

Observations of Complex Molecules in Low-Mass Protostars

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Abstract. Low-mass star forming regions are rich inventories of complex organic molecules. Furthermore, they show significant chemical diversity even among sources in a similar physical evolutionary stage (i.e. Class 0 sources). One distinct case is the hot corino chemistry characterized by rich existence of saturated complex organic molecules such as HCOOCH_3 and $\text{C}_2\text{H}_5\text{CN}$, whereas the other is the warm carbon-chain chemistry (WCCC) characterized by extraordinary richness of unsaturated complex organic molecules such as carbon-chain molecules. We here summarize these observational achievements during the last decade, and present a unified picture of carbon chemistry in low-mass protostellar cores. The chemical diversity most likely originates from the source-to-source difference in chemical compositions of grain mantles. In particular, the gas-phase abundance of CH_4 evaporated from grain mantles is thought to be a key factor for appearance of WCCC. The origin of the diversity and its evolution to protoplanetary disks are discussed.

Keywords. ISM: molecules, ISM: abundances, stars: formation

1. Introduction

So far more than 160 interstellar molecules have been identified mainly by radioastronomical observations, and about 1/3 of them are 'complex' molecules having 6 atoms or more (c.f. Herbst & van Dishoeck 2009). This clearly indicates the high chemical complexity of interstellar medium, which would ultimately be related to an origin of rich substances in our solar system. Hence, a detailed understanding of the chemical composition and its evolution in star forming regions is a central issue for astrochemistry.

Complex organic molecules (COMs) are classified into two general groups, saturated COMs and unsaturated COMs. Saturated COMs are fully or almost fully hydrogenated molecules such as CH_3OH , HCOOCH_3 , $(\text{CH}_3)_2\text{O}$, and $\text{C}_2\text{H}_5\text{CN}$. These molecules are known to exist abundantly in hot cores in high-mass star forming regions. Since the gas-phase chemical reactions cannot produce them efficiently, they are thought to be formed by grain surface reactions (e.g., Charnley *et al.* 1997; Watanabe & Kouchi 2002; Garrod & Herbst 2006; Herbst & van Dishoeck 2009). The produced molecules stay on grain mantles in the cold phase, and they are liberated into the gas phase after the birth of high-mass stars. Since 1980s, the hot core chemistry has extensively been studied to account for the observational results in various high-mass star forming regions and external galaxies (e.g., Blake *et al.* 1987; Millar *et al.* 1991; Nomura & Millar 2004; Herbst & van Dishoeck 2009). On the other hand, unsaturated COMs are represented by so called carbon-chain molecules having rich multiple bonds. They are known to exist abundantly and preferentially in young starless cores such as TMC-1. In fact, carbon-chain molecules are dominant organic molecules in TMC-1, according to the spectral line survey by Kaifu *et al.* (2004). Carbon-chain molecules are thought to be produced in the gas phase starting from C^+ and C, and hence, they are only abundant in young starless

cores, where C^+ and C have not been converted to CO completely (Suzuki *et al.* 1992; Benson *et al.* 1998).

In contrast to the extensive astrochemical studies on high-mass star forming regions and cold starless cores, chemistry of low-mass star forming regions was sparsely studied until 1990s. A pioneering study toward this direction is the spectral line survey of the low-mass Class 0 protostar, IRAS 16293-2422, by Blake *et al.* (1994) and van Dishoeck *et al.* (1995). They studied the chemical composition of this source in an unbiased way for the first time. Although they found rich CH_3OH and SO_2 , which can be recognized as a signature of the hot-core like chemistry, they could not detect the lines of larger COMs such as $HCOOCH_3$, $(CH_3)_2O$, and C_2H_5CN at that time, probably because of insufficient sensitivities in their observations. The chemical composition of low-mass star forming regions is of fundamental importance, because it can be regarded as the initial condition for chemical evolution to protoplanetary disks and planets. Thanks to great improvements of sensitivity in millimeter- and submillimeter-wave observations, such studies have extensively been carried out in 2000s, resulting in the following discoveries.

