CARBON CHAINS AND METHANOL TOWARD EMBEDDED PROTOSTARS

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ABSTRACT

Large interstellar organic molecules are potential precursors of prebiotic molecules. Their formation pathways and chemical relationships with one another and simpler molecules are of great interest. In this paper, we address the relationships between two classes of large organic molecules, carbon chains and saturated complex organic molecules at the early stages of star formation through observations of C2H and CH3OH. We surveyed these molecules with the IRAM 30 m telescope toward 16 deeply embedded low-mass protostars selected from the Spitzer c2d ice survey. We find that CH3OH and C2H are positively correlated, indicating that these two classes of molecules can coexist during the embedded protostellar stage. The C2H/CH3OH gas abundance ratio tentatively correlates with the CH4/CH3OH ice abundance ratio in the same lines of sight. This relationship supports a scenario where carbon chain formation in protostellar envelopes begins with CH4 ice desorption.

Key words: astrochemistry – ISM: molecules – stars: formation – stars: protostars

1. INTRODUCTION

Large organic molecules have been widely observed across different stages of star formation (Herbst & van Dishoeck 2009; Sakai & Yamamoto 2013). Their chemistry is of great interest because large interstellar molecules may serve as precursors to prebiotic chemistry on nascent planets. Large organic molecules also have great potential as molecular probes. In general, molecular abundance patterns contain information about the past and current environment in which they reside. This relationship can be exploited to constrain interstellar environments using molecular line observations if the chemistry of the target molecule is well understood. Larger molecules present numerous rotational lines at millimeter and centimeter wavelengths and are therefore especially appropriate from an excitation point of view. They suffer, however, from an often poorly constrained formation chemistry.

In this paper we explore how the relationship of two kinds of larger organic molecules constrain their chemistry. Interstellar organics are classified as either saturated organic molecules or unsaturated carbon chains. When saturated organic molecules reach sizes of six atoms or greater, they are known as complex organic molecules (COMs). Two classes of molecules have generally been supposed to form and exist in very different interstellar and circumstellar environments (Herbst & van Dishoeck 2009).

Carbon chain molecules were first observed in the cold, dark cloud TMC-1 in the form of cyanopolyynes (Little et al. 1977; Broten et al. 1978; Kroto et al. 1978). In such an environment, carbon chains form through efficient low-temperature ion-molecule reactions in the gas phase (Herbst & Leung 1989; Ohishi & Kaifu 1998). In 2008, Sakai et al. detected the first evidence of carbon chains in an unexpected region: the warm inner regions of a low-mass protostar. Detections toward a second source (Sakai et al. 2009a) suggested that carbon chains are common toward some classes of protostars. The term “warm carbon chain chemistry” (WCCC) was coined to describe this type of source. Based on low-temperature modeling, ion-molecule chemistry and chemical inheritance are not sufficient to produce the high abundance of carbon chains observed in WCCC sources. Sakai et al. (2008) proposed that additional carbon chains can be formed in protostellar envelopes when methane (CH4), a common interstellar ice, sublimes at 25 K (Öberg et al. 2008). In the gas phase, CH4 reacts with C+ to efficiently form carbon chains. This theory has been validated by chemical models (Hassel et al. 2011; Aikawa et al. 2012).

COMs were initially observed in hot cores present toward high-mass protostars (Blake et al. 1987). During the past two decades it has become clear, however, that COMs are abundant in many other circumstellar and interstellar environments as well (see e.g., Cazaux et al. 2003; Arce et al. 2008). COMs have even been detected toward cold cloud cores, the traditional sites of formation for carbon chains, (Öberg et al. 2010; Bacmann et al. 2012; Cernicharo et al. 2012). Based on experiments and models, COMs form efficiently on grain surfaces through energetic processing of simple ices and are released into the gas phase via thermal or nonthermal processes (Garrod & Herbst 2006; Garrod et al. 2008; Öberg et al. 2009b). Recent theoretical work has shown that COMs may also be formed in the gas phase following the desorption of methanol (CH3OH) (Balucani et al. 2015).

