Different Degrees of Nitrogen and Carbon Depletion in the Warm Molecular Layers of Protoplanetary Disks

Kenji Furuya1, Seokho Lee2, and Hideko Nomura1,3

1 National Astronomical Observatory of Japan, Osawa 2-21-1, Mitaka, Tokyo 181-8588, Japan; kenji.furuya@nao.ac.jp
2 Korea Astronomy and Space Science Institute, 776 Daedeok-daero, Yuseong-gu, Daejeon 34055, Republic of Korea
3 Department of Astronomical Science, The Graduate University for Advanced Studies (SOKENDAI), Osaka, Mitaka, Tokyo 181-8588, Japan

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Abstract

Observations have revealed that the elemental abundances of carbon and oxygen in the warm molecular layers of some protoplanetary disks are depleted compared to those in the interstellar medium by a factor of ~10–100. Meanwhile, little is known about nitrogen. To investigate the time evolution of nitrogen, carbon, and oxygen elemental abundances in disks, we develop a one-dimensional plane-parallel model that incorporates dust settling, turbulent diffusion of dust and ices, as well as gas-ice chemistry including the chemistry driven by stellar UV/X-rays and galactic cosmic rays. We find that gaseous CO in the warm molecular layer is converted to CO2 ice and locked up near the midplane via the combination of turbulent mixing (i.e., the vertical cold finger effect) and ice chemistry driven by stellar UV photons. The other hand, gaseous N2, the main nitrogen reservoir in the warm molecular layer, is less processed by ice chemistry and exists as it is. Then, nitrogen depletion occurs solely through the vertical cold finger effect of N2. As the binding energy of N2 is lower than that of CO and CO2, the degree of nitrogen depletion is smaller than that of carbon and oxygen depletion, leading to higher elemental abundance of nitrogen than that of carbon and oxygen. This evolution occurs within 1 Myr and proceeds further, when the α parameter for the diffusion coefficient is ≥10^{-3}. Consequently, the N2H+ / CO column density ratio increases with time. How the vertical transport affects the midplane ice composition is briefly discussed.

Unified Astronomy Thesaurus concepts: Astrochemistry (75); Protoplanetary disks (1300); Interstellar molecules (849)

1. Introduction

The formation of planets occurs in protoplanetary disks. The elemental compositions of gas and solids in disks directly set the elemental compositions of forming planets in the disks. Understanding the elemental compositions of gas and solids in disks is thus the first step in understanding how planets acquire their compositions (e.g., Öberg & Bergin 2021).

Recent observations have found that elemental abundances of volatile carbon and oxygen in some disks are different from those in the interstellar medium (ISM). In the three disks (TW Hya, DM Tau, and GM Aur), where gas mass is measured with the HD line observations (Bergin et al. 2013; McClure et al. 2016), the CO abundance in the warm molecular layer (T ≥ 20 K) is lower than the canonical value of 10^{-4} by factors of 10–100 (e.g., Favre et al. 2013; Zhang et al. 2019, 2021). As CO is the major carrier of volatile carbon, a reasonable hypothesis is that volatile elemental carbon is depleted in the gas phase by similar factors. Survey observations of disks in nearby star-forming regions have found that CO emission is much weaker than expected, even when the freeze-out of CO onto dust grains and photodissociation by stellar UV photons are considered in disk models (Ansdell et al. 2016; Long et al. 2017; Miotello et al. 2017). The faint CO emission may indicate that the CO abundance in the warm molecular layer in disks is typically lower than the canonical value. Alternatively, it may indicate that the gas mass of H2 is lower than expected in the disks. The timescale of carbon (and oxygen) depletion has been suggested to be fast (~1 Myr) based on the observations of CO isotopologues toward disks in different evolutionary stages/ages (Bergner et al. 2020b; Zhang et al. 2020). In addition, some disks show brighter C2H emission than expected, indicating a C/O ratio higher than unity at least in the C2H-emitting regions (Bergin et al. 2016; Miotello et al. 2019; Bosman et al. 2021a). The high C/O ratio indicates that the degree of oxygen depletion is more significant than that of carbon.

There are some proposed mechanisms to explain the depletion of volatile carbon and oxygen in the warm molecular layer: conversion of CO into less volatile species through chemistry driven by cosmic rays (CRs)/X-rays (e.g., Bergin et al. 2014; Furuya & Aikawa 2014), the so-called vertical cold finger effect (e.g., Meijerink et al. 2009; Kama et al. 2016; Xu et al. 2017), and a combination of both of these (Krijt et al. 2020). The vertical cold finger effect is the following phenomenon: Turbulence brings the gaseous molecules from the warm molecular layer to the disk midplane, where the dust temperature is low and molecules are frozen out onto large dust grains. As large dust grains are not fully coupled with the turbulent gas motion, they settle close to the midplane, trapping ices on them. As a result, the abundances of gaseous molecules in the disk atmosphere can decrease with time.

Compared to carbon and oxygen, our understanding of the nitrogen elemental abundance in disks is rather limited. The main carrier of nitrogen in the warm molecular layer is expected to be N2 or atomic N in the gas phase (e.g., Li et al. 2013), which are not directly observable. Some observational studies have concluded that the degree of nitrogen depletion is significantly smaller than that of carbon and oxygen. Cleaves et al. (2018) concluded that carbon and oxygen are depleted in
the observable gas of the IM Lup disk compared to the ISM elemental abundances by a factor of \( \sim 20 \) or even larger, whereas nitrogen is not significantly depleted (up to a factor of 4 compared to the ISM elemental abundance), based on the observations of CO, C2H, and HCN and the physical-chemical modeling of the disk. The estimated age of IM Lup is 0.5–1 Myr (Mawet et al. 2012), again indicating the timescale of carbon and oxygen depletion is fast. Anderson et al. (2019) found that the N2H+/CO flux ratio in 511 Myr old disks in Upper Scorpius is higher than that in \( \lesssim 2 \) Myr old disks, including the IM Lup disk. The high N2H+/CO flux ratio in the older disks may be due to N2, which is the parent molecule of N2H+, is less impacted by the physical and chemical processes in the gas phase and remains in the gas phase for a longer timescale than CO. It also may indicate that the degree of carbon depletion continues to be enhanced over time after \( \sim 2 \) Myr.

In addition to the elemental composition in disks, nitrogen abundance is relevant to the measurements of the disk gas mass; Trapman et al. (2022) showed that the combination of C18O line and N2H+ line can be a good proof of disk gas mass, assuming that N2 is not depleted in the disk gas. One of the biggest uncertainties in measuring the disk gas mass is the CO abundance in the warm molecular layer, as it is not necessarily the canonical value of 10^{-5} as mentioned above. As N2H+ is destroyed by CO, the C18O/N2H+ flux ratio is useful to constrain the CO abundance in the warm molecular layer (Trapman et al. 2022) if N2 is not depleted significantly in contrast to CO.

Theoretically, the elemental abundance of nitrogen in the warm molecular layer can be reduced as well as that of carbon. CO and N2 have similar volatility; laboratory experiments showed that the binding energy of N2 is slightly lower than that of CO, and their sublimation temperatures should be within a few degrees of each other (Fayolle et al. 2016). Then, the N2 abundance in the warm molecular layer can be reduced by the vertical cold finger effect like CO. In addition, the chemical conversion of N2 to less volatile species (NH3) driven by CRs/X-rays can occur after significant CO depletion (when the CO abundance becomes lower than \( \sim 10^{-5} \); Furuya & Aikawa 2014). For a quantitative understanding of the evolution of C/N/O elemental abundances in disks, models, that consider both gas-ice chemistry and the vertical cold finger effect are required. Several previous studies have investigated the detailed gas-ice chemistry in turbulent disks (e.g., Semenov & Wiebe 2011; Furuya et al. 2013; Furuya & Aikawa 2014). In these studies, however, dust grains were assumed to be dynamically well coupled with gas, and therefore, the vertical cold finger effect was not included. Other studies focused only on carbon and oxygen, and chemical processes other than adsorption and desorption of molecules were not considered (Xu et al. 2017; Krijt et al. 2018). Krijt et al. (2020) combined the dust evolution and grain surface chemistry of carbon and oxygen driven by CRs but ignored the chemistry driven by stellar UV photons; as growth and settling of dust proceeds, UV photons penetrate deeper into the disks, driving chemistry induced by UV photons (e.g., Akimkin et al. 2013; Van Clepper et al. 2022).