2. Hot Corino Chemistry and Warm Carbon-Chain Chemistry

First discovery was the detection of large saturated COMs such as $HCOOCH_3$, $(CH_3)_2O$, and C_2H_5CN in the low-mass star-forming region, IRAS16293-2422 (Cazaux *et al.* 2003), revealing that the hot-core like chemistry is also occurring even in a low-mass source. Furthermore, the interferometric observations showed that these molecules are distributed within a few 100 AU region (at temperature of ~ 100 K) around the protostar (Bottinelli *et al.* 2004b; Kuan *et al.* 2004). These results along with subsequent detections of the saturated COMs in other low-mass star forming regions clearly demonstrated that fairly complex organic molecules are already formed in the protostellar-core phase, which would be brought into protoplanetary disks. Then, it was thought that they may be related to an origin of pre-solar organic molecules found in meteorites (e.g., Cronin & Pizzarello 1997 and references therein). Just as in the case of the hot core chemistry in high-mass star forming regions, saturated COMs are formed on dust grains during cold and warm-up phases (Garrod & Herbst 2006), and are liberated into the gas phase in a small hot region (a few 100 AU) around the protostar, called hot corino. Now four Class 0 protostars (IRAS 16293-2422, NGC1333 IRAS4A, IRAS4B, and IRAS2A) are known to harbor hot corinos (Cazaux *et al.* 2003; Bottinelli *et al.* 2004a; Jørgensen *et al.* 2005; Sakai *et al.* 2006; Bottinelli *et al.* 2007).

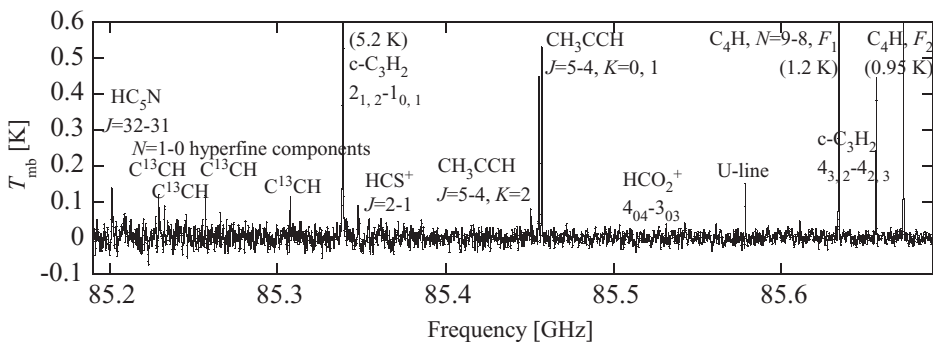


Figure 1. A portion of the spectral line survey toward L1527 observed with the Nobeyama 45 m telescope. Peak intensities are reduced by a factor of about 2 because of the narrow line width (~ 0.5 km s^{-1}) in comparison with the velocity resolution of the spectrometer (~ 0.8 km s^{-1}). In addition to the bright lines of C_4H and $c-C_3H_2$, even the very high excitation line of HC_5N ($J = 32 - 31$, $E_u = 67$ K) can be seen.

On the other hand, the extraordinary richness of unsaturated COMs such as C_4H , C_4H_2 , and HC_5N was found in the lukewarm region around the low-mass Class 0 protostar, L1527 (Sakai *et al.* 2008a). For instance, the high excitation lines of C_4H ($N = 9-8$), C_2H ($N = 3-2$) were detected with very high intensities (Figure 1). Emissions of various long carbon-chain molecules and their anions like C_4H^- and C_6H^- were also detected (e.g. Sakai *et al.* 2007, 2008b; Agúndez *et al.* (2008)) (Figure 2), while the lines of saturated COMs were not (Sakai *et al.* 2008c). Hence, the protostellar core L1527 has a completely different chemical composition from that of hot corinos. A small mapping observation of C_4H with the Nobeyama 45 m telescope shows that the distribution is concentrated toward the protostar in a few thousand AU. More importantly, the line width becomes broader toward the protostar position. It is therefore highly likely that carbon-chain molecules do exist even in the gas infalling to the protostar. This result is striking, since it had been thought that carbon-chain molecules are abundant only in young starless cores and deficient in the evolved starless cores and star forming cores (e.g., Suzuki *et al.* 1992; Benson *et al.* 1998). To account for these results, a new production scheme of carbon-chain molecules triggered by evaporation of CH_4 from ice mantles was proposed (Sakai *et al.* 2008a). It is called warm carbon-chain chemistry (WCCC). The sublimation temperature of CH_4 is 25 K (Collings *et al.* 2004), being much lower than

