-------|--------|--------|--------|--------|--------|
| Initial radii | 0.0275 | 0.0601 | 0.1313 | 0.2872 | 0.6279 |
| 1.0_MW | 0.0857 | 0.1185 | 0.1900 | 0.3471 | 0.6893 |
| 1.5_MW | 0.0853 | 0.1182 | 0.1898 | 0.3464 | 0.6888 |
| 2.0_MW | 0.0846 | 0.1174 | 0.1891 | 0.3458 | 0.6888 |
| 2.5_MW | 0.0821 | 0.1149 | 0.1868 | 0.3443 | 0.6894 |
| 3.0_MW | 0.0795 | 0.1122 | 0.1843 | 0.3420 | 0.6890 |
| 1.0_LMC | 0.0712 | 0.1038 | 0.1751 | 0.3312 | 0.6734 |
| 1.5_LMC | 0.0709 | 0.1036 | 0.1749 | 0.3309 | 0.6729 |
| 2.0_LMC | 0.0704 | 0.1030 | 0.1744 | 0.3305 | 0.6728 |
| 2.5_LMC | 0.0682 | 0.1009 | 0.1723 | 0.3290 | 0.6731 |
| 3.0_LMC | 0.0661 | 0.0987 | 0.1702 | 0.3270 | 0.6723 |
| 1.0_SMCI | 0.0556 | 0.0882 | 0.1595 | 0.3154 | 0.6566 |
| 1.5_SMCI | 0.0555 | 0.0881 | 0.1594 | 0.3153 | 0.6563 |
| 2.0_SMCI | 0.0552 | 0.0878 | 0.1592 | 0.3151 | 0.6562 |
| 2.5_SMCI | 0.0544 | 0.0870 | 0.1583 | 0.3145 | 0.6563 |
| 3.0_SMCI | 0.0535 | 0.0861 | 0.1574 | 0.3136 | 0.6560 |
| 1.0_SMCI_gdr500 | 0.0773 | 0.1100 | 0.1813 | 0.3372 | 0.6786 |

Note. Note that all models begin with the same grain-size distribution, given in the first line.

The Astrophysical Journal, 854:13 (16pp), 2018 February 10
Paula & Garrod
Figure 4. Plots of the fractional surface layer abundance plotted against the growth of the aggregate ice mantle. For a given point in the accretion history of the ice mantle, the composition of newly formed mantle material can be read from the surface abundances, aggregated across all grain-size bins. Model results with ISRF values of 1.5 are omitted.
| Model     | H$_2$O  | CO   | CO$_2$ | CH$_3$OH | CH$_4$ | NH$_3$ |
|-----------|---------|------|--------|----------|--------|--------|
|           | 10$^6$ yr | 5 × 10$^6$ yr | 10$^6$ yr | 5 × 10$^6$ yr | 10$^6$ yr | 5 × 10$^6$ yr | 10$^6$ yr | 5 × 10$^6$ yr | 10$^6$ yr | 5 × 10$^6$ yr | 10$^6$ yr | 5 × 10$^6$ yr |
| 1.0_smc  | 2.07(−5) | 8.41(−5) | 3.4    | 7.3      | 8.2    | 8.0    | 1.1    | 1.1     | 1.3    | 1.3     | 0.8    | 0.8    |
| 1.5_smc  | 2.00(−5) | 7.93(−5) | 2.0    | 4.4      | 11.3   | 9.3    | 2.3    | 2.3     | 4.3    | 4.3     | 2.3    | 2.3    |
| 3.0_smc  | 1.94(−5) | 7.53(−5) | 0.8    | 1.6      | 14.3   | 15.6   | 1.1    | 2.2     | 2.2    | 2.2     | 2.2    | 2.2    |
| 1.0_smc_gdr500 | 8.35(−6) | 7.70(−5) | 3.7    | 7.4      | 5.4    | 1.4    | 4.1    | 7.1     | 0.3    | 0.1     | 1.8    | 0.9    |