Both models and observations thus reveal that both carbon chains and complex organics can form at a range of temperatures and may therefore coexist in some sources. Based on a small sample source (two WCCC sources and three hot corinos), Sakai et al. (2008, 2009a) found that carbon chains and COMs are not detected in large abundances in the same low-mass protostellar sources, however. They suggest that this anti-correlation stems from differences in star formation time scales, which results in different compositions of the ice grains in the protostellar envelope, for WCCC versus hot corino sources. If the starless core phase is short, the bulk of the carbonaceous ice form from accretion of C atoms. The carbon atoms are hydrogenated to form CH3 and the release of CH4 during protostellar formation promotes WCCC. If the starless core is long-lived, most of the carbon atoms in the gas phase have had time to react and form CO, resulting in CO-
dominated ice. CH$_3$OH, which forms through CO hydrogenation, is the starting point of COM chemistry on grains (Sakai & Yamamoto 2013).

In this study, we explore the relationship between the COM precursor CH$_3$OH and the prototypical carbon chain C$_2$H in a sample of embedded protostars selected from the Spitzer c2d (cores to disk) ice survey. We further explore the relationship between C$_2$H and CH$_3$OH, and ice abundances in the same lines of sight. In Section 2 we describe our source sample and selection criteria. The IRAM 30 m observations are described in Section 3. The results and discussion are in Sections 4 and 5, respectively, and the conclusions are in Section 6.

2. SAMPLE SELECTION

Our sources were selected from the Spitzer c2d ice sample (Evans et al. 2003; Boogert et al. 2008). From the 51 sources in the Spitzer c2d ice sample presented in Boogert et al. (2008), we initially constrained ourselves to the northern low-mass sources, as they are easily observable with the IRAM 30 m, leaving us with 26 sources. The sources are characterized into different classes based on their spectral energy distributions, and in particular their IR spectral indices, $\alpha_{\text{IR}}$, defined as the slope between 2 and 24 $\mu$m. We chose sources with $\alpha_{\text{IR}} > 0.3$, which defines class 0/I sources (Wilking et al. 2001). These sources are often but not always associated with young embedded young stellar objects (YSOs); this cut left us with 19 sources. We then removed B1-b, IRAS 03301+3111, and EC 92 from our sample. B1-b was removed because previous observations of this source exist. IRAS 03301+3111 was removed because the upper limits on the ice abundances did not place any strong constraints on the data and EC 92 was removed because it was not resolvable from SVS 4-5 within the beam of the IRAM 30 m.

Table 1 lists the source coordinates, bolometric luminosities, envelope masses, and the IR SED indices together with the H$_2$O, CH$_3$OH, and CH$_3$O$_2$ ice abundances of our final sample. Our sources span $\alpha_{\text{IR}}$ from 0.34 to 2.70 and are situated in the Perseus, Taurus, Serpens, L1014, and CB244 clouds. The envelope masses are between 0.1 and 17.7 $M_{\odot}$ and the bolometric luminosities are between 0.32 and 38 $L_{\odot}$. Previous observations of WCCC sources fall within our range of bolometric luminosities (Chen et al. 1997; André et al. 2000). The H$_2$O ice column is between 0.4–39 $\times$ 10$^{18}$ cm$^{-2}$ and the $N_{\text{CH}_3OH}/N_{\text{H}_2O}$ and $N_{\text{CH}_3OH}/N_{\text{H}_2O}$ are 2%–25% and 1.6%–11%, respectively. Six of our sources (B1-a, B5 IRS 1, L1489 IRS, IRAS 04108+2803, SVS 4-5, and IRAS 03235+3004) were part of a study by Öberg et al. (2014) on COMs, including CH$_3$OH, in low-mass protostars. For these sources we recalculate the CH$_3$OH column densities using the CH$_3$OH integrated line intensities from Öberg et al. (2014) and our rotation diagram method.