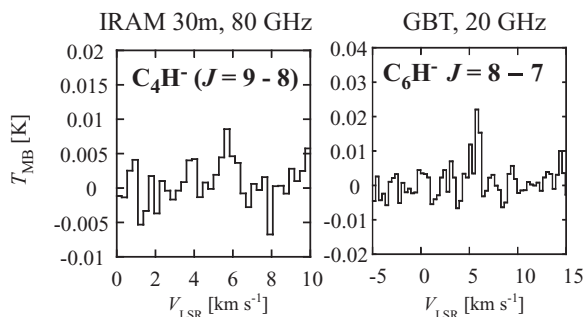


Figure 2. Spectral line profiles of carbon-chain anions observed toward L1527 (Sakai *et al.* 2007, 2008b).

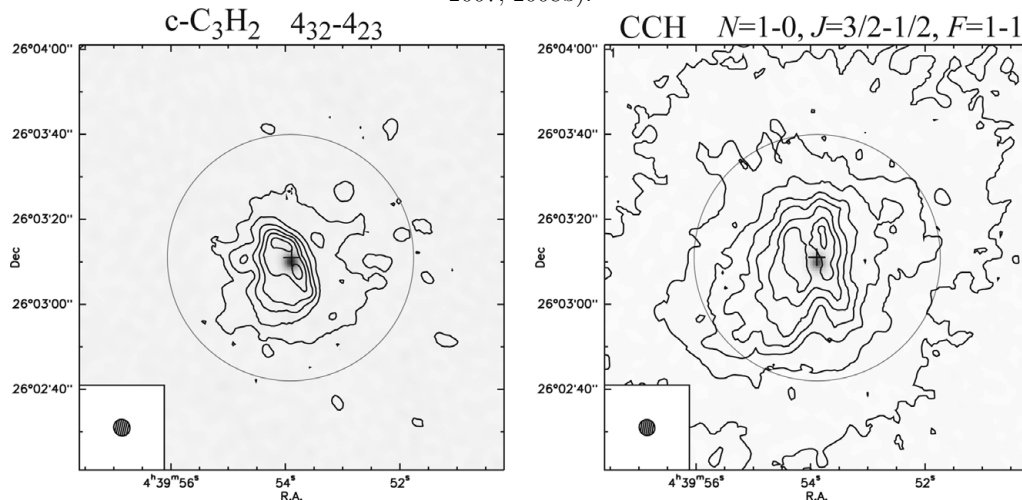


Figure 3. Integrated intensity maps of $c-C_3H_2$ and CCH observed toward L1527 with PdBI (Sakai *et al.* 2010). The maps are prepared by combining the single dish (IRAM 30 m) data to recover the extended component. The circles represent a field of view of PdBI.

that of H_2O . Hence, CH_4 is evaporated in a warm region extending to a few thousand AU, and reacts with C^+ in the gas phase to produce various carbon-chain molecules. The basic mechanism of WCCC was independently confirmed by chemical model calculations (Aikawa *et al.* 2008; Hassel *et al.* 2008; Harada & Herbst 2008).

An important question is then whether such peculiar chemistry is specific to L1527 or not. With this in mind, we searched for a similar source among many low-mass protostars, and finally found the second WCCC source, IRAS 15398-3359, in Lupus molecular cloud 1 ($d = 150$ pc) (Sakai *et al.* 2009a). Its spectral features resemble those in L1527, and various carbon-chain molecules are as abundant as in L1527. Furthermore, the distribution of the high excitation line of CCH ($N = 4 - 3$) shows central concentration around the protostar. According to the Spitzer observations, a deep infrared absorption feature of solid CH_4 is seen toward this source (Öberg *et al.* 2008), implying a favorable condition for WCCC. The discovery of the WCCC source outside the Taurus region suggests that WCCC can no longer be ascribed to a peculiarity of a particular region, but should be regarded as one of characteristic chemical features of low-mass protostellar cores.