In this study, we investigate the time evolution of carbon-, nitrogen-, and oxygen-bearing species in a disk, considering the vertical cold finger effect and gas-ice chemistry, which includes the chemistry driven by stellar UV/X-rays and the galactic CRs. The rest of this paper is organized as follows. Our numerical model is described in Section 2, and the numerical results are presented in Section 3. We discuss the timescale of elemental depletion, the temporal evolution of column densities of gas-phase species, and the midplane ice composition in Section 4. Our findings are summarized in Section 5.

## 2. Model

### 2.1. Numerical Setup

Figure 1 shows an outline of our modeling processes. We first obtain the self-consistent solution of the density and temperature profiles of the gas and dust in the vertical direction of a disk, irradiated by stellar UV and X-rays. The gas surface density profile in the disk is taken from the TW Hya disk model developed in Cleaves et al. (2015) with the global dust-to-gas mass ratio of 0.01. The size distribution of dust in an entire disk follows a power law with an index of \(-3.5\) with minimum \((a_{\text{min}})\) and maximum radii \((a_{\text{max}})\) of 0.1 \(\mu\)m and 1 mm, respectively. The dust size distribution is discretized into 50 logarithmically spaced bins.

Dust temperature is obtained from the radiative equilibrium using the RADMC-3D code (Dullemond et al. 2012). Gas temperature is obtained by solving the steady-state balance between heating and cooling, considering simplified chemistry (Lee et al. 2021). Gas density distribution is determined from the hydrostatic equilibrium, while the distribution of dust with different radius is obtained by solving the steady-state balance between settling and turbulent stirring (e.g., Takeuchi & Lin 2002). Our vertical gas distribution is different from that in Cleaves et al. (2015), which was calculated assuming a Gaussian profile and the parametric gas scale height. We have...
confirmed that the degree of carbon and nitrogen depletion discussed in Section 3 does not change significantly whether using the vertical gas distribution from the hydrostatic equilibrium or the parametric distribution in Cleeves et al. (2015). The dust-settling velocity and the diffusion coefficient for turbulent stirring are given later in this section.

The input stellar spectrum is composed of the observed UV spectrum of TW Hya (Dionatos et al. 2019), added to a blackbody component with an effective temperature of 4110 K (Andews et al. 2012). As our model is one-dimensional plane parallel, the stellar flux at a radius $R$ from the star is assumed to be absorbed at the surface of the disk and half of the flux diffuses into the vertical direction toward the midplane. The stellar flux at wavelength $\nu$ at the surface of the disk ($z_c(R) = 0.8R$ in our models) is given by

$$F(\nu, R) = \frac{1}{2 \pi R^2 + z_c(R)^2},$$

(1)

where $L_{\nu}(\nu)$ is the stellar spectrum. The stellar flux at each height $z$ is calculated by RADMC-3D (Dullemond et al. 2012). The dust opacity for UV and longer wavelengths is calculated with the dsharp_opac package from Birnstiel et al. (2018), assuming the dust composition listed in their Table 1. In addition to dust, we consider polycyclic aromatic hydrocarbons (PAHs) as a source of UV opacity (Weingartner & Draine 2001) and gas heating. We assume a PAH radius of $\sim 5\text{ A}$ (Weingartner & Draine 2001) and that PAHs are always dynamically coupled with gas. The average Galactic PAH-to-dust mass ratio is 4.6% (Draine & Li 2007), while the PAH abundance in disks is lower than that value by a factor of 10–100 (Geers et al. 2006). In our models, the PAH-to-dust mass ratio in an entire disk is assumed to be 0.05%, i.e., 100 times lower than the Galactic average value. X-ray ionization rate is calculated by the analytical formula (Igea & Glassgold 1999; Bai & Goodman 2009), with the stellar X-ray luminosity of $10^{30}\text{ erg s}^{-1}$. The nonattenuated CR ionization rate is set to be $10^{-18}\text{ s}^{-1}$, and the CR ionization rate of each disk position is calculated with the attenuation column of 96 g cm$^{-2}$ (Umebayashi & Nakano 1981).

Next, we solve gas and ice chemistry, considering the vertical transport of gas and ice, under the physical conditions obtained in the first step:

$$\frac{\partial n_i}{\partial t} + \frac{\partial (n_i V_f)}{\partial z} - \frac{\partial \phi_i}{\partial z} = P_i - L_i,$$

(2)

$$\phi_i = -m_i D_i \frac{\partial}{\partial z} \left( \frac{n_i}{m_i} \right),$$

(3)

where $n_i$ is the number density of species $i$ and $z$ is the height from the midplane. $P_i$ and $L_i$ represent the production rate and the loss rate, respectively, of species $i$ by chemical reactions (see Section 2.2). The second term on the left-hand side of Equation (2) describes the vertical settling of dust, while the third term describes the turbulent diffusion. The dust-settling velocity is $V_f = -\Omega_K^2 R z_c$, where $\Omega_K$ is the Keplerian orbital frequency (Nakagawa et al. 1981). Assuming the Epstein regime, the dimensionless stopping time $\tau_s$ is defined as $\tau_s = \rho_{\text{int}} \Omega K a / \rho g c_s^2$, where $\rho_{\text{int}}$ is the internal density of dust (1.68 g cm$^{-3}$), $a$ is the radius of dust, $\rho g$ is the mass density of gas, and $c_s$ is the local sound velocity. The diffusion coefficient is parameterized as $D_i = \alpha c_s^2 / \Omega_K$ (Shakura & Sunyaev 1973), where $\alpha$ is assumed to be $10^{-3}$ in this study, unless otherwise stated. The Schmidt number, $S_c$, describes the strength of coupling between gas and dust and is given by $1 + \tau_s^2$ (Youdin & Lithwick 2007). For gas-phase species, $V_f = 0$ and $S_c = 1$.

For the numerical integration of Equation (2), the first-order operator-splitting method is employed; we first integrate the equation between times $t$ and $t + \Delta t$ without the source terms of chemical reactions. Next, we integrate the equation without the transport terms (i.e., only with the terms of chemical reactions) between times $t$ and $t + \Delta t$ at each height $z$. In the time integration of the chemical reaction terms, we rebin the dust size distribution into eight bins (that is, icy species on eight different dust populations are distinguished from each other) to shorten the computational time. The dust sizes for each of the eight dust populations are $(a_{\text{min,}j}, a_{\text{max,}j}) = (0.10 \mu m, 0.32 \mu m), (0.32 \mu m, 1.0 \mu m), (1.0 \mu m, 3.2 \mu m), (3.2 \mu m, 10 \mu m), (10 \mu m, 32 \mu m), (32 \mu m, 100 \mu m), (100 \mu m, 320 \mu m), (320 \mu m, 1 \text{ mm})$, where $a_{\text{max,}j}$ and $a_{\text{min,}j}$ are the maximum and minimum radius for each dust bin, respectively. Even if we used the larger number (e.g., 12) of dust bins for rebinning, the numerical results presented in Section 3 remained almost unchanged.

The averaged radius $\langle \sigma_f \rangle$ of each dust bin for calculations of the chemistry is defined as follows (Vasyunin et al. 2011):

$$\langle \sigma_f \rangle(z) = \int_{a_{\text{min,}j}}^{a_{\text{max,}j}} a^2 f(a, z) da / \int_{a_{\text{min,}j}}^{a_{\text{max,}j}} a^2 f(a, z) da,$$

(4)

where $f$ is the number density of grains with size between $a$ and $a + da$. Dividing the total mass of each dust population per unit volume ($\rho_d(a_j)$) by the mean mass of one dust grain $(4\pi a^2_5 \rho_d / 3)$, we can obtain the number of grains with the averaged radius $\langle \sigma_f \rangle$ per unit volume. The temperature for each dust bin ($T_d$) is defined by the area-weighted average temperature (Gavino et al. 2021) because the rate coefficients of gas–dust interactions are proportional to the surface area in general:

$$T_d(\langle \sigma_f \rangle, z) = \frac{\int_{a_{\text{min,}j}}^{a_{\text{max,}j}} T_d(a, z) a^2 f(a, z) da}{\int_{a_{\text{min,}j}}^{a_{\text{max,}j}} a^2 f(a, z) da}. $$

(5)