3. OBSERVATIONS

All sources were observed with the IRAM 30 m telescope using the EMIR 90 GHz receiver and the Fourier Transform Spectrometer (FTS) backend. Six of the sources (B1-a, B5 IRS 1, L1489 IRS, IRAS 04108+2803, SVS 4-5, and IRAS 03235+3004) were observed on 2013 June 12–16 at 93–101 GHz and 109–117 GHz. The remaining sources were observed on 2014 July 23–28 at 92–100 GHz and 108–116 GHz. The
spectral resolution for both sets of observations was 200 kHz and the sideband rejection was $-15$ dB (Carter et al. 2012).

The pointing accuracy was checked every 1–2 hr and found to be within $2''$–$3''$. Focus, which was checked every 4 hr, remained stable with corrections of $<0.4$ mm. For the data set obtained in 2013 June, both the position-switching and wobbler-switching modes were used during observations, but the position-switching spectra has been excluded from this paper because of severe baseline instabilities; only wobbler switching was used for the 2014 July observations with a wobbler throw of $2'$. We exclude IRAS 03254+3050 from further analysis due to the significant self-absorption in the molecular targets of this study. No other source displayed signs of self-absorption in CH$_3$OH or C$_4$H. We also inspected the shapes of stronger lines, e.g. CN, in individual integrations and found no self-absorption in any high-density tracing line. This indicates a lack of dense material in the off position and therefore a low probability of CH$_3$OH and C$_4$H-emitting, material in the wobble off positions.

The spectra were reduced using CLASS$^2$ with a global baseline fit to each 4 GHz spectral chunk using four to seven line-free windows. Individual scans were baseline subtracted and averaged, and antenna temperature, $T_{a}$, was converted to main beam temperature, $T_{mb}$, by applying forward and beam efficiency values of 0.95 and 0.81. Using literature source velocities, the spectra were converted to rest frequency with additional adjustments made based on the CH$_3$OH 2-1 ladder. The CH$_3$OH 2-1 ladder emission was compared with previous observations for a subset of sources and was found to agree within 10% (Öberg et al. 2009a).

4. RESULTS

CH$_3$OH is detected in all 15 analyzed sources and C$_4$H in 13 sources at greater than 3$\sigma$. Two C$_4$H upper limits are also reported. Figures 1 and 2 display the CH$_3$OH and C$_4$H lines.

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$^2$ http://www.iram.fr/IRAMFR/GILDAS
toward all observed sources. For ease of comparison, the CH$_3$OH lines in Figure 1 are ordered in decreasing CH$_3$OH brightness from the top down. Figure 2 is ordered identically. Tables 2 and 3 list the integrated intensity of the CH$_3$OH and C$_4$H lines, respectively. The integrated intensity of CH$_3$OH lines of sources studied by Öberg et al. (2014) can be found in Table 2 of that paper. Most CH$_3$OH and all C$_4$H lines could be fit by a single Gaussian. Toward SVS 4-5 and B1-c, the
Table 3
Integrated C$_2$H Line Intensities in K km s$^{-1}$

| Source          | 95.150 GHz $N = 10-9$, $F = 11-10$ | 95.189 GHz $N = 10-9$, $F = 9-8$ | 114.183 GHz $N = 12-11$, $F = 12-11$ | 114.221 GHz $N = 12-11$, $F = 11-10$ |
|-----------------|------------------------------------|----------------------------------|----------------------------------------|---------------------------------------|
| B1-a            | 0.088[0.005]                       | 0.094[0.004]                     | 0.054[0.012]                           | 0.036[0.010]                          |
| SVS 4-5         | 0.142[0.007]                       | 0.130[0.008]                     | 0.090[0.013]                           | 0.112[0.010]                          |
| B1-c            | 0.119[0.008]                       | 0.111[0.004]                     | <0.027                                 | <0.023                                |
| IRAS 23238+7401 | 0.066[0.004]                       | 0.047[0.003]                     | 0.031[0.005]                           | 0.027[0.006]                          |
| L1455 IRS3      | 0.055[0.005]                       | 0.041[0.004]                     | <0.017                                 | <0.019                                |
| B5 IRS 1        | 0.138[0.008]                       | 0.124[0.010]                     | 0.059[0.010]                           | 0.068[0.016]                          |
| L1455 SMM1      | 0.092[0.010]                       | 0.081[0.005]                     | 0.041[0.006]                           | 0.061[0.009]                          |
| IRAS 03245+3002 | 0.070[0.005]                       | 0.061[0.007]                     | 0.052[0.009]                           | 0.023[0.007]                          |
| L1014 IRS       | 0.054[0.005]                       | 0.062[0.006]                     | 0.19[0.003]                            | <0.012                                |
| IRAS 04108+2803 | 0.022[0.003]                       | 0.030[0.007]                     | <0.017                                 | ...                                   |
| IRAS 03235+3004 | 0.163[0.003]                       | 0.147[0.004]                     | 0.062[0.005]                           | 0.106[0.007]                          |
| L1489 IRS       | ...                                 | <0.013                           | ...                                    | ...                                   |
| HH 300          | 0.047[0.006]                       | 0.038[0.005]                     | <0.021                                 | <0.022                                |
| IRAS 03271+3013 | 0.062[0.004]                       | 0.055[0.010]                     | 0.043[0.011]                           | 0.022[0.006]                          |
| L1448 IRS1      | ...                                 | ...                              | ...                                    | ...                                   |