Note: Abundances shown are absolute for water ice or relative to water, in percent, for other species. Two subcolumns are given for each species; the left subcolumn shows the abundance at 10$^6$ yr while the right subcolumn shows the abundance at 5 × 10$^6$ yr.
| Model         | H$_2$O  | CO     | CO$_2$   | CH$_3$OH | CH$_4$ | NH$_3$  |
|---------------|---------|--------|----------|----------|--------|---------|
|               | 10$^6$ yr | 5 × 10$^6$ yr | 10$^6$ yr | 5 × 10$^6$ yr | 10$^6$ yr | 5 × 10$^6$ yr | 10$^6$ yr | 5 × 10$^6$ yr | 10$^6$ yr | 5 × 10$^6$ yr |
| 1.0_MW        | 6.41(−5) | 1.51(−4) | 1.86(−5) | 7.74(−5) | 1.67(−5) | 3.33(−5) | 5.30(−6) | 1.70(−5) | 4.44(−6) | 5.57(−6) | 1.41(−5) | 2.54(−5) |
| 1.5_MW        | 6.03(−5) | 1.47(−4) | 1.72(−5) | 7.73(−5) | 1.84(−5) | 3.49(−5) | 4.76(−6) | 1.61(−5) | 4.01(−6) | 5.12(−6) | 1.32(−5) | 2.37(−5) |
| 2.0_MW        | 5.65(−5) | 1.39(−4) | 1.48(−5) | 7.14(−5) | 2.11(−5) | 4.24(−5) | 4.19(−6) | 1.49(−5) | 3.87(−6) | 4.94(−6) | 1.28(−5) | 2.32(−5) |
| 2.5_MW        | 4.86(−5) | 1.12(−4) | 8.63(−6) | 4.77(−5) | 2.79(−5) | 6.95(−5) | 3.18(−6) | 1.21(−5) | 3.77(−6) | 4.74(−6) | 1.27(−5) | 2.32(−5) |
| 3.0_MW        | 4.15(−5) | 8.51(−5) | 3.35(−6) | 2.53(−5) | 3.41(−5) | 9.62(−5) | 2.00(−6) | 8.63(−6) | 3.69(−6) | 4.54(−6) | 1.26(−5) | 2.31(−5) |
| 1.0_LMC       | 4.28(−5) | 1.38(−4) | 6.08(−6) | 3.42(−5) | 6.93(−6) | 1.29(−5) | 2.64(−6) | 1.22(−5) | 6.71(−7) | 1.12(−6) | 2.27(−6) | 4.34(−6) |
| 1.5_LMC       | 4.14(−5) | 1.37(−4) | 5.48(−6) | 3.38(−5) | 7.82(−6) | 1.41(−5) | 2.36(−6) | 1.15(−5) | 5.98(−7) | 1.03(−6) | 2.23(−6) | 4.28(−6) |
| 2.0_LMC       | 4.00(−5) | 1.33(−4) | 4.64(−6) | 3.07(−5) | 8.93(−6) | 1.82(−5) | 2.08(−6) | 1.07(−5) | 5.71(−7) | 9.87(−7) | 2.20(−6) | 4.25(−6) |
| 2.5_LMC       | 3.67(−5) | 1.17(−4) | 2.51(−6) | 1.81(−5) | 1.17(−5) | 3.40(−5) | 1.46(−6) | 8.00(−6) | 5.43(−7) | 8.91(−7) | 2.18(−6) | 4.22(−6) |
| 3.0_LMC       | 3.40(−5) | 1.01(−4) | 8.96(−7) | 6.85(−6) | 1.40(−5) | 4.93(−5) | 7.91(−7) | 4.53(−6) | 5.12(−7) | 7.83(−7) | 2.15(−6) | 4.19(−6) |
| 1.0_SMC       | 2.13(−5) | 8.55(−5) | 9.13(−7) | 6.68(−6) | 1.24(−6) | 1.93(−6) | 8.54(−7) | 5.47(−6) | 5.95(−8) | 1.99(−7) | 3.82(−7) | 1.00(−6) |
| 1.5_SMC       | 2.10(−5) | 8.52(−5) | 8.23(−7) | 6.68(−6) | 1.46(−6) | 2.21(−6) | 7.60(−7) | 5.25(−6) | 4.93(−8) | 1.86(−7) | 3.79(−7) | 9.97(−7) |
| 2.0_SMC       | 2.07(−5) | 8.41(−5) | 7.11(−7) | 6.13(−6) | 1.70(−6) | 3.22(−6) | 6.63(−7) | 4.85(−6) | 4.36(−8) | 1.75(−7) | 3.77(−7) | 9.95(−7) |
| 2.5_SMC       | 2.00(−5) | 7.98(−5) | 4.02(−7) | 3.55(−6) | 2.26(−6) | 7.42(−6) | 4.53(−7) | 3.44(−6) | 3.84(−8) | 1.49(−7) | 3.75(−7) | 9.92(−7) |
| 3.0_SMC       | 1.94(−5) | 7.53(−5) | 1.52(−7) | 1.24(−6) | 2.79(−6) | 1.18(−5) | 2.23(−7) | 1.66(−6) | 3.37(−8) | 1.18(−7) | 3.72(−7) | 9.88(−7) |
| 1.0_SMC_gdr500 | 8.35(−6) | 7.70(−5) | 3.09(−7) | 5.70(−6) | 4.48(−7) | 1.07(−6) | 3.43(−7) | 5.50(−6) | 2.16(−8) | 7.19(−8) | 1.52(−7) | 6.75(−7) |

**Table 6**

Absolute Abundances for Relevant Ice-mantle Species in the Model Grid

**Note.** Same data as from Table 5. Abundances are shown for two times for each species and model; the left subcolumn shows abundance at 10$^6$ yr, while the right subcolumn shows abundances at 5 × 10$^6$ yr.
serve to increase the fraction of OH going toward CO₂ formation via increased CO mobility, while the production of H₂O decreases in turn.