Recently, we conducted an interferometric observation of carbon-chain molecules and their related molecules toward L1527 with PdBI, and confirmed that carbon-chain molecules are distributed within a few thousand AU around the protostar, as shown in Figure 3 (Sakai *et al.* 2010). The distributions show a steep increase inward of a radius of 500-1000 AU from the protostar, implying an abundance jump by an order of magnitude. The radius corresponds to the dust temperature of 20-30 K, which is just around the evaporation temperature of CH_4 . This result further supports the WCCC in L1527. More interestingly, a small dip (500 AU scale) can be seen toward the protostar position. We carried out a simple radiative transfer calculation by employing the density and temperature structure of the L1527 protostellar core reported by Jørgensen *et al.* (2002), and found that the abundance of the carbon-chain molecules decreases in the innermost part by a factor of 10. Nevertheless, carbon-chain molecules are thought to survive partly in the gas infalling to the protostar, since the blue- and red-shifted components by ~ 1 km s $^{-1}$ are centrally concentrated (See Figures 2-4 of Sakai *et al.* (2008a)). Hence, it is likely that a portion of carbon-chain molecules produced in the Class 0 phase will be delivered to the protostellar disk.

3. Origin and Future of the Chemical Diversity

So far, it has been thought that the chemical compositions of low-mass star forming regions are more or less uniform, and hence, the chemical evolution from a protostellar disk to a protoplanetary disk has no significant variations. However, the above observational

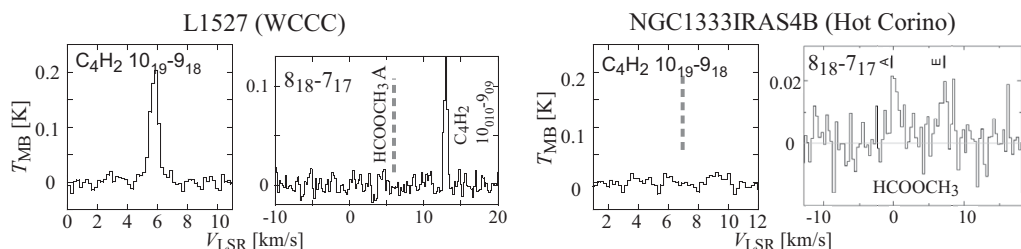


Figure 4. Chemical diversity of the Class 0 sources. In the WCCC source L1527, the carbon-chain molecules are abundant, whereas the complex organic molecules tend to be deficient. In the hot corino source NGC1333 IRAS4B, the situation is opposite. The C_4H_2 and HCOOCH_3 spectra in L1527 are taken from Sakai *et al.* (2008a) and Sakai *et al.* (2008c), respectively. The HCOOCH_3 spectrum in NGC1333 IRAS4B is from Sakai *et al.* (2006).

results clearly demonstrate diversity of chemical compositions in low-mass protostellar cores. At present, we know the hot corino and WCCC sources as the two extreme cases. These two types of sources show exclusive nature in chemical compositions. In hot corinos, unsaturated COMs such as carbon-chain molecules are generally deficient, whereas in WCCC sources, saturated COMs such as HCOOCH_3 are deficient (Figure 4). This implies that the chemical evolution to the protoplanetary disk is not a single pathway, and the chemical compositions of protoplanetary disks could be different from source to source.

3.1. Carbon Chemistry around Low-Mass Protostar

To consider the origin of the chemical diversity, we first summarize the chemical processes which would occur during the temperature raise due to protostellar activities. We start from a cold ($T < 10$ K) dense starless core, where most of the molecules except for H_2 are depleted on dust grains and no carbon chemistry is occurring. After the birth of the protostar, the temperature starts to rise. We can define the following three major steps in carbon-chemistry.

(1) Restart of carbon-chemistry ($T \sim 20$ K): At about 20 K, CO is evaporated from grain mantles, which restarts the basic carbon-chemistry by the $\text{He}^+ + \text{CO} \rightarrow \text{C}^+ + \text{O} + \text{He}$ reaction. The produced C^+ reacts with H_2 to form CH_2^+ , and then makes various organic molecules. This is essentially the same as the conventional carbon chemistry in young starless cores (e.g., Herbst 1983). Since the $\text{C}^+ + \text{H}_2$ reaction is a slow radiative-association process, the efficiency to produce organic molecules is not very high.

(2) Warm carbon-chain chemistry ($T \sim 25$ K): When the temperature is raised up to 25 K, CH_4 can be evaporated. This realizes a temporary carbon-rich condition in the gas phase. Since C^+ already exists in stage (1), CH_4 reacts with C^+ to produce carbon-chain molecules. For this process to be effective, the fractional abundance of CH_4 relative to H_2 in the gas phase should be higher than several times 10^{-7} . In this case, CH_4 can be a major reactant for C^+ in place of OH and other molecules. Note that H_2O is still frozen on dust grains, and does not contribute to the C^+ destruction in this stage.