Figure 3. Rotation diagrams for CH$_3$OH. The black dashed lines represent the fit to the lines. When a line could not be fit, denoted by the red dot–dash line, the average rotational temperature was used to derive the column density. Where no error bars are seen, the errors bars are smaller than the symbols.
CH$_3$OH lines display substantial wings, probably due to outflows in the beam, and these features were fit with 2–3 Gaussian components. Only the narrow central Gaussian components were used to derived the listed column densities, since their properties agreed the best with the C$_4$H line characteristics in the same lines of sight.

To determine the column densities of CH$_3$OH and C$_4$H, we used the rotation diagram method of Goldsmith & Langer (1999) and assumed optically thin lines and local thermodynamic equilibrium at a single temperature. Figures 3 and 4 display the rotation diagrams obtained for CH$_3$OH and C$_4$H, respectively. Sources observed by Öberg et al. (2014) were refit using a single-component rotation diagram to be consistent with the column density determinations of C$_4$H and the new CH$_3$OH observations.

Table 4 lists the derived column densities and rotational temperature obtained from the rotation diagram analysis. In situations where there were not enough lines with S/N > 3σ, the rotational temperature is assumed to be the average of the observed rotational temperatures; in these cases, $T_{\text{rot}}$ is italicized. On average, $T_{\text{rot}}$ for CH$_3$OH is $13 \pm 2$ K and $24 \pm 5$ K for C$_4$H. It is important to note that for this class of objects the CH$_3$OH rotational temperatures do not necessarily reflect the kinetic temperatures, but are rather lower limits (Öberg et al. 2014). The difference in excitation temperature for CH$_3$OH and C$_4$H thus cannot be used to constrain the relative emission regions of CH$_3$OH and C$_4$H.

The observed column density distributions of C$_4$H and CH$_3$OH are displayed in Figure 5 along with their respective average column densities. The column densities of both species span approximately an order of magnitude and the average column densities of $9.1 \times 10^{13}$ cm$^{-2}$ and $1.0 \times 10^{14}$ cm$^{-2}$ for C$_4$H and CH$_3$OH, respectively, are similar. The WCCC sources from Sakai et al. (2008, 2009a, 2009b) overlap with the high end of our C$_4$H distribution. Classical hot corino sources (Maret et al. 2005; Sakai et al. 2009a) overlap with the high end of the CH$_3$OH distribution and the low end of our distribution for C$_4$H. However, as seen below, classical hot corino sources form a distinct subgroup when simultaneously taking into account the column densities of both species compared with any sources in our sample.