### 2.2. Chemical Reaction Network

The chemical network used in this work is based on that in Furuya & Aikawa (2014), which includes gas-phase reactions, the interaction between gas and (icy) grain surfaces, and grain surface reactions. UV photodissociation/photoionization rates are calculated by convolving the local radiation field and the photodissociation/photoionization cross sections (Heays et al. 2017). The self-shielding and mutual shielding factors for the photodissociation of H$_2$ and CO are taken from Visser et al. (2009). Shielding factors for N$_2$ photodissociation are taken from Li et al. (2013). The binding energies of CO, CO$_2$, H$_2$O, and N$_2$ are set at 1150 K, 2600 K, 5700 K, and 1000 K, respectively.
2.3. Initial Compositions

Initially, we assume spatially uniform volatile elemental abundances throughout the disk. Our underlying initial elemental abundances for H:He:C:N:O:Na:Mg:Si:S:Fe are 1.00:9.75(−2):1.00(−4):6.00(−6):2.20(−4):2.25(−9):1.09(−8):9.74(−9):1.14(−8):2.74(−9), respectively, where $a/b$ means $a \times 10^{-b}$. Then, the initial elemental [C/N] and [C/O] ratios are $\sim 2$ and $\sim 0.5$, respectively. For initial molecular abundances, we assume that all hydrogen is in H$_2$, all carbon is in CO, the remaining oxygen is in H$_2$O, and all nitrogen is in N$_2$. The other elements are assumed to exist as either atoms or atomic ions in the gas phase. All CO and N$_2$ are assumed to be entirely present in the gas phase.

In another scenario, both thermal desorption and photodesorption of water ice cause the depletion of volatile oxygen in the disk. In this scenario, due to thermal desorption and even larger dust grains suppress the emission from inner warm dust regions, we assume that all hydrogen is in H$_2$, all carbon is in CO, the remaining oxygen is in H$_2$O, and all nitrogen is in N$_2$. The other elements are assumed to exist as either atoms or atomic ions in the gas phase. All CO and N$_2$ are assumed to be entirely present in the gas phase. We determine the initial partitioning of H$_2$O among ice mantles of eight different dust populations as follows. All H$_2$O is assumed to be present in ice mantles, and the number density of H$_2$O ice on each dust population is assumed to scale with $\rho_d(\sigma_T, z)/\Sigma_d(\sigma_T, z)$, i.e., larger-sized dust grains have the larger amount of H$_2$O ice.

Our two-step approach assumes that large dust grains are already settled, and the depletion of elemental carbon, nitrogen, and oxygen in the disk upper layers has not occurred yet at the beginning of our simulations. The first assumption would be verified because observations of Class 0/I sources have found that their inner (<1000 au) dense regions already contain millimeter-sized dust grains (e.g., Miotello et al. 2014; Harsono et al. 2018; Galametz et al. 2019). In addition, the presence of dust ring structures observed in some Class 0/I disks may indicate that dust coagulation and settling have already started in the young disks (e.g., Sheehan & Eisner 2018; Nakatani et al. 2020; Ohashi et al. 2021). The second assumption would be justified as well, at least for carbon and nitrogen: Class 0/I disks are warmer than Class II disks (i.e., the vertical cold finger effect is less efficient) with no signs of CO freeze-out in the inner $\sim$100 au (van’t Hoff et al. 2020) and with the CO abundance close to the canonical value (Zhang et al. 2020). As N$_2$ is more volatile than CO, it would be reasonable to assume N$_2$ is entirely present in the gas phase.

The situation for water (i.e., oxygen) is less clear. H$_2$O emission has been detected in the inner warm ($\gtrsim 100$ K) regions (inner envelope and/or a disk), where water ice has sublimated, of several Class 0 sources at spatial scales of 100 au (Persson et al. 2012; Jensen et al. 2019). Harsono et al. (2020) reported nondetection of H$_2$O emission toward Class I disks at scales of 100 au, possibly because abundant large (millimeter-sized or even larger) dust grains suppress the emission from inner warm dust regions. Theoretically speaking, one can consider two extreme scenarios about water in Class 0/I disks. In one scenario, due to thermal desorption and/or photodesorption of water ice, followed by photodissociation of water in the gas phase, water ice on dust grains is uncovered in the upper layers of Class 0/I disks (still, water ice can exist close to the midplane). As a result, dust coagulation and settling would not cause the depletion of volatile oxygen in the disk upper layers. In this case, the volatile oxygen abundance would be uniformly $\sim 10^{-4}$ in Class 0/I disks (oxygen in CO is not counted here). In another scenario, both thermal desorption and photodesorption are negligible, and coagulation and settling of dust covered by water ice cause the depletion of volatile oxygen in the disk upper layers. In this case, the volatile oxygen abundance scales with the local dust-to-gas mass ratio in Class 0/I disks. Reality would be somewhere between the two extremes, depending on stellar properties and disk physical structures. The former scenario is assumed in our fiducial models, while the latter scenario is discussed in Section 4.4.
abundances of nitrogen and carbon become similar at $R = 80$ au. At $R = 20$ au, the temperatures of all dust populations are higher than the freeze-out temperature of CO and N$_2$ even at the midplane. Then, the cold finger effect does not work, and the gas-phase abundances of CO and N$_2$ in the warm molecular layers are their canonical values.

The bottom panels in Figure 4 show the molecular abundances at 1 Myr in our full model, where both transport processes and gas-ice chemistry are considered. At $R = 80$ au, CO$_2$ ice is the major reservoir of elemental carbon and oxygen at $z/R \lesssim 0.1$, as well as CO ice and H$_2$O ice. CO$_2$ ice is formed by the surface reaction CO + OH $\rightarrow$ CO$_2$ + H at $z/R \sim 0.1$–0.2, where stellar UV radiation is not significantly attenuated and transported into the midplane, where UV radiation is completely shielded, by dust settling and turbulent mixing. The source of oxygen for the CO$_2$ formation is H$_2$O ice and atomic oxygen, the latter of which is transported from the disk upper layers. N$_2$ does not easily react with radical species on the grain surface in contrast to CO. Owing to the much larger binding energy of CO$_2$ (and H$_2$O) compared to that of N$_2$, elemental carbon and oxygen are easily locked up as ices near the midplane than nitrogen. Consequently, nitrogen becomes the third most abundant element in the gas phase after hydrogen and helium at $R = 80$ au.

At $R = 20$ au, inside the CO snow line, CO$_2$ ice is formed at $z/R \sim 0.1$ by the surface reaction CO + OH $\rightarrow$ CO$_2$ + H and transported into the midplane by dust settling and turbulent mixing like at $R = 80$ au. Because of the CO$_2$ formation, the gas-phase CO abundance becomes lower than the canonical value by a factor of $\sim 2$ at 1 Myr. The abundance of CO$_2$ ice remains lower than those of CO gas and H$_2$O ice at $R = 20$ au. The main limiting factor of CO$_2$ formation is the amount of available oxygen for the chemistry. At 80 au (outside the CO snow line), atomic O and H$_2$O ice at $z/R \gtrsim 0.1$ are abundant enough to convert a significant fraction of CO gas into CO$_2$ ice because CO near the midplane is frozen out onto dust grains and thus is abundant only in the gas phase at $z/R \gtrsim 0.1$. H$_2$O ice below $z/R \lesssim 0.1$ does not contribute to the CO$_2$ formation,
because H₂O ice is mostly on large (>100 μm) dust grains, which are dynamically decoupled from the gas, and because the stellar UV radiation to dissociate H₂O ice is significantly attenuated. At 20 au (inside the CO snowline), however, atomic O and H₂O ice at z/R > 0.1 are not abundant enough, because CO gas is present throughout (both in the surface layer and at the midplane). As a result, the conversion of CO gas into CO₂ ice is not very efficient inside the CO snow line compared to outside the CO snow line.

Our models ignore the radial drift of dust grains. As discussed in Appendix B, the size of dust grains that contributes to the grain surface chemistry efficiently is <100 μm, and larger dust grains do not play a significant role in the chemistry. The dimensionless stopping time of 100 μm-sized dust grains is ~10⁻³ and ~5 × 10⁻³ at the midplane of R = 20 au and 80 au, respectively. For a 100 μm-sized dust grain, the timescale of drifting from 80 au to 30 au (i.e., around the CO snowline) is evaluated to be >1 Myr using Equations (17) and 18 in Brauer et al. (2008). Then, the impact of radial drift on our results on the carbon and nitrogen depletion outside the CO snow line would be not significant. Inside the CO snow line, the radial drift of CO-ice mantled dust grains from the outer regions, followed by the sublimation of CO ice, can enhance the CO-gas abundance (e.g., Krijt et al. 2020). This effect would not be negligible, as not a small amount of CO is present on large dust grains (≥100 μm).