(3) Hot corino chemistry ($T = 70 - 100$ K): The ice mantle will be evaporated at this temperature. Complex organic molecules trapped in the ice mantle will also be released into the gas phase, which realizes the hot corino chemistry. At the same time, the $\text{C}^+ + \text{CH}_4$ reaction will be suppressed, because overwhelming H_2O molecules act as the main destructor of C^+ . The $\text{C}^+ + \text{H}_2\text{O}$ reaction just reproduces CO through HCO^+ . This would result in the deficiency of carbon-chain molecules.

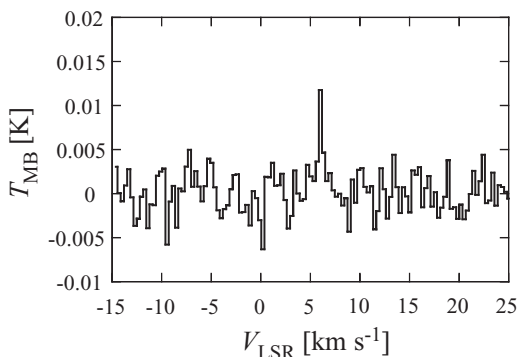


Figure 5. Spectral line profile of CH_3D ($J_K = 1_0 - 0_0$) observed toward L1527 with HHST.

According to the above picture, the WCCC becomes effective only when the gas-phase CH_4 abundance is higher than several times 10^{-7} . In this case, the chemical evolution will proceed in order of (1), (2), and (3). If the CH_4 abundance is not enough for WCCC, the evolution will proceed from (1) to (3) directly by skipping stage (2). Hence, the gas-phase CH_4 abundance is a key factor for appearance of WCCC. In fact, we have recently detected the rotational spectral line of CH_3D toward the prototypical WCCC source, L1527, and have found that the derived CH_4 abundance ($f = (4.3 - 15.2) \times 10^{-6}$) indeed fulfills this criterion (Figure 5). A significant spread in the $\text{CH}_4/\text{H}_2\text{O}$ abundance ratio in the solid phase is seen in infrared observations of low-mass protostars (Öberg *et al.* 2008). Considering that the difference of the CH_4 abundance would be amplified in abundances of carbon-chain molecules through their formation processes, it is highly likely that the abundance of CH_4 supplied from grain mantles would control the chemical composition in the low-mass protostars. In the present stage, it is not certain whether the WCCC sources have a hot corino activity in the closest vicinity of the protostar. However, the hot corino activity should be weak even if it does exist, since the CH_3OH lines ($J_K = 7_K - 6_K$) are much weaker in the WCCC sources than in the hot corino sources (Jørgensen *et al.* 2007; Sakai *et al.* in prep) and large saturated COMs are not detected in L1527. This situation is schematically shown in Figure 6.

From the above considerations, the chemical diversity would not originate from a simple evolutionary effect, but the different chemical compositions of grain mantles are needed to be considered. This is consistent with the fact that the hot corino sources are not always more evolved than the WCCC sources.

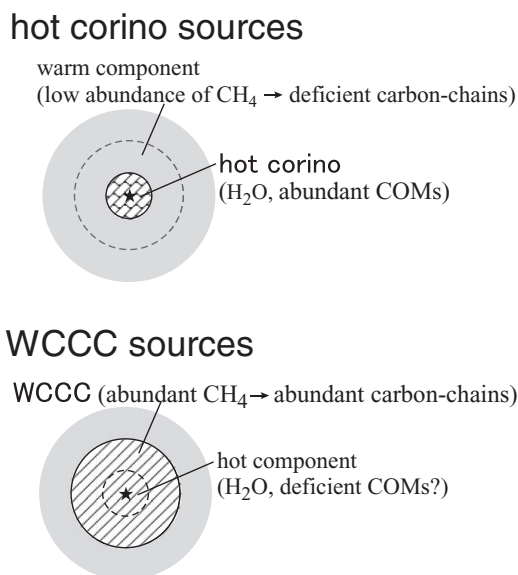


Figure 6. Physical appearance of the hot corino sources and the WCCC sources. In the hot corino sources, carbon-chain molecules are deficient over the protostellar core, whereas saturated COMs are abundant in the vicinity of the protostar (a few hundred AU). In the WCCC sources, carbon-chain molecules are distributed abundantly in a lukewarm region near the protostar (a few thousand AU). On the other hand, large saturated COMs are not detected, indicating that the hot corino activity is very weak.