Figure 4. Rotation diagrams for C$_4$H. The black dashed lines represent the fit to the lines. When a line could not be fit, denoted by the red dot–dash line, the average rotational temperature was used to derive the column density. Where no error bars are seen, the errors bars are smaller than the symbols.
Table 4

| Source         | N(CH$_3$OH) $10^{13}$ cm$^{-2}$ | T$_{rot}$(CH$_3$OH)$^a$ K | N(C$_4$H) $10^{11}$ cm$^{-2}$ | T$_{rot}$(C$_4$H)$^b$ K |
|---------------|-------------------------------|----------------------------|-------------------------------|------------------------|
| B1-ab         | 44 [14]                      | 13 [3]                     | 11.9 [2.8]                    | 22 [4]                 |
| SVS 4-5b      | 49 [19]                      | 13 [4]                     | 10.6 [2.1]                    | 35 [8]                 |
| B1-c          | 7.3 [2.2]                    | 17 [5]                     | 13.3 [0.7]                    | 24 [5]                 |
| IRAS 23238    | 9.4 [4.4]                    | 12 [5]                     | 6.7 [1.0]                     | 23 [3]                 |
| +7401         |                               |                            |                              |                        |
| L1455 IRS3    | 5.9 [3.6]                    | 10 [4]                     | 5.5 [0.5]                     | 24 [5]                 |
| B5 IRS1       | 7.7 [2.0]                    | 13 [6]                     | 17.4 [2.6]                    | 22 [2]                 |
| L1455 SMM1    | 6.4 [3.3]                    | 13 [6]                     | 8.8 [2.8]                     | 26 [7]                 |
| IRAS 03245    | 6.6 [1.2]                    | 17 [3]                     | 7.6 [3.5]                     | 24 [9]                 |
| +3002         |                               |                            |                              |                        |
| L1014 IRS     | 3.7 [2.4]                    | 11 [6]                     | 15.8 [4.2]                    | 16 [2]                 |
| IRAS 04108    | 4.5 [1.9]                    | 12 [4]                     | 3.1 [0.4]                     | 24 [5]                 |
| +2803$^a$     |                               |                            |                              |                        |
| IRAS 03235    | 5.1 [0.3]                    | 13 [2]                     | 18.3 [7.4]                    | 24 [7]                 |
| +3004$^b$     |                               |                            |                              |                        |
| L1489 IRS1    | 3.0 [0.6]                    | 13 [2]                     | <1.5                         | 24 [5]                 |
| HH 300        | 1.0 [0.4]                    | 13 [2]                     | 4.9 [0.6]                     | 24 [5]                 |
| IRAS 03271    | 1.8 [0.2]                    | 13 [2]                     | 6.9 [2.5]                     | 27 [7]                 |
| +3013         |                               |                            |                              |                        |
| L1448 IRS1    | 1.0 [0.2]                    | 13 [2]                     | <3.6                         | 24 [5]                 |

Notes.

$^a$ $T_{rot}$ values in italics are assumed rotational temperatures and are based on the average $T_{rot}$ in the source with standard deviation errors. The listed errors are the 1σ uncertainty.

$^b$ Sources observed by Öberg et al. (2014).

Figure 6 displays the column density correlation plots for CH$_3$OH and C$_4$H, both absolute and normalized to the H$_2$O ice column. As H$_2$O ice is the first ice to form and the last to desorb during star formation, its column should be a good proxy of the envelope material in the line of sight (Boogert et al. 2015).

For both column density correlation plots, there appears to be a positive correlation. To determine the statistical significance of the correlation, a Spearman’s (rho) rank correlation tests were performed. The absolute column densities are not significantly correlated. By contrast, the normalized (to water ice) column densities are significantly positively correlated at the >99% level applying the Spearman’s rank correlation test.

In Figure 6 the warm carbon chain source, L1527, is displayed as a teal square and falls within our observed columns for both CH$_3$OH and C$_4$H (Sakai et al. 2008, 2009b). The red diamonds display three classic hot corino sources (Maret et al. 2005; Sakai et al. 2009b). The three hot corino sources and the WCCC source L1527 in Figure 6 display an anti-correlation. This is consistent with the anti-correlation noted by Sakai et al. (2008). When combing the hot corino and WCCC sources with our sample, we see two distinct regions: a positive correlation for low to medium column densities of CH$_3$OH, while the hot corino sources occupy a unique space characterized by high CH$_3$OH and low C$_4$H column densities.