3.2. Depletion Factors of Carbon and Nitrogen

We define depletion factors of element X as

\[ f_{\text{depl}}(X) = \frac{[X/H]_0}{[X/H]_\infty}, \]

where \([X/H]_0\) is the initial elemental abundance of X with respect to H, and \([X/H]_\infty\) is the elemental abundance of X with respect to H in the gas above the snow surfaces of CO for carbon and N₂ for nitrogen (see Zhang et al. 2019; Krijt et al. 2020). A larger value of \(f_{\text{depl}}(X)\) means that the depletion of element X in regions above the snow surface is more significant. We define the position of the CO snow surface as the height below which multilayered CO ice can be present on at least one of the eight dust populations. We compare total desorption rate of CO by thermal desorption and photodesorption with its adsorption rate for each dust population, assuming the gas-phase CO abundance is 10⁻² and grain surfaces are covered by one monolayer of CO ice. The snow surface of CO is defined as the height above which the adsorption rate of CO is greater than the desorption rate for all dust populations. A similar definition is applied to the snow surface of N₂. The positions of the snow surfaces are the same among different models as long as we adopt the same disk physical model.

Figure 5 shows \(f_{\text{depl}}(\text{C})\) and \(f_{\text{depl}}(\text{N})\) as functions of R in the static model (left panel), the model without surface chemistry (middle panel), and our full model (right model) at t = 0.1 Myr, 0.3 Myr, and 1 Myr. As we ran our models only at R = 20, 30, 50, 80, and 100 au, we cannot infer the exact radial positions of the CO and N₂ snow lines; the CO snow line is located at around 30 au, while the N₂ snowline is located at around 50 au. In the static model, \(f_{\text{depl}}(\text{N})\) is almost unity (i.e., no significant depletion) regardless of R, while \(f_{\text{depl}}(\text{C})\) is ~3–5 well outside the CO snow line. In the model without surface chemistry, \(f_{\text{depl}}(\text{C})\) is in the range of ~2–20 outside the CO snow line.
while it is close to unity inside the CO snow line. At $R = 50$ au, the CO snow surface is close to the midplane compared to that at $R \geq 80$ au, leading to the lower efficiency of the vertical cold finger effect. The radial profile of $f_{\text{depl}}(N)$ basically follows that of $f_{\text{depl}}(C)$, and $f_{\text{depl}}(C)/f_{\text{depl}}(N)$ is $\sim 1–2$. In the full model, $f_{\text{depl}}(N)$ is similar to that in the model without surface chemistry, because nitrogen in the warm gas is depleted only by the cold finger effect of N$_2$. $f_{\text{depl}}(C)$ in the full model is the largest ($\sim 3–30$) among the three models, because of the combination of the vertical cold finger effect and the surface chemistry, which converts CO into CO$_2$. Consequently, $f_{\text{depl}}(C)/f_{\text{depl}}(N)$ can be as high as $\sim 3–5$ in the full model, i.e., carbon is more depleted than nitrogen by a factor of $\gtrsim 3$ outside the CO snow line, leading to a higher abundance of gas-phase nitrogen than that of gas-phase carbon. We also run some additional models to explore the parameter dependence of $f_{\text{depl}}(C)$ and $f_{\text{depl}}(N)$, varying $\xi_{\text{CR}}$, $a_{\text{max}}$, and $a_{\min}$ (see the Appendix C in details). We confirmed that these parameters did not affect our qualitative chemical results. Then, the combination of the cold finger effect and the grain surface chemistry results in larger depletion of carbon than nitrogen outside the CO snow line within 1 Myr once the dust grains have settled toward the midplane, making nitrogen the third most abundant element in the gas phase after hydrogen and helium. Our full model is consistent with the observations toward the IM Lup disk with the age of 0.5–1 Myr, where carbon and oxygen are depleted compared to the ISM abundance by a factor of $\sim 20$ or even larger, whereas nitrogen depletion is less significant (Cleeves et al. 2018).
respectively, in the static model factors monotonically increase with time. The depletion factors monotonically increase with time.

4. Discussion

4.1. Timescale of Elemental Depletion: UV-driven Chemistry versus CR-driven Chemistry

In our full model, outside the midplane CO snow line, the volatile carbon abundance in the warm molecular layer can be reduced by a factor of more than 10 within 1 Myr due to the combination of the vertical cold finger effect and the chemical conversion of CO into CO$_2$ ice driven by stellar UV photons. On the other hand, the nitrogen abundance in the warm molecular layer is reduced solely due to the vertical cold finger effect of N$_2$. Here we discuss which processes determine the evolutionary timescale of the elemental abundances in the warm molecular layer.

When turbulent mixing is switched off (the static model), the chemical conversion of CO into CO$_2$ ice occurs only in limited regions ($z/R \sim 0.1$–0.2). In the full model, however, CO$_2$ ice formed at $z/R \sim 0.1$–0.2 can be transported to the midplane via turbulent mixing and dust settling, while CO near the midplane and in the disk upper layers can be transported to the regions at $z/R \sim 0.1$–0.2 via turbulent mixing. Then, the CO$_2$-rich regions expand with time. The timescale of this process is limited by mixing because the timescale of the freeze-out of CO and atomic O onto dust grains ($\tau_{fr}$) and that of the chemistry driven by stellar UV photons ($\tau_{phd}$) are shorter than the mixing timescale. The turbulent mixing timescale is given by $\tau_{mix} \sim (0.1r)^2/D_z$. For example, $\tau_{mix}$ is $\sim 3 \times 10^4$ yr at $R = 20$ au, $\sim 8 \times 10^4$ yr at 50 au, and $\sim 2 \times 10^5$ yr at 100 au in our models, where $\alpha$ is assumed to be $10^{-3}$. The freeze-out timescale $\tau_{fr}$ is given by

$$\tau_{fr} \approx 3000 \left( \frac{10^{-24} \text{ cm}^2/\text{H \sigma_d}}{\sigma_d} \right) \left( \frac{10^9 \text{ cm}^{-3}}{n_H} \right) \text{ yr},$$

where $\sigma_d$ is the total dust cross section per hydrogen nuclei, and $n_H$ is the number density of hydrogen nuclei. As OH ice is produced by H$_2$O ice photodissociation, $\tau_{phd}$ is given by

$$\tau_{phd} \approx 100(\chi/1)^{-1} \text{ yr}. \quad (8)$$

Cosmic-ray/X-ray-induced UV photons are less important than the stellar UV; the FUV flux induced by CRs in the dense molecular cloud core environment, where $\xi$ is $\sim 10^{-17}$ s$^{-1}$, is $\sim 10^4$ photons cm$^{-2}$ s$^{-1}$. As $\chi = 1$ corresponds to the FUV flux of $\sim 10^5$ photons cm$^{-2}$ s$^{-1}$, the CR/X-ray-induced UV photons are negligible unless $\xi \gtrsim 10^{-14}$ s$^{-1}$ (see Figure 2). Then, $\tau_{mix}$ is much shorter than $\tau_{fr}$ and $\tau_{phd}$.