3.2. Origin of the Different Mantle Compositions

As seen in the above unified picture of carbon chemistry in low-mass star forming regions, hot corino chemistry and the WCCC would reflect the different chemical compositions of grain mantles. This difference would reflect the past history during the starless core phase, when the grain mantle had grown up. One important factor is the duration time of the starless-core phase (Sakai *et al.* 2009a) (Figure 7). It could depend on large-scale environmental effects including magnetic field strength and turbulent energy input. The WCCC prefers the short starless-core phase. In this case, more carbon atoms are depleted directly onto dust grains before being converted to CO in the gas phase, which makes more CH₄ on dust grains by hydrogenation. In contrast, the hot corino chemistry requires the long starless-core phase. In this case, CO is mainly depleted onto dust grains to form saturated COMs, whereas CH₄ is hardly produced.

The short starless-core phase for the WCCC sources is also supported by the deuterium fractionation ratios. Sakai *et al.* (2009b) observed many deuterated carbon-chain molecules, and found that the deuterium fractionation ratios are moderate (2-7 %). The CH₂DOH/CH₃OH ratio is derived to be lower than 3 %, which is much lower than that found in hot corinos (Parise *et al.* 2006). The observed ratios mean less degree of the CO depletion, which is consistent with the short time scale of the starless-core phase.

The two cases shown in Figure 7 are the extreme ones, and the intermediate case would be possible, depending on the length of the starless-core phase. In this way, the continuous chemical variation shown in our C₄H survey (Sakai *et al.* 2009a) can naturally be interpreted. If this is the case, we would be able to obtain novel information on the past contracting process of the parent core from what type of chemistry is now occurring near the protostar. We think that this can be a new approach to understanding physical processes in the early stages of star formation.

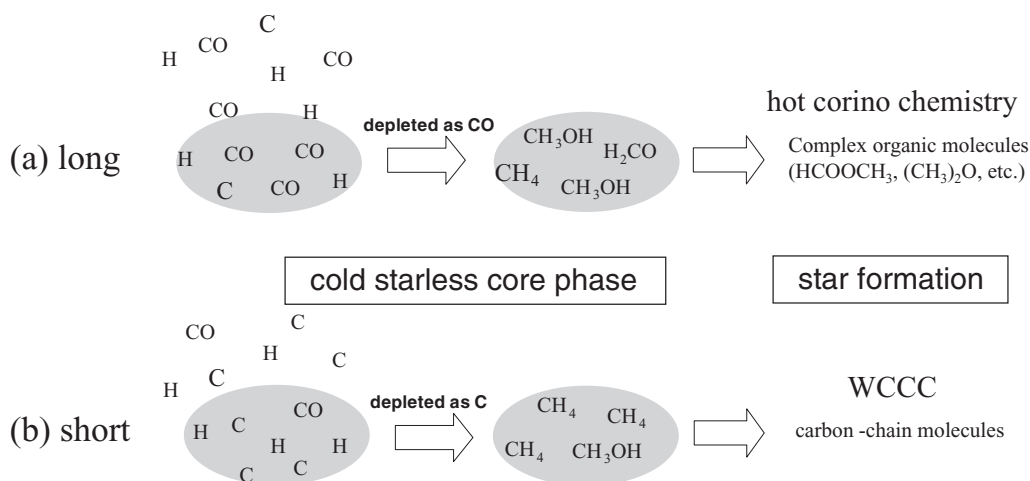


Figure 7. Origin of chemical variation. The two extreme cases are shown. The case (a) represents the chemical evolution for a long starless core phase. Most of the C atoms are converted to the CO molecules in the gas phase, which then deplete onto dust grains. They then form CH₃OH, H₂CO, and more complex organic molecules through hydrogenation reactions and radical reactions on the grain surfaces. On the other hand, the case (b) corresponds to a short starless-core phase in which a certain amount of the C atoms deplete directly onto the dust grains, and then form CH₄ effectively through hydrogenation. This realizes WCCC.