The difference between our sample and the hot corino sources suggest that CH$_3$OH/C$_4$H may trace an evolutionary sequence. We used the IR spectral indices, $\alpha_{IR}$, as a proxy for age since $\alpha_{IR}$ decreasing signifies an increasing age (Wilking et al. 2001). We find no relationship for the CH$_3$OH/C$_4$H ratio to $\alpha_{IR}$, indicating that there is no evolutionary sequence within our sample. Instead observed variations in the CH$_3$OH/C$_4$H ratio in our sample (visible in Figure 6 as a large spread in CH$_3$OH column densities for any specific C$_4$H column density) seems to be the result of different initial ice compositions.

Figure 7 shows a positive correlation between the C$_4$H/CH$_3$OH gas and the ice phase CH$_3$/CH$_3$OH. The correlation is not statistically significant due to the many ice upper limits; however, it does suggest a relationship between gas and ice abundances for these species. When CH$_3$H gas and CH$_4$ ice, and CH$_3$OH ice and gas are considered separately, there seems to be a stronger relationship between the gas and ice phase hydrocarbons (Figure 7, bottom) than between CH$_3$OH gas and ice (Figure 7, middle).

5. DISCUSSION

In this study, we observed 16 embedded protostars to determine the relationship between CH$_3$OH and C$_4$H. We find that there is a positive correlation between the column density of CH$_3$OH and C$_4$H. Several of the sources have COM detections in addition to CH$_3$OH (Öberg et al. 2014). WCCC and COM chemistry are thus not mutually exclusive during the embedded stages of star formation. Rather, carbon chain and COM formation seem to follow one another up until the onset of an efficient hot corino chemistry. Once the hot corino has formed, CH$_3$OH and C$_4$H are no longer correlated (Maret et al. 2005).

Aikawa et al. (2012) modeled the chemistry from a prestellar core up to the formation of the protostellar envelope and found that both carbon chains and COMs can be present in the colder outer envelope. Aikawa et al. (2012) attribute the formation of the carbon chains to an increase in the C$^+$ abundance in
The presence of CH$_3$OH in the envelope is due to nonthermal sublimation of CH$_2$OH ice. Contrary to C$_2$H, CH$_3$OH is also abundant toward the protostellar core due to thermal sublimation. The abundance of CH$_2$OH in the protostellar core can be many orders of magnitude higher than the outer envelope emission, but its contribution to observed emission can be quite negligible if the volume of thermally sublimated CH$_2$OH is small compared with the protostellar envelope volume. Should the emission from the thermally sublimated CH$_2$OH dominate the CH$_3$OH envelope emission, the source would be considered a hot corino.

Within our source sample, envelope ice abundances explain variations in the C$_2$H/CH$_3$OH ratio. The CH$_3$OH ice and gas columns (Figure 7, middle) are not clearly related, however. If all CH$_2$OH in all of the sources originated from nonthermal desorption there should be a correlation between CH$_2$OH gas and ice abundances. On the other hand, if some CH$_3$OH is due to thermal desorption, the source luminosity will influence the CH$_2$OH emission, muddling the expected CH$_2$OH gas and ice correlation. As we observe no correlation, it is likely that we are probing both thermal and nonthermal desorption processes.

The observed tentative C$_2$H–CH$_4$ ice correlation indicates that the formation of C$_2$H depends on the initial abundance of CH$_4$ ice. The thermal sublimation of CH$_4$ ice to promote WCCC was initially suggested by Sakai et al. (2008) and is consistent with current chemical models (Hassel et al. 2011; Aikawa et al. 2012). Not all C$_2$H may originate from this process, however, as some may be inherited from the molecular cloud. An unusually high contribution of inherited C$_2$H may explain the outlier with a high C$_2$H gas column and a low CH$_4$ ice upper limit (IRAS 03271+3010) in Figure 7. A possible explanation for such a high contribution may be that this source is very young.