On the other hand, many previous modeling studies show that CO is converted into less volatile species via the chemistry driven by CRs and X-rays (e.g., Bergin et al. 2014; Furuya & Aikawa 2014). In brief, CO is destroyed by He$^+$ to produce C$^+$ and atomic O, which are eventually locked up in icy CO$_2$, icy CH$_4$, and icy carbon-chain molecules. As these molecules are much less volatile than CO, they are present in ice mantles even inside the CO snow line. As the rate-limiting step of the CO-gas reprocessing chemistry is the ionization of He by CRs/X-rays to produce He$^+$, the timescale is given by

$$\tau_{CR\text{chem}} \approx \frac{x_{\text{CO}}}{\xi_{\text{He}^+}}$$

$$\approx 2 \times 10^7 \left( \frac{x_{\text{CO}}}{1 \times 10^{-4}} \right) \left( \frac{\xi_{\text{He}^+}}{5 \times 10^{-19} \text{ s}^{-1}} \right)^{-1} \text{ yr}, \quad (9)$$

where $x_i$ is the abundance of species $i$, and $\xi_{\text{He}^+}$ is the ionization rate of He atom (Furuya & Aikawa 2014), which is half of the ionization rate of H$_2$. Then, $\tau_{CR\text{chem}}$ is much larger than $\tau_{phd}$ and $\tau_{mix}$. N$_2$ can also be converted into less volatile species (NH$_3$ ice) by the following pathway (Willacy 2007; Furuya & Aikawa 2014): $\text{N}_2 + \text{H}^+ \rightarrow \text{N}_3^+ + e^- \rightarrow \text{NH}$. Once NH is formed, it is adsorbed onto dust grains, followed by subsequent
hydrogenation to form NH$_3$ ice. The timescale of the N$_2$ conversion into NH$_3$ ice is slightly longer than $\tau_{\text{CRchem}}$, as it occurs only after the significant depletion of CO gas (when the CO abundance is lower than $\sim 10^{-3}$); otherwise, N$_2$H$^+$ is destroyed by CO and N$_2$ is reformed (Furuya & Aikawa 2014).

$\tau_{\text{CRchem}}$ is much shorter than $\tau_{\text{phd}}$ and $\tau_{\text{mix}}$, and thus the chemistry driven by CRs (and X-rays) is less important than that driven by stellar UV photons. Even if the higher value for $\xi_{\text{CR}}$ of $10^{-16}$ s$^{-1}$ is assumed, the above conclusion holds, because $\tau_{\text{CRchem}}$ is still larger than $\tau_{\text{fr}}, \tau_{\text{phd}},$ and $\tau_{\text{mix}}$. Indeed, the depletion factors of carbon and nitrogen do not change significantly between the model with $\xi_{\text{CR}} = 10^{-18}$ s$^{-1}$ and that with $\xi_{\text{CR}} = 10^{-16}$ s$^{-1}$ (see Appendix C).

4.2. Dependence on the Strength of Turbulence

In our models presented so far, the $\alpha$ parameter for the vertical diffusion coefficient is assumed to be $10^{-3}$. As discussed in Section 4.1, the timescale of carbon and nitrogen depletion is mostly determined by the turbulent mixing timescale, and thus the $\alpha$ parameter should affect the timescale and the degrees of carbon and nitrogen depletion at a given time. Recent observational studies have put constraints on the strength of the turbulence in the warm molecular layers for some disks on the basis of the molecular line observations. Flaherty et al. (2020) constrained the nonthermal gas motion ($\delta v$) in disks around DM Tau, MWC 480, and V4046 Sgr, based on the $^{12}$CO 2–1 observations and parametric disk models. Converting $\delta v$ to $\alpha$ by $\alpha = (\delta v/c_s)^2$, they found that $\alpha \sim 8 \times 10^{-2}$ for the DM Tau disk, $\alpha < 3 \times 10^{-3}$ for the MWC 480 disk, and $\alpha < 1 \times 10^{-2}$ for the V4046 Sgr disk in the gas traced by $^{12}$CO 2–1, i.e., not the disk midplane. Similar observational studies toward the disks around TW Hya and HD 162936 indicate $\alpha < 7 \times 10^{-3}$ and $\alpha < 3 \times 10^{-3}$, respectively (Teague et al. 2016; Flaherty et al. 2017, 2018).

These observational studies seem to indicate that the strength of the turbulence is not strong ($\alpha \lesssim 10^{-3}$) in disks in general, but the turbulence is strong ($\alpha \gtrsim 10^{-2}$) in some disks. To explore the impact of the $\alpha$ parameter on the model results, we recalculated the entire modeling process (Figure 1) with $\alpha = 10^{-2}$ and $\alpha = 10^{-4}$ as the value of the $\alpha$ parameter also affects the disk physical conditions. Figure 6 shows $f_{\text{depl}}(\text{C})$ and $f_{\text{depl}}(\text{N})$ in full models with $\alpha = 10^{-2}$ (left panel) and $\alpha = 10^{-4}$ (right panel). As the mixing timescale is inversely proportional to $\alpha$, $f_{\text{depl}}(\text{C})$ already reaches $\sim 10$ at 0.1 Myr at $R \gtrsim 80$ au in the model with $\alpha = 10^{-2}$. Both $f_{\text{depl}}(\text{C})$ and $f_{\text{depl}}(\text{N})$ reach the steady-state values within 1 Myr in the model with $\alpha = 10^{-2}$. In the model with $\alpha = 10^{-3}$, $f_{\text{depl}}(\text{N})$ almost reaches the steady-state value within 1 Myr, while $f_{\text{depl}}(\text{C})$ does not. We reran the model with $\alpha = 10^{-3}$ for 3 Myr and confirmed that $f_{\text{depl}}(\text{C})$ reaches $\sim 50$ and $\sim 60$ at $R = 80$ au and $R = 100$ au, respectively, at 3 Myr, while $f_{\text{depl}}(\text{C})$ at $R \lesssim 50$ au almost reaches the steady-state value within 1 Myr. In the model with $\alpha = 10^{-4}$, the depletion factors are less than 10 even at 1 Myr, because of the long mixing timescale (e.g., longer than 1 Myr at $R > 50$ au). Therefore, a relatively large value of $\alpha$ ($\gtrsim 10^{-3}$) is favorable for the significant depletion of carbon and making the warm molecular layer enriched in nitrogen relative to carbon within 1 Myr.

On the other hand, Anderson et al. (2019) found that the N$_2$H$^+$/CO flux ratio is higher in 5–10 Myr disks than in younger disks with the age of <2 Myr. If this trend primarily traces the evolution of volatile elemental abundances, the depletion of carbon should continue in 5–10 Myr. Because the time it takes for the depletion factors to reach steady state is shorter for higher $\alpha$ values, our model with $\alpha = 10^{-4}$ or $10^{-3}$ may be more consistent with the finding by Anderson et al. (2019) rather than the model with $\alpha = 10^{-2}$. Taken together, to explain the observed CO (or carbon) depletion timescale by our models, a reasonable value of $\alpha$ is $\sim 10^{-3}$.

4.3. Column Densities of Gas-phase Molecules

Here we discuss how the column densities of gas-phase species evolve with time in our full model with $\alpha = 10^{-3}$. Figure 7 shows the column densities of CO and N$_2$, their protonated species (HCO$^+$ and N$_2$H$^+$), and the tracer of the elemental carbon-to-oxygen ratio in the gas phase (hereafter $\text{C/O}_{\text{gas}}$; C$_2$H and HCN) at $t = 0.1$, 0.3, 1, and 3 Myr. For comparisons, we ran an additional static model, where grain surface chemistry, except for desorption and adsorption processes, was turned off (i.e., there is no depletion of carbon, oxygen, and nitrogen in the warm molecular layers). The molecular column densities predicted by this additional model at 1 Myr are shown by black dashed lines in the figure.

The column densities of CO and HCO$^+$ decrease with time, reflecting the gradual loss of CO from the warm molecular
layer via the combination of the chemical conversion of CO and the vertical cold finger effect. The N$_2$ column density decreases with time at $>50$ au, due to the vertical cold finger effect only. The column density of N$_2$ is larger than that of CO, indicating that N$_2$ is the second most abundant molecule in the gas phase. The column densities of N$_2$ decrease with time, whereas the N$_2$H$^+$ column density increases slightly with time rather than decreases. As N$_2$H$^+$ is destroyed by CO, the decrease of the gas-phase CO abundance leads to the enhanced N$_2$H$^+$ abundance (e.g., Aikawa et al. 2015), canceling the decrease of the gas-phase N$_2$ abundance. As a result, the column density ratio of CO to N$_2$H$^+$ increases with time at least until 3 Myr. This result may be consistent with the observations by Anderson et al. (2019), who found that the N$_2$H$^+$/CO flux ratio in 511 Myr old disks in Upper Sco is higher than that in younger disks with the age of $<$2 Myr. Trapman et al. (2022) showed that the combination of C$^{18}$O and N$_2$H$^+$ lines is useful to constrain disk gas mass, adopting a static thermal-chemical disk model, assuming that nitrogen is not depleted. Our results do not fully support their assumption of the nondepletion of nitrogen. However, the combination of C$^{18}$O and N$_2$H$^+$ lines would be useful to constrain the disk gas mass, because the carbon depletion is more significant than the nitrogen depletion, and thus the N$_2$H$^+$/CO ratio can be used as a probe of the carbon (CO) depletion.