4. Summary and Implications

During the last decade, chemical compositions of low-mass star-forming regions have been investigated extensively, as summarized above. Now, we recognize the significant chemical diversity even among sources in a similar physical evolutionary stage. Nevertheless, we still have many unknowns on the chemical evolution of protostellar cores, some of which are highlighted below:

(1) We do not know whether the hot corino activity exists inside the WCCC sources, as mentioned above. According to the unified picture, the hot corino chemistry would occur in the vicinity of the protostar even for the WCCC sources. However, the hot corino activity is known to be weak in these sources. This means that saturated COMs are not well produced in the WCCC sources for some reasons. To address this problem, we have to study the weak hot corino activity in the WCCC sources with sensitive and high-resolution observations. Furthermore, it is necessary to understand the formation mechanism of saturated COMs on grain mantles in more detail.

(2) How unique are the WCCC and the hot corino chemistry among the low-mass star forming regions? We need to investigate chemical compositions of more low-mass protostellar cores for statistical arguments.

(3) How is the chemical diversity of the Class 0 sources brought into the later stages? Although the relation between hot corinos and protostellar disks is still unknown, saturated COMs are actually distributed within a few 100 AU region around the protostar. On the other hand, carbon-chain molecules also exist in the closest vicinity of the protostar (< 500 AU) in the WCCC sources (Sakai *et al.* 2010). Thus, the chemical variation would be delivered to the protoplanetary disks. Its detailed processes are needed to be clarified.

Here we stress that the above questions are only major ones. We still have a big gap between chemistry of star-forming regions and that of protoplanetary disks. In the next decade, a dramatic progress is expected in this area with the full operation of ALMA.

Finally, we mention unique importance of COMs in tracing the chemical evolution. Observations of 'fundamental' molecules such as CO, HCN and HCO⁺ are essential to study the current physical structures and kinematics of star-forming regions. Their relatively high abundances ensure bright emissions in many sources to make such a business easy. However, fundamental species appear everywhere, and it is difficult to extract chemical characteristic of each source from their observations. On the other hand, COMs are much more sensitive to chemical and physical environments and are suitable for chemical characterization. A drawback is faintness of the lines, and hence, sensitive observations are necessary. If we can overcome this for instance with ALMA, complex molecules will give us fruitful information, not "complex" information.

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Discussion

DOUG JOHNSTONE: You suggest that the difference between Hot Corino Sources and WCCC sources is due to the speed with which they collapse but how important might the environment of the core be? For example, a core at the edge of a cloud may live in a higher radiation field?

NAMI SAKAI: I agree that environmental effects are important. We should concretely identify what types of environmental effects discriminate between the hot corino chemistry and WCCC. One important factor would be the large scale star-formation activity in the region where the protostar resides. Although the number of the sample is limited, a region harboring hot corinos is usually a formation site of star clusters, whereas a region harboring WCCC sources is relatively quiescent. Such a difference in the large-scale environment may affect the contracting speed of the clouds. The position of the cores in a parent cloud could also be a possible cause, as you mention. More statistics are essential.

E. F. VAN DISHOECK: It is not clear to me why you so easily dismiss the information on the "spread" in observed CH₄ ice abundances toward pre-stellar cores and protostars, since these data should probe close to the sublimation temperature of CH₄ ice.

NAMI SAKAI: We think that the CH₄ ice abundance would strongly depend on the density distribution and the temperature structure, and hence, we have directly measured the gas-phase CH₄ abundance in a warm region to test our WCCC scenario. However, I agree that we should more carefully make use of the CH₄ ice abundances reported so far, because a factor of difference in the CH₄ abundance would cause a big difference in the abundances of complex species.

MARTIN CORDINER: Are there any other observational tracers to test the idea a rapid freeze-out produces elevated ice CH₄ abundances?

NAMI SAKAI: The molecular D/H ratios would be an independent tracer. The relatively low fractions observed in L1527 suggest the freeze-out of gaseous species in early stages of chemical evolution of its parent cloud.

S. VITI: TPD experiments (e.g. Collings *et al.* 2004, Viti *et al.* 2004) show that not all the CO and CH₄ evaporate at 20 K and 25 K respectively. In fact you should have about 40 % of CH₄ still on the grains up to ~70 K. How does this agree your conclusion?

NAMI SAKAI: Thank you very much for your comments. It would not affect seriously on our conclusion. Even if that portion (~40 %) of the CH₄ ice still remains on grains and is released into the gas phase in the hot (> 70 K) region, carbon-chain production would not be effective, because H₂O becomes the main destructor of C⁺ in such a hot region. However, your point will be important for detailed modeling.