In addition to ice abundances, the chemistry of C$_2$H and CH$_3$OH may depend on environmental parameters such as envelope mass and bolometric luminosity. A higher bolometric luminosity should result in a larger hot corino region. If this is the main regulator for the COMs–carbon chain relationship, the CH$_3$OH/C$_2$H ratio would increase toward more luminous protostars. We do not find any correlation between this ratio and source luminosity (Tables 1 and 4). It is more difficult to assess the importance of the initial envelope mass on the chemistry, since envelope mass evolves with time. A current low envelope mass measurement may signify either a low-mass protostar or an older more massive protostar. We do not find any correlation between the CH$_2$OH/C$_2$H ratio and envelope mass alone (Tables 1 and 4). The small sample size prevented a more detailed analysis of the combined influence of mass and age on the chemistry. We also do not see any relationships between these environmental parameters and the absolute column densities of C$_2$H and CH$_3$OH.

As reported in Section 4 we also find no correlation with $\alpha_{IR}$, an age indicator, and the CH$_3$OH/C$_2$H ratio. For young embedded protostars the “age” of the system does not seem to affect the relative importance of carbon chain and COM chemistry, i.e., C$_2$H and CH$_3$OH coexist in the envelope at this evolutionary stage. In Figure 6 the boomerang shape may indicate an evolutionary trend when comparing these young objects with more evolved ones. This is consistent with models. As the protostar transitions into the hot corino stage, the temperature is high enough to both destroy carbon chains and thermally desorb CH$_3$OH, resulting in an anti-correlation in the observed C$_2$H and CH$_3$OH column densities (Aikawa et al. 2012).

6. CONCLUSIONS

We surveyed 16 northern sources selected from the Spitzer c2d ice sample using the IRAM 30 m and found the following.

1. C$_2$H and CH$_3$OH coexist and are correlated at the deeply embedded stage of low-mass protostellar evolution. This can be explained by lukewarm environments in the protostellar envelopes that promote WCCC alongside nonthermal desorption of CH$_3$OH.

2. The CH$_3$OH/C$_2$H correlation does not extend into the hot corino phase. This is indicative of an evolutionary sequence where carbon chains and COMs coexist in
luke warm protostellar envelopes, but once a hot corino forms, COMs are enhanced and carbon chains are destroyed.

3. The ice and gas abundances are related in these sources based on a tentative correlation between CH$_3$OH/C$_2$H gas ratio and CH$_3$OH/CH$_4$ ice ratio. It is likely that the C$_2$H gas and CH$_4$ ice correlation is what is driving this relationship, suggesting that WCCC is intimately connected to the CH$_4$ ice abundance.

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Figure 7. Ice and gas correlation plots from our sample. The top plot displays the CH$_3$OH to CH$_4$ ice ratio vs. the C$_2$H$_2$ to CH$_3$OH gas ratio. The middle plot displays the ice CH$_3$OH vs. the gas CH$_3$OH columns and the bottom plot displays the ice CH$_4$ vs. the gas C$_2$H$_2$ columns. Both of the bottom two plots are normalized to the H$_2$O ice column density and the gray data points indicate the upper limits.
An error was found in the calculation of the presented CH₃OH and C₄H column densities. For both CH₃OH and C₄H, there was a conversion error (log₁₀ to natural log) when fitting the rotational temperature in Figures 3 and 4 of the original article. When corrected, the rotational temperatures decrease by a factor of $\sim 2$ for all sources which affects the partition function value and hence, the column densities. As a result of this error, the CH₃OH column densities were underestimated by a factor of $\sim 4$, and the C₄H column densities by a factor of $\sim 2.5$ toward all the sources in the sample. In addition, we found an error in the treatment of the C₄H hyperfine splitting. When corrected, the C₄H column densities are an additional factor of $\sim 2$ lower.

Table 1 updates Table 4 in the original article, listing the recalculated column densities and rotational temperatures. The updated rotational diagrams for CH₃OH and C₄H are shown in Figures 1 and 2, respectively. Figures 3 and 4 display the updated Figures 5 and 6 from the original article. The authors would like to emphasize that these errors do not change or affect the conclusions of the original article.