3.2. CO Ice Behavior

CO is efficiently formed in the gas phase and accretes onto the grain surface. At early times in the model nearly all surface CO reacts with OH to form CO₂ owing to mobile CO on the warm (≥12 K) dust. If the dust temperature remains high after collapse, CO₂ efficiently forms at late times as well. At post-collapse densities, the hydrogenation of CO into the short-lived HCO also becomes an important process, with possible outcomes of reverting to CO or forming stable H₂CO. H₂CO can then be further hydrogenated to form methanol, CH₃OH. These reactions serve to destroy CO ice; however, if accretion rates are comparable to the rate of these destruction reactions, the transport of CO to the mantle phase can proceed before the destruction of all surface CO, leading to non-negligible CO mantle abundances and less efficient conversion to methanol.

Figure 4 shows low CO abundances pre-collapse for all models. Post-collapse, the behavior is determined by the dust temperature and the accretion rate. Accretion rate is driven by the amount of carbon, oxygen, and other heavy elements in the model; it is lowest in SMC models and highest in MW models. Higher accretion rates will drive more surface CO into the inert mantle simply by building up the ice layers more quickly, leading to higher CO ice abundances in the mantles. The post-collapse dust temperature determines the efficiency of CO₂ formation; for models with less than 2.5 times the base stellar intensity, an inversion in the CO/CO₂ ratio is seen at the end of collapse, while a stronger ISRF allows strong CO₂ formation even to Aᵥ of 10.6. This depletes CO levels for the entirety of the model.

The surface abundances of the five grain populations are shown separately in Figures 5 and 6 for two models, 1.0_LMC and 3.0_LMC. In Figure 5, the abundance of CO is seen to increase dramatically as the model collapses and grain temperatures drop below the 12 K threshold. The exact time of the abundance turnover is different for the individual grain populations, as each has a different temperature. Figure 6 shows a model dominated by CO₂ for all but the largest grains owing to elevated dust temperatures induced by the elevated ISRF value of 3.0. The relative drop in temperature is also more extreme, and the finite number of time steps is apparent in these plots owing to a rapid transition in chemical behavior.

3.3. CH₃OH Ice Behavior

Hydrogenation of CO to CH₃OH has two steps with activation energy barriers that produce short-lived radicals, HCO and CH₂OH/CH₃O. Hydrogenation of HCO will form products of either H₂CO or H₂ + CO with equal probability, an assumption of our model. Once formed, H₂CO is fairly robust to reverting to a less-hydrogenated form, reacting with a hydrogen atom to form CH₂O or CH₃OH more readily than HCO + H₂. Hydrogen addition to H₂CO and abstraction from CH₂OH are fast, as manifested in the constant ratio of surface abundances between the two species across all models.

The total abundance of CH₃OH ice in the models shown in Table 6 has little spread, with variation of only a factor of two to four across models with an order of magnitude less elemental carbon abundance (MW to SMC). Notably, the amount of CH₃OH relative to the amount of CO on the grain surface increases as the elemental carbon abundance decreases across models. The change is primarily driven by a strong decrease in CO ice abundance as elemental abundances decrease, from MW to LMC to SMC values. For a set of models with equal elemental abundances, the abundance of CH₃OH drops by a factor of two to four as the ISRF increases from 1.0 to 3.0, showing a decrease in formation efficiency at higher dust temperatures.

3.4. CH₄ and NH₃ Ice Behavior

These ices form primarily through successive hydrogenation on grain surfaces. NH₃ ice has a linear pathway with little branching, though N₂ can be a significant nitrogen carrier for models with high nitrogen abundance. CH₄ ice shows similar behavior; the primary formation of CH₄ begins with atomic carbon. The sharp decline in CH₄ ice abundance shown in Figure 4 at early time is indicative of gas-phase atomic carbon reacting to form CO in the gas phase and the atomic abundance decreasing rapidly. Because nitrogen has no equivalent reservoir, its ice behavior is more consistent throughout mantle formation.

The total abundance of NH₃ ice shown in Table 6 reflects a consistent fraction of total nitrogen found in NH₃ ice across models with varying elemental nitrogen abundance. However, CH₄ ice does not follow this trend, with elevated abundance of CH₄ per carbon atom in models with increased elemental carbon abundance. This reflects the increasing C/O ratio in models with increasing carbon abundance. Models with increased C/O ratio take longer to convert gas-phase atomic carbon into CO; as the formation of surface hydrocarbons requires accretion of atomic carbon, models that sustain a reservoir of atomic carbon in the gas show elevated CH₄ abundances.