C$_2$H is considered a tracer of [C/O]$_{\text{gas}}$ because its abundance depends on whether [C/O]$_{\text{gas}}$ is higher than unity or not (e.g., Bergin et al. 2016; Miotello et al. 2017; Bosman et al. 2021a). In our full model, the C$_2$H column density increases with time by a factor of $\sim$10 at most, because [C/O]$_{\text{gas}}$ becomes close to, but is still lower, than unity both inside and outside of the CO snow line (see panels (e) and (f) of Figure 4). The HCN column density remains almost unchanged with time in our full model.

The C$_2$H and HCN column densities in our model ($\sim$10$^{12}$–10$^{13}$ cm$^{-2}$ and $\sim$10$^{11}$–10$^{13}$ cm$^{-2}$, respectively) at 1 Myr are still one to two orders of magnitude lower than that observed in the outer regions (outside of the CO snowline) of Class II disks (Bergin et al. 2016; Bergner et al. 2020a; Guzmán et al. 2021). The underestimation of the C$_2$H and HCN column densities in our model indicates a need for additional processes to make [C/O]$_{\text{gas}}$ higher than unity.

The rationale for $0.5 \lesssim$ [C/O]$_{\text{gas}}$ $\lesssim$ 1 both inside and outside of the CO snow line in our model is as follows. Inside the CO snow line, only the oxygen-rich species, H$_2$O and CO$_2$, can freeze out near the midplane. Then, the gas becomes dominated by CO over time, leading to [C/O]$_{\text{gas}}$ $\sim$ 1. Outside the CO snow line, there are two CO reservoirs at $t = 0 \, \text{yr}$: One is the gas-phase CO in the warm molecular layer and another is the CO ice on small dust grains near the midplane. As CO is assumed to be present in the gas phase at $t = 0 \, \text{yr}$, it is preferentially frozen out onto smaller grains; smaller grains dominate the dust cross section, and dust temperature does not depend on the size near the midplane. Some CO ice near the midplane is transported upward, enriching the warm molecular layers in CO. Atomic O and CO in the surface layer are consumed by the CO$_2$ formation at a similar rate, but this enrichment process partially cancels out the CO depletion in the surface layers. As a result, [C/O]$_{\text{gas}}$ becomes $>0.5$ but does not exceed unity.

A promising process for enhancing [C/O]$_{\text{gas}}$ is the destruction of carbon grains by photoablation as proposed by Bosman et al. (2021b). The carbon abundance locked up in refractory carbon dust is $10^{-4} \times 100 \Delta_d/g$, where $\Delta_d/g$ is the dust-to-gas mass ratio. To enhance [C/O]$_{\text{gas}}$ considerably ($\sim$2), the carbon abundance released in the gas phase should be comparable to or larger than the gas-phase carbon abundance.

**Figure 7.** Radial profiles of the column densities of selected gas-phase molecules in the full model at 0.1, 0.3, 1, and 3 Myr. The column densities at 3 Myr are shown only at $R = 50$, 80, and 100 au. At the inner radii, the column density almost reaches the steady-state values within 1 Myr. For comparisons, black dashed lines show the column densities predicted by the static model without grain surface chemistry (i.e., no depletion of carbon and nitrogen in the warm molecular layers) at 1 Myr.
Then, the following relation should hold, \( f_{\text{depl}}(C) \Delta d_{g} / \Delta g \gtrsim 10^{-2} \) (Bosman et al. 2021b), assuming complete photoablation of refractory carbon dust. In our model with \( \alpha = 10^{-2} \) at 1 Myr, the requirement is satisfied at \( z / R \lesssim 0.2 \), even if complete photoablation of carbon grains is assumed. Below \( z / R \lesssim 0.1 \), however, stellar UV is significantly attenuated (\( \chi \ll 1 \)) and/or the dust temperature is too low, leading to the freeze-out of gas-phase carbon. Taken together, only very limited regions \( (z / R \sim 0.1-0.2) \) might be able to become \([C/O]_{\text{gas}} > 1\) by photoablation. Even if so, locally high \([C/O]_{\text{gas}}\) would be smeared out by turbulent mixing in a relatively short timescale (e.g., \( \tau_{\text{mix}} \sim 2 \times 10^{5} \) yr at \( R = 100 \) au). Therefore, as noted in Van Clepper et al. (2022), carbon grain destruction may be ongoing over the course of grain growth, rather than solely after the grain growth.

4.4. Comparisons with Previous Studies

Krijt et al. (2020) studied the depletion of carbon and oxygen combining the dust evolution and grain surface chemistry of carbon and oxygen driven by CRs but ignored the chemistry driven by stellar UV photons. One of the most significant differences between their study and ours is that they considered the formation of pebbles from small grains in disks, while we assumed that pebbles already exist at the beginning of our simulations. In Krijt et al. (2020), the formation and the vertical settling of pebbles transport \( H_{2}O \) ice to the midplane. This process leads to \([C/O]_{\text{gas}} \sim 1\) because CO is much more volatile than \( H_{2}O \). On the other hand, in our models, we assumed that pebbles already exist at \( t = 0 \) yr and the ISM-like elemental abundance throughout the disk (i.e., \([C/O]_{\text{gas}} \sim 0.5\) in the disk upper layers, where \( H_{2}O \) is efficiently dissociated by stellar UV photons). As noted in Section 2.3, what happens to water in young disks, where the growth of small dust grains has already started, remains unclear. The model by Krijt et al. (2020) would correspond to the scenario where the sublimation/photodesorption of water ice is negligible, and coagulation and settling of dust covered by water ice cause the depletion of volatile oxygen in the disk upper layers because their model did not consider the chemistry induced by stellar UV and the disk is cold. Our model corresponds to another extreme scenario where water ice on dust grains is uncovered due to thermal desorption and/or photodesorption of water ice in the disk upper layers, and dust coagulation and settling do not cause the depletion of volatile oxygen in the disk upper layers. Reality would be somewhere between the two extremes, depending on stellar properties and disk physical structures. Note that the oxygen abundance in the disk upper layers would also be related to the photoablation of carbon grain; if the photoablation occurs efficiently during the formation and settling of pebbles, \( H_{2}O \) ice, which covers dust grains, would be photodesorbed at the same time.

In order to check the impact of elemental oxygen abundance available for the CO formation on our results, we reran our full model assuming that the initial \( H_{2}O \) abundance scales with the local dust-to-gas mass ratio, i.e., \(10^{-4} \times (\Delta d_{g} / \Delta g)^{1/2}\). In other words, the initial \( H_{2}O \)-to-dust mass ratio is uniform inside the disk. As \( \Delta d_{g} / \Delta g \) is \( \sim 10^{-3} \) or lower at \( z / R \gtrsim 0.1 \) (see Figure 2), the elemental abundance of oxygen not locked up in CO is lower than that in our fiducial models by a factor of \( \sim 10 \) or even larger. We confirmed that \( f_{\text{depl}}(C) \) in the model with the uniform \( H_{2}O \)-to-dust mass ratio is between that in the fiducial full model and that in the model without grain surface chemistry (Figure 8). We also confirmed that \([C/O]_{\text{gas}} \) at 1 Myr is close to unity as in the fiducial full model. Therefore, our qualitative chemical results are not sensitive to the initial oxygen abundance.

Regarding \([C/O]_{\text{gas}} \) at 1 Myr or later, our model predicted that \([C/O]_{\text{gas}}\) becomes larger than the initial value of \( \sim 0.5 \), but does not exceed unity. Van Clepper et al. (2022), who combined a toy model of the pebble formation and a gas-ice astrochemical model (but surface chemistry was ignored except for hydrogenation, i.e., the CO2 formation does not occur in their model), also predicted that \([C/O]_{\text{gas}}\) does not exceed unity. On the other hand, Krijt et al. (2020) predicted that eventually, \([C/O]_{\text{gas}}\) in the warm molecular layers can become larger than unity. The difference in the predicted \([C/O]_{\text{gas}}\) can be explained by CR-driven chemistry versus UV-driven chemistry. The rationale why \([C/O]_{\text{gas}} > 1\) can be realized in Krijt et al. (2020) is that they assumed \( C^{+} \), which is produced by the destruction of CO by \( He^{+} \), is eventually locked up in \( CH_{4} \), while atomic \( O \) is locked up in \( H_{2}O \) and/or \( CO_{2} \). As \( CH_{4} \) is more volatile than \( H_{2}O \) and \( CO_{2} \), it can more easily go back to the gas phase and enhance \([C/O]_{\text{gas}}\) in the warm molecular layer. In the model by Krijt et al. (2020), the effect of stellar UV on chemistry was ignored in contrast to our models. More comprehensive simulations with dust settling, growth, and photoablation with both CR- and UV-driven chemistry are required for better understanding of the evolution of carbon, nitrogen, and oxygen in protoplanetary disks.

