Depletion of gaseous CO in protoplanetary disks by surface-energy-regulated ice formation

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Empirical constraints of fundamental properties of protoplanetary disks are essential for understanding planet formation and planetary properties. Carbon monoxide (CO) gas is often used to constrain disk properties. However, estimates show that the CO gas abundance in disks is depleted relative to expected values, and models of various disk processes impacting the CO abundance could not explain this depletion on observed ~1 Myr timescales. Here we demonstrate that surface energy effects on particles in disks, such as the Kelvin effect, that arise when ice heterogeneously nucleates onto an existing particle can efficiently trap CO in its ice phase. In previous ice formation models, CO gas was released when small ice-coated particles were lofted to warmed disk layers. Our model can reproduce the observed abundance, distribution and time evolution of gaseous CO in the four most studied protoplanetary disks. We constrain the solid and gaseous CO inventory at the midplane and disk diffusivities and resolve inconsistencies in estimates of the disk mass—three crucial parameters that control planetary formation.

With a consideration of surface energy effects such as the Kelvin effect (Methods), the process of CO ice nucleation in protoplanetary disks requires substantially larger supersaturations of CO gas (S > ~100) than the process of condensational growth (S > ~1). Thus, once nucleation occurs, condensational growth onto the nucleated particles quickly becomes the dominant ice formation process and rapidly depletes the CO gas in the regions of the disk near the midplane where it is initially supersaturated, creating a vertical concentration gradient (Fig. 1a). This concentration gradient is reduced by diffusive mixing that funnels CO gas from the upper warm layers to the disk midplane. The ongoing process of ice condensation readily depletes the fresh supply of CO gas such that it does not reach the critical supersaturation needed to nucleate new ice particles throughout the bulk of the disk after the first few thousand years of the disk’s lifetime. The initial fraction of particles that are coated in CO ice is thus primarily set at this early stage. CO gas is incorporated into solid CO on a timescale that is relatively fast once gas diffuses towards the disk midplane; thus, the CO gas mole fraction will be substantially depleted throughout the vertical extent of the disk (Fig. 1a) over a vertical diffusion timescale (Supplementary Fig. 3).

The progressive depletion of CO gas is facilitated by the condensation of CO onto large CO-coated ice particles, which have the lowest surface energy barriers (Methods). These large ice particles form from the initial population of CO-nucleated ice particles that grow, first via condensational growth and later via coagulation, before eventually drifting radially inwards towards the host star (Methods). For evolved disks, most of the solid CO mass is therefore located on the largest ice-coated particles in the size distribution (Fig. 1b). These large ice particles settle below the warm layers to a region of the disk that is too cold for CO evaporation and that is optically thick to ultraviolet (UV) photons, such that ice photodesorption does not occur (Fig. 1b). This settling of large grains is prevalent along the ice-forming regions of the disk (Fig. 2a), leading to a large sequestration of volatile material in the disk midplane.

If the effects of surface energy on ice nucleation are neglected, ice preferentially and continuously forms on small grains that are lofted efficiently to warm layers where they release CO ice back into the gas phase (Supplementary Fig. 2) and limit the maximum amount of gaseous CO depletion (Fig. 1b). In other words, by considering surface energy effects that largely prevent small grains from bearing CO ice, we circumvent the problem of CO resupply to the warm layers through lofting and evaporation of small CO ice grains (Fig. 1b).