Figure 5 shows the ice compositions of individual grain sizes in the distribution, specifically for the 1.0_LMC model. CH₄ behavior on the largest grain size differs from its counterparts at early times (∼3 × 10⁵ yr). CH₄ surface abundance is greater than CO₂ for the largest grain; this is caused primarily by the difference in temperature between the grain sizes, with lower temperatures enhancing hydrogenation rates of atomic carbon. The destruction of atomic carbon on large grains is almost entirely through C + H → CH, while on small grains roughly 20% of carbon reacts via C + OH → CO + H. Additionally, the warmer temperatures on small grains permits diffusion of the CH₃ radical, opening new pathways for destruction of CH₃ via, e.g., CH₃ + H₂ → C₂H₆, a molecule not yet detected in interstellar regions but strongly detected in the coma of Comet Hyakutake (Mumma et al. 1996). Ethane surface and mantle abundances are highest on the small grains, with a C₂H₆/CH₄ grain abundance ratio in the model 1.0_LMC of 1.0 at 3 × 10⁵ yr, dropping to 0.1 at 10⁶ yr.

3.5. Gas-to-dust Ratio

The gas-to-dust ratio was fixed at a value of 175 throughout the model grid. This is known to vary with environment, but we chose to keep it fixed to disentangle its effects from the effects of changing elemental abundances and dust temperatures. We ran an additional model with an ISRF value of 1.0 and SMC abundances at a gas-to-dust ratio of 500 to test the robustness of the grid results.
The aggregate mantle of the reduced dust model is shown in Figure 7, below the equivalent grid model with a ratio of 175; absolute ice abundances are given in Table 6. The decreased aggregate cross-sectional area lowers the total accretion rate. This serves to lower CO₂ abundance, which requires accretion of CO during the warm pre-collapse phase. Other species are comparable between the two models, due to the long post-collapse phase from $10^6$ to $5 \times 10^6$ yr. The comparable

![Figure 5](image-url)
abundances of solid species cause mantles to be appreciably thicker in the model with gas-to-dust ratio set at 500, seen in Table 4.

Notably, the model with an increased gas-to-dust ratio also exhibits enhanced CH$_3$OH abundance. The increased formation efficiency of CH$_3$OH appears to be directly connected to the heavy atom accretion rate onto grain surfaces, the key driver of inert ice-mantle growth. If the ice mantle does not grow quickly enough to sequester CO, long surface times coupled with high hydrogen accretion rates produce a high CH$_3$OH abundance.

Figure 6. Fractional layer compositions, as in Figure 5, but for the model 3.0_LMC.
Figure 8 shows the model results overlaid on the observations. For each model we plot two points per panel; for the top panel, the smaller leftward point shows the ice composition at $8 \times 10^5$ yr, while the large rightward point shows the composition at 10$^6$ yr. The bottom panel shows the same models at times of $10^6$ and $5 \times 10^6$ yr. The choice of time spent at post-collapse density is arbitrary, and because physical conditions do not change significantly during this time, the composition follows a roughly straight line between these points. The MW and SMC abundance models appear to match observations more closely at earlier times, while the LMC observations have variation such that model matches are found at both early and late times.

Models with MW abundances show compositions enriched in CO$_2$ and CO/CH$_3$OH, with the relative enrichment between the two set by the stellar flux parameter. As no observations lie near the high-flux galactic abundance models, these models do not appear to represent any observed MYSO and can be ignored.

LMC MYSOs demonstrate large variation in composition, from extreme CO/CH$_3$OH depletion (as in SMC sources) to highly enriched in CO$_2$. Models with LMC-like elemental abundances fall across the ensemble of LMC MYSOs, though there is considerable overlap between LMC and galactic sources. The models separate cleanly on this plot, implying additional effects not addressed in the model setup. Variation in local metallicity may cause blending, as metal-poor MW YSOs may appear chemically similar to LMC MYSOs. Parameters beyond our model, such as variation in collapse speed or ice
processing, may also play a role. Models are able to fit LMC observations at the full range of stellar flux parameter tested.

Models with the most depleted elemental abundances fall near the observed SMC MYSOs, matching the low (undetected) CO abundance and presence of CO2. The models lying closest to observed YSO abundances have high stellar flux values, though the models cannot fully reproduce the spread in CO2 abundances and typically overproduce CO/CH3OH. Of note, the composition of SMC models in Figure 4 shows a roughly equal abundance of surface CO and CH3OH, while observational upper limits exist only for CO. Tightening the abundance constraints on these two species would provide strong evidence for the validity of our CO surface chemistry.