4.5. Ice Compositions in the Midplane

Although the main topic of this study is the gas-phase elemental abundance in the warm molecular layers, we discuss ice compositions in the disk midplane briefly, because the chemical compositions in the warm molecular layer and those in the midplane are related to each other through turbulent mixing. We only focus on the most abundant species in the ISM ice and cometary ice, i.e., \( H_{2}O \), \( CO \), and \( CO_{2} \) for C- and O-bearing species, and \( N_{2} \) and \( NH_{3} \) for N-bearing species.

Figure 9 shows the total abundances of selected icy molecules (i.e., the sum of the ice abundances on eight dust populations) in the disk midplane in the static model (left), in the full model with \( \alpha = 10^{-4} \) (middle), and in the full model...
with $\alpha = 10^{-3}$ (right) at 1 Myr. In the static model, the ice composition in the midplane is mostly determined by the assumed initial compositions and the balance between adsorption and desorption, because the timescale of the chemistry driven by CRs is longer than 1 Myr for $\xi_{CR} \lesssim 10^{-17}$ s$^{-1}$ (e.g., Furuya & Aikawa 2014). When the turbulent mixing is considered, we see the increases of the H$_2$O, CO, and N$_2$ abundances outside their snow lines by a factor of a few compared to the initial abundances, and the efficient formation of CO$_2$ ice, the abundance of which reaches more than 10% of the H$_2$O abundance within 1 Myr. Note that CO$_2$ ice is abundantly present in the ISM ice (CO$_2$/H$_2$O $\sim$ 30%; Boogert et al. 2015), while there is no CO$_2$ at the beginning of our simulations. Therefore, the impact of the vertical mixing on the abundant (>10$^{-5}$ per H) ice molecules in the disk midplane is limited, if ice in disks were inherited from the ISM ice.

On the other hand, if we look at the ice compositions of each dust population, the situation is different. Figure 10 shows radial profiles of abundances of selected icy molecules on small (0.1–0.32 $\mu$m), middle (3.2–10 $\mu$m), and large (0.32–1 mm) sized dust populations in the full model with $\alpha = 10^{-3}$ at 1 Myr. The abundance of NH$_3$ is below 10$^{-6}$ and not shown in the figure.

Figure 9. Radial profiles of the total abundances of selected icy molecules (i.e., the sum of the ice abundances on eight dust populations) in the static model (left), in the full model with $\alpha = 10^{-4}$ (middle), and in the full model with $\alpha = 10^{-3}$ (right) at 1 Myr. Arrows on the right-hand margin indicate the initial abundances of H$_2$O, CO, and N$_2$. The abundance of NH$_3$ is below 10$^{-6}$ and not shown in the figure.

Figure 10. Radial profiles of abundances of selected icy molecules in the disk midplane.

5. Summary

We investigated the temporal evolution of elemental abundances of volatile carbon, nitrogen, and oxygen in the warm molecular layer (≥20 K) of a protoplanetary disk, considering both the vertical cold finger effect and gas-ice chemistry. We developed a one-dimensional plane-parallel model that incorporates dust settling, turbulent diffusion of dust
and ices, as well as gas-ice chemistry including the chemistry driven by stellar UV/X-rays and the galactic CRs. Our main findings are summarized as follows.

1. Outside the CO snow line, the elemental abundance of carbon in the warm molecular layer can be reduced by a factor of >10 via the combination of the vertical cold finger effect of CO and the chemical conversion of CO into CO$_2$ driven by stellar UV photons. On the other hand, the gaseous N$_2$, the main nitrogen reservoir in the warm molecular layer, is less processed by the stellar UV-driven chemistry and exists as it is. As the binding energy of N$_2$ is lower than that of CO and CO$_2$, the degree of nitrogen depletion in the warm molecular layer is smaller than that of carbon and oxygen, leading to higher elemental abundance of nitrogen than those of carbon and oxygen.

2. The degree of carbon and nitrogen depletion and the depletion timescale are independent of the assumed CR ionization rate, at least, when $\xi_{\text{CR}}$ is less than $10^{-16}$ s$^{-1}$, but depends on the strength of turbulence. In the case when the $\alpha$ value for the diffusion coefficient is $10^{-3}$, the CO abundance in the warm molecular layers beyond the midplane CO snow line can become lower than the ISM abundance by factors of >10 within 1 Myr. The CO abundance continues to decrease until at 3 Myr. On the other hand, the N$_2$ abundance reaches steady state within 1 Myr. When $\alpha = 10^{-2}$, both CO and N$_2$ abundance reaches steady state within 1 Myr. When $\alpha = 10^{-3}$, the depletion factors of carbon and nitrogen are less than a factor of $\lesssim$5 in 1 Myr.

3. As a result of more significant depletion of elemental carbon and oxygen than nitrogen, the N$_2$H$^+$/CO column density ratio increases with time in particular for the outer disk regions (outside the N$_2$ snowline).

4. In our models, elemental carbon-to-oxygen ratio in the gas phase ([C/O]$_{\text{gas}}$) becomes larger than 0.5, but does not exceed unity both inside and outside of the midplane CO snow line. A promising mechanism for enhancing [C/O]$_{\text{gas}}$ would be the destruction of carbon grains by photoablation during the course of grain growth (Sections 4.3 and 4.4; see also Bosman et al. 2021a; Van Clepper et al. 2022).

5. The compositions of ice mantles at the midplane can be different, depending on dust size. Because the largest dust grains (1 mm in our models) settled close to the midplane and the surface area per unit gas volume is small, their ice mantle compositions do not change significantly. On the other hand, smaller grains do not preserve their initial ice compositions.

6. The size-dependent dust temperature (i.e., larger grains have lower temperatures, assuming radiative equilibrium) is crucial for the efficiency of the vertical cold finger effect (see Appendix A for details).

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Software: RADMC-3D (Dullemond et al. 2012), dshar-p_opac (Birnstiel et al. 2018), Matplotlib (Hunter 2007).

Appendix A

Importance of Size-dependent Dust Temperature for the Vertical Cold Finger Effect

In previous studies of the vertical cold finger effect of CO, the temperature of a dust grain is independent of its size, that is, dust grains with different sizes have the same temperature (e.g., Kama et al. 2016; Xu et al. 2017). Here, we show that this assumption can underestimate the impact of the vertical cold finger effect.

We ran the model without grain surface chemistry (see Section 3.1), employing two different assumptions for the dust temperature of the eight dust populations. In one model, the dust temperature of dust populations is calculated in the same way as in our fiducial model. Consequently, larger dust populations are colder than smaller ones. In another model, all dust populations are assumed to have the same temperature (hereafter, the single-$T_d$ model), and the dust temperature is assumed to be the area-weighted temperature averaged in the range between 0.1 $\mu$m and 1 mm (i.e., the entire size range in our fiducial models). The left panel of Figure A1 compares the vertical distribution of the gas-phase CO abundance in the two models at $R = 80$ au at 1 Myr. The gas-phase CO abundance is much larger (i.e., the efficiency of the vertical cold finger effect is lower) in the single-$T_d$ model compared to the fiducial model. As discussed in Kama et al. (2016), in the single-$T_d$ model, the ratio of the dust cross section contributed by large dust grains that settled below the CO snow surface to the total dust cross section (denoted as $\Delta_X$) is the critical parameter for

![Figure A1](image-url)
determining the efficiency of the vertical cold finger effect. If \( \Delta X \) is small, most gas-phase CO adsorb onto small grains. The CO-ice coated small grains can be transported above the CO snow surface by turbulent mixing, and the CO ice can sublimate into the gas phase. Thus, the vertical cold finger effect is not efficient. As shown in Figure 2, the total cross section is dominated by small grains in our model. Then, the vertical cold finger effect is not efficient in the single-\( T_d \) model.