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### Table 1

| Source          | N(CH₃OH) $10^{13}$ cm$^{-2}$ | T$_{rot}$(CH₃OH)$^a$ K | N(C₄H) $10^{13}$ cm$^{-2}$ | T$_{rot}$(C₄H)$^a$ K |
|-----------------|------------------------------|-------------------------|-----------------------------|-----------------------|
| B1-a$^b$        | 10.2 [3.2]                   | 5.8 [1.3]               | 2.5 [0.6]                   | 9.6 [1.7]             |
| SVS 4-5$^b$     | 11.2 [4.3]                   | 5.8 [1.6]               | 2.2 [0.4]                   | 15 [3]               |
| B1-c            | 1.7 [0.5]                    | 7.2 [2.0]               | 2.7 [0.2]                   | 10 [2]               |
| IRAS            | 2.2 [1.0]                    | 5.4 [2.2]               | 1.4 [2.2]                   | 10 [1]               |
| 23238+7401      |                             |                         |                            |                      |
| L1455 IRS3      | 1.5 [0.9]                    | 4.4 [1.9]               | 1.1 [0.3]                   | 10 [2]               |
| B5 IRS 1$^b$    | 1.8 [0.5]                    | 5.7 [1.3]               | 3.6 [0.5]                   | 9.5 [1.0]            |
| L1455 SMM1      | 1.5 [0.8]                    | 5.7 [2.7]               | 1.8 [0.5]                   | 11 [7]               |
| IRAS            | 1.5 [0.3]                    | 7.4 [1.4]               | 1.6 [0.7]                   | 10 [4]               |
| 03245+3002      |                             |                         |                            |                      |
| L1014 IRS       | 0.88 [0.56]                  | 4.8 [2.4]               | 3.2 [0.8]                   | 6.9 [1.0]            |
| IRAS 04108 +2803$^b$ | 1.0 [0.4]                   | 5.1 [1.6]               | 0.64                        | 10 [2]               |
| IRAS 03235 +3004$^b$ | 1.2 [0.8]                   | 5.7 [1.0]               | 3.8 [1.5]                   | 10 [3]               |
| L1489 IRS$^b$   | 0.69 [0.14]                  | 5.7 [1.0]               | <0.32                       | 10 [2]               |
| HH 300          | 0.24 [0.09]                  | 5.7 [1.0]               | 1.0 [3.2]                   | 10 [2]               |
| IRAS            | 0.42 [0.04]                  | 5.7 [1.0]               | 1.4 [0.5]                   | 10 [3]               |
| 03271+3013      |                             |                         |                            |                      |
| L1448 IRS1      | 0.23 [0.04]                  | 5.7 [1.0]               | <0.73                       | 10 [2]               |

**Notes.**

$^a$ T$_{rot}$ values in italics are assumed rotational temperatures and are based on the average T$_{rot}$ in the source with standard deviation errors.

$^b$ Sources observed by Öberg et al. (2014).
Figure 1. Updated Rotation Diagrams for CH₃OH displaying the recalculated column densities and rotational temperatures. The black dashed lines represent the fit to the lines. When a line could not be fit, denoted by the red dot-dash line, the average rotational temperature was used to derive the column density. Where no error bars are seen, the errors bars are smaller than the symbols.
Figure 2. Updated Rotation Diagrams for C$_2$H displaying the recalculated column densities and rotational temperatures. The black dashed lines represent the fit to the lines. When a line could not be fit, denoted by the red dot-dash line, the average rotational temperature was used to derive the column density. Where no error bars are seen, the errors bars are smaller than the symbols.
Figure 3. Updated histograms of the column density of C₄H and CH₃OH with the recalculated column densities. The solid bars are detections and line-filled bars indicate upper limits. The average column density is also listed in the upper left hand corner.
Figure 4. Updated correlation plots for the column density of C$_4$H and CH$_3$OH from our sample using the recalculated column density values. The left plot displays the pure column density correlation where the black data points are our data, the teal square is L1527 (Sakai et al. 2008, 2009), and the red diamonds are three hot corino sources (Maret et al. 2005; Sakai et al. 2009). The right plot displays the CH$_3$OH to C$_4$H correlation following a normalization using the H$_2$O ice column density.

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