The increased CH3OH abundance relative to CO in SMC models is an unexpected result. CH3OH formation requires CO surface residence times to be longer than the mantle deposition timescale to allow sufficient time for hydrogenation. In this way, the balance between CO and CH3OH is determined primarily by the accretion rate of elements heavier than hydrogen. With long CO surface residence times, CO2 production will also be increased if dust temperatures are above the necessary threshold for CO surface mobilities.

As discussed by Garrod & Pauly (2011), the main reaction that forms grain-surface CO2, i.e., \( \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \), involves internal barriers whose behavior in the gas phase may be approximated by a single, modest (80 K) barrier. On grain surfaces, this barrier is much lower than the barrier to the diffusion of either CO or OH, meaning that, upon meeting, these reactants will usually be confined together long enough for the reaction to take place, giving the reaction an effective efficiency close to unity.

Garrod & Pauly (2011) determined a minimum temperature of around 12 K for CO to be efficiently converted to CO2 on grains, corresponding to the temperature at which CO becomes sufficiently mobile on the grain surface, not only to be able to meet its reaction partner OH, but for the rate of reaction of CO + OH to be able to compete effectively with the reaction \( \text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H} \), which in this model has an activation energy barrier of 2100 K, again based on gas-phase estimates, following Garrod & Pauly (2011). For the latter reaction, in spite of its ability to occur through tunneling, the diffusion of H2 away from its reaction partner, OH, is nevertheless more probable than reaction. This means that tunneling through the reaction barrier is the rate-limiting step in the reaction, and not the diffusion of H2. Consequently, variation of the diffusion rate of H2 with temperature affects neither the rate of the \( \text{H}_2 + \text{OH} \) reaction nor the ability of the CO + OH reaction to compete with it. Variations in temperature do, however, affect the average population of H2 on the grain surfaces, which is determined almost entirely by the balance between the rate of accretion of gas-phase H2 molecules onto the grains and the rate at which they thermally desorb back into the gas. The variation in the H2 population with temperature has a direct effect on the competition between the CO + OH and H2 + OH reactions, with higher temperatures acting to reinforce the dominance of CO, due to the reduction in H2 population.

The suggested threshold temperature of 12 K for CO-to-CO2 conversion is necessarily approximate, as it is representative of a range of temperatures for which CO2 conversion may range from close to 100% down to a low-temperature conversion ratio somewhere on the order of 10% (or less). As discussed above, the threshold will be somewhat dependent on the rate of accretion of H2 onto the grains, which scales with gas density. The picture is further complicated by the effects specifically studied in this paper, in which a range of grain sizes and temperatures contribute to an aggregate composition, in some cases including grains that fall above and below the threshold of efficient CO2 production. For models presented in this paper, peak CO2 surface formation is found on grains with temperatures in the range of roughly 14–18 K; we do not explore temperatures above 18 K, where thermal evaporation of species likely curtails CO2 formation, while temperatures lower than 14 K allow for H2 + OH to compete noticeably in the destruction of surface OH.

However, we may consider how much variation there could be in the guideline threshold temperature through various influences. The discussion in the above paragraphs demonstrates that the main determinants of this temperature are the diffusion rate of CO, the desorption rate of H2, and the accretion rate of H2. A simplistic consideration of the balance between the rates of these processes at a nominal temperature of 12 K indicates that an order-of-magnitude increase in gas density, increasing the accretion rate of H2 by the same factor, would produce a commensurate increase in the threshold temperature of \( \sim 0.8 \) K. The adoption of an H2 binding energy 10% smaller than the 430 K used in our model would increase the threshold temperature by 0.65 K. The use of a CO diffusion barrier equal to 30% of the CO binding energy, rather than the 35% we adopt here, would decrease the threshold temperature by \( \sim 0.83 \) K. (The review by Cuppen et al. (2017) suggest that this ratio for CO lies between 30% and 40%).

It should be noted that changing each of the above parameters in the opposite sense would produce a similar variation in the threshold temperature in the other direction. However, each of the determined variations has been calculated in isolation, and it is unclear how a combination of different parameters would affect the overall threshold. Under certain conditions, the models also fall into the so-called accretion limit, under which modified-rate equations become active in the model (see Garrod 2008). Such conditions will change the simple treatment of the balance between processes that we consider above. A robust determination of the sensitivity of the threshold temperature to each parameter demands a more rigorous testing of the parameter space using the full chemical/physical model. The continuing refinement of laboratory measurements of CO and H2 binding and diffusion properties will also be very valuable to this effort.

### 4.1. Thermal Ice Processing

The models produce a reasonable fit to observations, though a general trend exists in overproduction of (CO + CH3OH). This may not be a simple model issue, but instead a comparison of model results to observations in different physical regimes. These MYSOs are highly luminous objects, and thermal processing of the envelope is likely to have occurred in many sources. In this case, the most volatile ices may be under-abundant owing to evaporation when compared to the final model output, which ends prior to a grain heating and ice evaporation phase.