However, in the fiducial model, where smaller grains have higher temperatures, the net adsorption rate (i.e., the adsorption rate of gas-phase CO minus the desorption rate of CO ice) of the large dust grains can be larger than that of the small dust grains, even if \( \Delta X \ll 1 \) (see the right panel of Figure A1). Then, the single-\( T_d \) model underestimates the efficiency of the vertical cold finger effect.

The vertical cold finger effect was originally introduced through an analogy with the radial cold finger effect (Stevenson & Lunine 1988; Meijerink et al. 2009). As the dust temperature is essentially the same in the disk midplane irrespective of its size, the size-dependent dust temperature discussed here is not relevant for the radial cold finger effect, but is critically important for the vertical cold finger effect.

Appendix B

Roles of Different-sized Dust Grains in Disk Chemistry

Figures B1 and B2 show the vertical distribution of the abundances of selected icy species on the eight dust populations at \( R = 80 \) au and \( 20 \) au, respectively. At \( R = 80 \), the formation of CO\(_2\) ice occurs mainly on the middle-sized grain populations (\(~\)10 \( \mu \)m), because gas-phase CO preferentially freeze out on those populations at \( z/R \sim 0.1 \) (right panel of Figure A1), where stellar UV is not fully shielded. Large dust populations (\( \gtrsim 100 \mu \)m) are dynamically decoupled from the gas, and elements locked up in H\(_2\)O, CO, and N\(_2\) ices on the large dust grains do not contribute to the active chemistry at \( z/R \gtrsim 0.1 \).

At \( R = 20 \) au, on the other hand, the formation of CO\(_2\) ice occurs mainly on small dust populations (\(~\)1 \( \mu \)m or less), because the dust temperatures for all dust populations are too high for the CO freeze-out, and thus dust populations with larger total cross sections (i.e., small populations) are more important for the surface chemistry. Then, the important dust size for CO\(_2\) formation depends on the distance from the star. As at \( R = 80 \) au, large dust populations (\( \gtrsim 100 \mu \)m) are dynamically decoupled from the gas, and oxygen locked up in H\(_2\)O ice on the large dust grains do not contribute to the chemistry at \( z/R \gtrsim 0.1 \).

As discussed above, different-sized dust grains contribute to the disk chemistry in different ways. Disk chemical models often adopt the single-grain approximation, where gas-ice chemistry is described assuming a single-grain size and temperature (see Gavino et al. 2021 and references therein). It is clear that the disk chemistry with turbulent mixing cannot be represented by models with the single-grain approximation. A similar argument was made by Gavino et al. (2021) for the case of static disk chemical models.
Appendix C

Parameter Dependence

C.1. Cosmic-Ray Ionization Rate

In the models presented in Section 3, the galactic CR ionization rate was assumed to be $\xi_{\text{CR}} = 10^{-18}$ s$^{-1}$. Here we explore the impact of assumed values of $\xi_{\text{CR}}$ on our results. For this sake, we reran the static model and the full model with $\xi_{\text{CR}} = 10^{-16}$ s$^{-1}$. There has been no clear observational evidence of higher values of $\xi_{\text{CR}}$ in disks than in the dense ISM ($\sim 10^{-17}$ s$^{-1}$). Cleeves et al. (2015) concluded that the emission lines of HCO$^+$ and N$_2$H$^+$ from the TW Hya disk are best reproduced by the model with a low CR ionization rate of $10^{-19}$ s$^{-1}$. Seifert et al. (2021) concluded that $\xi_{\text{CR}}$ in the inner 100 au regions of the IM Lup disk is $10^{-20}$ s$^{-1}$ by modeling HCO$^+$ and N$_2$H$^+$ emission, while that in the outer regions is $\gtrsim 10^{-17}$ s$^{-1}$. Aikawa et al. (2021) concluded that $\xi_{\text{CR}} \gtrsim 10^{-18}$ s$^{-1}$ in the disks around IM Lup, AS 209, and HD 163296 on the basis of the comparisons between observationally derived column densities of HCO$^+$, N$_2$H$^+$, and N$_2$D$^+$ and those predicted by a generic disk model (Aikawa et al. 2018). Then, the assumed value of $10^{-16}$ s$^{-1}$ may be considered as an upper limit of $\xi_{\text{CR}}$ in the Class II disk environments.

Figure C1 compares the depletion factors of carbon and nitrogen in the models with $\xi_{\text{CR}} = 10^{-16}$ s$^{-1}$ with those in the models with $\xi_{\text{CR}} = 10^{-18}$ s$^{-1}$ at 1 Myr. In the static model case, the model with $\xi_{\text{CR}} = 10^{-16}$ s$^{-1}$ shows higher depletion factors of carbon and nitrogen in particular inside the CO snow line ($\lesssim 30$ au) and N$_2$ snow line ($\lesssim 50$ au), respectively, although the depletion factors are less than $\sim 10$. This is because CR-driven chemistry converts gas-phase CO and gas-phase N$_2$ near the midplane, where stellar UV and X-ray cannot penetrate, into less volatile icy molecules. The timescale of the chemistry ($\tau_{\text{CRchem}}$) is longer than 1 Myr when $\xi_{\text{CR}} = 10^{-18}$ s$^{-1}$, whereas the timescale is the order of $10^5$ yr when $\xi_{\text{CR}} = 10^{-16}$ s$^{-1}$ (see Section 4.1). In the full model case, the assumed value of $\xi_{\text{CR}}$ does not significantly affect the depletion factors of carbon and nitrogen because $\tau_{\text{CRchem}}$ is larger than $\tau_{\text{ph}}$ and $\tau_{\text{mix}}$, even when $\xi_{\text{CR}} = 10^{-16}$ s$^{-1}$. Therefore, we conclude that the CR ionization rate is less important for the chemistry of carbon (and nitrogen) depletion in the warm gas ($\gtrsim 20$ K) than had been previously thought, when the dust grains have settled and UV radiation penetrates close to the midplane. However, CRs are the important parameter for determining the turbulence state of protoplanetary disks, since they control the ionization rate and the status of the magnetorotational instability (e.g., Sano et al. 2000). Thus, the CRs still indirectly play a key role in carbon and nitrogen depletion through turbulence.

C.2. Maximum and Minimum Sizes of Dust Grains

In the models presented in Section 3, the maximum size of dust grains ($a_{\text{max}}$) is fixed to be 1 mm, as often assumed in disk chemical models (e.g., Zhang et al. 2021). On the other hand, (sub)millimeter polarization observations of some disks have suggested that $a_{\text{max}}$ is $\sim 100$ $\mu$m (e.g., Kataoka et al. 2016, 2017).
Adopting the lower value of $a_{\text{max}}$ affects the degrees of carbon and nitrogen depletion for several reasons. First, the dust temperatures are lowered, and thus the efficiency of the vertical cold finger effect is increased. Second, on the other hand, the relative fraction of the cross section of small dust grains, which are dynamically coupled to the gas, to the total dust cross section increases, lowering the efficiency of the vertical cold finger effect.

Third, the mass fraction of large dust grains, which are dynamically decoupled from the gas, decreases, leading to a larger amount of excess oxygen to convert CO to CO$_2$ ice via the chemistry driven by stellar UV flux. This indicates the third effect is the most important at $R \lesssim 50$ au.

The smallest dust grains ($0.1 \mu$m) in our models are not fully dynamically coupled with gas (see panel (c) in Figure 2). To check the impact of the presence of even smaller dust grains, we also recalculated the entire modeling process with $a_{\text{min}} = 0.01 \mu$m rather than $a_{\text{min}} = 0.1 \mu$m. We confirmed that adopting the smaller value of $a_{\text{min}}$ does not affect the depletion factors significantly (right panel of Figure C2).

ORCID iDs

Kenji Furuya https://orcid.org/0000-0002-2026-8157
Seokho Lee https://orcid.org/0000-0002-0226-9295
Hideko Nomura https://orcid.org/0000-0002-7058-7682

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Figure C2. Dependence of depletion factors of elemental carbon (red lines) and nitrogen (blue lines) on $a_{\text{max}}$ (left panel) and $a_{\text{min}}$ (right panel) at 1 Myr. In the left panel, the solid, dashed, and dotted lines represent the models with $a_{\text{max}} = 1$ mm, 100 $\mu$m, and 10 $\mu$m, respectively. In the right panel, the solid and dashed lines represent the models with $a_{\text{min}} = 0.1 \mu$m and 0.01 $\mu$m, respectively.