Collings et al. (2003a, 2003b) find via temperature-programmed desorption (TPD) studies that CO bound to a CO substrate desorbs at temperatures of \( \sim 25 \) K. TPD studies of CO bound to an H2O surface find desorption temperatures between 30 and 70 K, depending on the nature of the H2O ice deposition. Residual CO ice is able to linger in the H2O ice
until \( \sim 140 \text{ K} \), when \( \text{H}_2\text{O} \) ice crystallization causes so-called “volcano-desorption.” If temperatures reach \( \gtrsim 70 \text{ K} \), \text{CO}_2 \) will begin desorption from an \( \text{H}_2\text{O} \) surface (Fayolle et al. 2011; Noble et al. 2012). Entrapment of \text{CO}_2 in the \( \text{H}_2\text{O} \) ice will prevent complete removal of \text{CO}_2, though relative loss is dependent on ice thickness, mixing ratio, and other parameters. Complete loss is not expected until \( \text{H}_2\text{O} \) crystallization. The temperatures quoted here apply to laboratory timescales of minutes to hours, but fitting the desorption rates to an activation energy barrier via the Polanyi–Wigner equation provides a useful quantity for models with astrophysical timescales (see, e.g., the desorption of \text{CO} at roughly 25 K in Garrod 2013).

These experimental results provide evidence for the observations having gone through some amount of mantle desorption; models with a complete collapse to high densities and a following warm-up phase may better account for this effect.

4.2. Comparison to Polar and Apolar Ice Features

We have used a single-point model to trace the collapse of the envelope; this approach cannot fully reproduce the signature of envelope shells with varying age. The outer regions of the envelope may be chemically younger than the central source, and this difference in total ice formation between regions may be significant depending on the age of the outer envelope. Ice formed in this young environment would be \text{CO}_2-rich and \text{CO}-poor, while significant freeze-out in the inner high-density region forms a significant surface abundance of nearly pure \text{CO} (Pontoppidan et al. 2003). The densities reached in our models are not sufficiently high to achieve such strong freeze-out of \text{CO} that it becomes dominant, although in the MW models it comes close. Figure 12 of Garrod & Pauly (2011) shows a high-density collapse in which \text{CO} eventually dominates \( \text{H}_2\text{O} \). However, it is unclear whether apolar \text{CO} signatures require numerical dominance over the total surface \( \text{H}_2\text{O} \) abundance, or whether these signatures can be achieved with some fractional abundance of \text{CO}, combined with some surface self-segregation mechanism that is effective even at low temperatures.

4.3. Cosmic-ray Ionization Rate

The cosmic-ray ionization rate, \( \zeta \), was held fixed throughout our model grid at a value of \( 1.3 \times 10^{-17} \text{ s}^{-1} \). Other chemical model work in the Magellanic Clouds has used either the galactic local value or an enhanced value (Chin et al. 1998; Acharyya & Herbst 2015, 2016). Data on \( \zeta_{\text{LMC}} \) and \( \zeta_{\text{SMC}} \) are scarce; Abdo et al. (2010a) analyzed a Fermi-LAT > 100 MeV gamma-ray map of the LMC and found the globally averaged cosmic-ray ionization rate to be 20%–30% of the local MW value. Regional variability can be significant, with cosmic-ray sources in the LMC causing nearby regions to have ionization rates higher than the globally averaged value. SMC studies lack the sensitivity and resolution required for anything other than a global measurement; this value is depleted by at least a factor of six to seven with respect to the local galactic value (Abdo et al. 2010b).

4.4. Comparison to Low-mass YSOs

The model results presented here have been compared with high-mass YSOs owing to the availability of such data for the Magellanic Clouds. However, low-mass YSOs in the MW generally demonstrate a larger solid-phase \text{CO}_2/\text{H}_2\text{O} ratio than high-mass sources (see, e.g., Öberg et al. 2011). Due to the simple free-fall collapse model we employ here, the models do not directly address differences between high- and low-mass sources. It is plausible that the dust temperature differences investigated here could be responsible for such variations, perhaps with the envelopes of lower-mass sources spending longer periods at higher temperatures more conducive to \text{CO}_2 production. The inclusion of a more explicit temperature structure in the models would help to elucidate this issue.

5. Summary

Our results suggest that gas-grain models of cold cloud collapse can produce ice-mantle abundances that match reasonably well to observations in a variety of environments. We conclude the following:

1. The values of ISRF intensity and elemental abundances chosen provide an adequate distribution of ice abundances that cover the observed ice abundances in YSOs. Models with strongly enhanced ISRF intensity at MW elemental abundances are excluded, while SMC models with enhanced ISRF are preferred.

2. LMC models lie near observed YSOs for every value of the ISRF intensity modeled, characterizing the large spread in LMC YSO ice abundances. This may be indicative of large local fluctuations in the LMC ISRF.

3. The ISRF intensity strongly affects the relative abundance of \text{CO}_2 to \text{CO}/\text{CH}_3\text{OH}, with higher ISRF values leading to \text{CO}_2 enhancement. This is caused by a temperature threshold for \text{CO} moblity on grain surfaces, leading to efficient production of \text{CO}_2 at dust temperatures \( \gtrsim 12 \text{ K} \).

4. Increasing model elemental abundances (and corresponding C/O ratio) decreases the \( \text{H}_2\text{O} \) abundance against the other ices; this is evidenced by model values moving parallel to the \( \text{H}_2\text{O} \) ternary axis with changes in elemental abundance.

5. Our models indicate that the lack of \text{CO} in SMC sources is most likely caused by a combination of low elemental abundances and high ISRF intensity.

6. \text{CH}_3\text{OH} abundance is found to be enhanced in low-metallicity environments relative to \text{CO}. The enhancement is caused by the relatively slow accretion rate in the low-metallicity models; \text{CO} is more efficiently hydrogenated owing to longer surface residence time, and the production of \text{CH}_3\text{OH} increases. This is an important start for the formation of complex organic molecules in LMC and SMC hot cores.

We leave some issues to be addressed in future work. Thermal processing of the ice is important for matching observed ice abundances, and it is not included in these models. We find significant growth in the [dust + mantle] radius, which affects both the dust temperature and surface chemistry; however, we assume a \( Q_{\text{abs}} \) of carbonaceous dust for temperature calculations, though the \( Q_{\text{abs}} \) of ice will differ. We also use a grain-size distribution found for silicate grains; this could be resolved by using values for silicate or carbonaceous grains throughout, or by attempting to model both populations.

Future models could investigate the dependence on cosmic-ray ionization rate, a parameter with large variation across the
LMC. The rate of collapse may also be important, as it sets the heavy atom accretion rate. Follow-up models will address behavior in collapse to higher densities (∼10⁷ cm⁻³), including a warm-up phase for comparison to a newly detected hot core in the LMC (Shimonishi et al. 2016b).

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References
Abdo, A. A., Ackermann, M., Ajello, M., et al. 2010a, A&A, 512, A7
Abdo, A. A., Ackermann, M., Ajello, M., et al. 2010b, A&A, 523, A46
Acharyya, K., & Herbst, E. 2015, ApJ, 812, 142
Acharyya, K., & Herbst, E. 2016, ApJ, 822, 105
Barrett, P., Hunter, J., Miller, J. T., Hsu, J.-C., & Green, T.P. 2005, in ASP Conf. Ser. 347, Astronomical Data Analysis Software and Systems XIV, ed. P. Shopbell, M. Britton, & R. Ebert (San Francisco, CA: ASP), 91
Bernard, J.-P., Reach, W. T., Paradis, D., et al. 2008, AJ, 136, 919
Boogert, A. C. A., & Ehrenfreund, P. 2004, in ASP Conf. Ser. 309, Astrophysics of Dust, ed. A. N. Witt, G. C. Clayton, & B. T. Draine (San Francisco, CA: ASP), 547
Boogert, A. C. A., Pontoppidan, K. M., Knez, C., et al. 2008, ApJ, 678, 985
Brooke, T. Y., Sellgren, K., & Geballe, T. R. 1999, ApJ, 517, 883
Brown, P. D., Charnley, S. B., & Millar, T. J. 1998, MNRAS, 231, 409
Caldwell, D. A. 1997, PhD thesis, Rensselaer Polytechnic Institute
Cardelli, J. A., Clayton, G. C., & Mathis, J. S. 1989, ApJ, 345, 245
Chiar, J. E., Gerakines, P. A., Whittet, D. C. B., et al. 1998, ApJ, 498, 716
Chin, Y.-N., Henkel, C., Millar, T. J., Whiteoak, J. B., & Marx-Zimmer, M. 1998, A&A, 330, 901
Collings, M. P., Dever, J. W., Fraser, H. J., & McCoustra, M. R. S. 2003a, Ap&SS, 285, 633
Collings, M. P., Dever, J. W., Fraser, H. J., McCoustra, M. R. S., & Williams, D. A. 2003b, ApJ, 583, 1058
Cuppen, H. M., Morata, O., & Herbst, E. 2006, MNRAS, 367, 1757
Cuppen, H. M., van Dishoeck, E. F., Herbst, E., & Tielens, A. G. G. M. 2009, A&A, 508, 275
Cuppen, H. M., Walsh, C., Lamberts, T., et al. 2017, SSRv, 212, 1
Dartois, E., Schutte, W., Geballe, T. R., et al. 1999, A&A, 342, L32
Draine, B. T., & Lee, H. M. 1984, ApJ, 285, 89
Fayolle, E. C., Öberg, K. I., Cuppen, H. M., Visser, R., & Limmertz, H. 2011, A&A, 529, A74
Fuchs, G. W., Cuppen, H. M., Ioppolo, S., et al. 2009, A&A, 505, 629
Galametz, M., Hony, S., Galliano, F., et al. 2013, MNRAS, 431, 1596
Garrod, R. T. 2008, A&A, 491, 239
Garrod, R. T. 2013, ApJ, 765, 60
Garrod, R. T., & Pauly, T. 2011, ApJ, 735, 15
Gerakines, P. A., Whittet, D. C. B., Ehrenfreund, P., et al. 1999, ApJ, 522, 357
Gibb, E. L., Whittet, D. C. B., Boogert, A. C. A., & Tielens, A. G. G. M. 2004, ApJS, 151, 35
Gibb, E. L., Whittet, D. C. B., Schutte, W. A., et al. 2000, ApJ, 536, 347
Harper, M., Weinstein, B., Simon, C., et al. 2015, python-ternary: Ternary Plots in Python, Zenodo, doi:10.5281/zenodo.34938
Heikkinen, A., Johansson, L. E. B., & Olofsson, H. 1999, A&A, 344, 817
Krugel, E. 2003, The Physics of Interstellar Dust (Bristol: IOP Publishing Ltd.)
Kurt, C. M., & Dufour, R. J. 1998, RMxAA, 7, 202
Loizides, F., & Schmidt, B. 2016, Positioning and Power in Academic Publishing: Players, Agents and Agendas (Amsterdam: IOS Press)
Madden, P., & Dickinson, M. 2014, ARA&A, 52, 415
Madden, S. C., Cormier, D., & Rémy-Ruyer, A. 2016, in IAU Symp. 315, From Interstellar Clouds to Star-forming Galaxies: Universal Processes?, ed. P. Jablonka, P. André, & F. van der Tak (Cambridge: Cambridge Univ. Press), 191
Madden, S. C., Rémy, A., Galliano, F., et al. 2012, in IAU Symposium, Vol. 284, The Spectral Energy Distribution of Galaxies—SED 2011, ed. R. J. Tuffs & C. C. Popescu (Cambridge: Cambridge Univ. Press), 141
Mathis, J. S. 1990, ARA&A, 28, 37
Mathis, J. S., Rumpl, W., & Nordsieck, K. H. 1977, ApJ, 217, 425
Mumma, M. J., Disanti, M. A., del Rio Russo, N., et al. 1996, Sci, 272, 1310
Noble, J. A., Conigui, E., Dulieu, F., & Fraser, H. J. 2012, MNRAS, 421, 768
Öberg, K. I., Boogert, A. C. A., Pontoppidan, K. M., et al. 2011, ApJ, 740, 109
Oliveria, J. M., van Loon, J. T., Chen, C.-H. R., et al. 2009, ApJ, 707, 1269
Oliveria, J. M., van Loon, J. T., Sloan, G. C., et al. 2011, MNRAS, 411, L36
Oliveria, J. M., van Loon, J. T., Sloan, O. C., et al. 2013, MNRAS, 428, 3001
Pauly, T., & Garrod, R. T. 2016, ApJ, 817, 146
Peimbert, A. 2003, ApJ, 584, 735
Pontoppidan, K. M., Fraser, H. J., Dartois, E., et al. 2003, A&A, 408, 981
Pradhan, A. C., Murthy, J., & Pathak, A. 2011, ApJ, 743, 80
Roman-Duval, J., Gordon, K. D., Meixner, M., et al. 2014, ApJ, 797, 86
Russell, S. C., & Dopita, M. A. 1992, ApJ, 384, 508
Shimonishi, T., Onaka, T., Kouchi, A. 2004, A&A, 376, 650
Shimonishi, T., Onaka, T., Kawamura, A., & Aikawa, Y. 2016b, ApJ, 827, 72
Spitzer, L. 1978, Physical Processes in the Interstellar Medium (New York: Wiley-Interscience)
van Loon, J. T., Oliveira, J. M., Gordon, K. D., Sloan, G. C., & Engelbracht, C. W. 2010, AJ, 139, 1553
van Loon, J. T., Oliveira, J. M., Wood, P. R., et al. 2005, MNRAS, 364, L71
Vangioni-Flam, E., Lequeux, J., Maucherat-Joubert, M., & Rocca-Volmerange, B. 1980, A&A, 90, 73
Watanahe, N., & Kouchi, A. 2002, ApJL, 571, L173
Watanahe, N., Nagaoka, A., Shiraki, T., & Kouchi, A. 2004, ApJ, 616, 638
Watanahe, N., Shiraki, T., & Kouchi, A. 2003, ApJL, 588, L121
Zucconi, A., Walmsley, C. M., & Galli, D. 2001, A&A, 376, 650