The amount of observed CO gas in protoplanetary disks varies with semi-major axis and the disk age. Depletion occurs quickly immediately exterior to the midplane CO ice line because gas can quickly diffuse to the disk midplane and form ice (Fig. 2b). The vertical diffusion timescale increases in the outer disk where the scale heights are large due to disk flaring such that the timescale of depletion varies by orders of magnitude across a given system (Supplementary Fig. 3). As a result, while the depletion of CO at the midplane in the outer disk is large due to the low midplane temperature, the observed depletion in the upper, warmer layer will be minimal if the vertical diffusion timescale is longer than the current age of the system. Thus, in the outer disk, the amount of observed depletion varies with semi-major axis and increases with time such that the disk will become more depleted in gaseous CO as it evolves (Fig. 2b). In other words, the amount of CO gas depletion in the outer disk is simply a function of the fraction of the disk diffusion timescale that has elapsed since the system’s birth (Fig. 3). This is in agreement with recent observations of gaseous CO where very young disks (<1 Myr) do not appear to be depleted in CO gas while older systems (>1 Myr) can be depleted significantly. The observed timescale of depletion can be naturally explained by this model, while previous ice formation models and chemical models with interstellar medium (ISM) cosmic ray rates generally require ~3 Myr to deplete CO by an order of magnitude given expected cosmic ray abundances. Depending on the speed of particle growth and drift, there can also be a local enhancement of CO gas around the ice line once solid CO ice particles have drifted inwards and released their volatile material. This feature is initially very narrow in radial extent and is diffusively broadened with time (Fig. 2b). The CO-enriched gas interior to the disk’s critical semi-major axis is then accreted onto the host star.
Fig. 1 | The distribution of gaseous CO is regulated by preferential condensation of CO onto large particles. a. The initial CO abundance (black line) is first depleted (grey line) in the regions where it is supersaturated (dark blue shaded region). CO from the upper layers is then mixed downwards and depleted on a vertical diffusion timescale. Without radial resupply, the final CO gas mole fraction will be constant with height and fixed to the midplane CO saturation mole fraction (solid red line). If the Kelvin effect is not included, then CO would abundantly condense on small grains as well. These small grains can be lofted and will release their volatile components in the warm upper layers, thus limiting the maximum amount of depletion possible at a given semi-major axis (dashed red line). b. A fiducial distribution of ice-coated particles (green) and ice-free grains (blue) at a given disk semi-major axis \( r = 30 \text{ au} \), here for TW Hya at 5 Myr. The growth of the large particles is limited by particle drift (blue dashed line). The remaining CO-ice-coated particles settle to the disk midplane (black dashed line) and are not readily lofted to the upper regions of the disk where surface layer heating occurs (red dashed line) or where the disk becomes optically thin to UV photons (the UV optical depth \( \tau_{\text{UV}} = 1 \), dashed orange line). The ice particles are thus unable to release their volatile material due to either evaporation or photodesorption.

Fig. 2 | The radial evolution of CO in the disk around TW Hya. a. Ice-coated particles settle vertically throughout the radial extent of the disk (ice scale height is the black solid line and small particle scale height is the dash-dot line) below the surface layer heated region (that is, the ice formation region, dark blue), which we approximate as beginning at an altitude, \( z \), that is two scale heights, \( H \), above the midplane (red dashed line), based on more detailed modelling and observations\(^{15,19} \). The ice-coated particles also remain below the region that is optically thin (with a UV optical depth \( \tau_{\text{UV}} < 1 \) to UV photons, orange dashed line), allowing CO to be sequestered in solids. The small particle scale height extends throughout the disk to heights where evaporation and photodesorption can occur (light blue shaded region). b. The amount of CO gas depletion defined as the initial (interstellar) gas–phase CO-to-H\(_2\) ratio divided by the final ratio (unitless, blue lines) in protoplanetary disks varies with semi-major axis and increases with time such that the disk will become more depleted in gaseous CO in the outer disk as it evolves. The results were calculated using disk parameters for the disk around TW Hya (Methods).

We model four systems and compare them with observations in Fig. 4. We constrain the bulk disk diffusive properties and the composition of solid and gaseous material in the disk midplane as a function of both semi-major axis and time. The observed depletion is not always directly correlated with disk age in the observed sample, as some young disks are very depleted in CO gas while some older disks are not\(^{16} \). The amount of depletion from initial values depends sensitively on the diffusion present in the system. Thus, in addition to the system age, the primary factor that controls the distribution of gaseous CO is the level of diffusion in the disk. We thus optimize the fit of our model to the data by varying the level of diffusion present in the system (Methods). Our empirical constraints of the diffusion parameter (Table 1) all fall within a range of plausible values\(^{1} \) and are qualitatively consistent with estimates from non-thermal gas velocities\(^{15–18} \) (Methods).

While the relative CO abundance depends sensitively on the diffusion present in the system, the total CO mass present in the system depends on the total disk mass. This modelling demonstrates that CO gas is indeed depleted in systems such that a simple conversion from CO gas emission to other fundamental properties such as the total disk mass is not appropriate without modelling non-equilibrium ice formation including surface energy effects.
With the modelling presented in this work, disk masses estimated from CO agree with those estimated from dust line modelling\(^{19–21}\), lower limits from hydrogen deuteride observations (when relevant)\(^{5,22}\) and dust emission (with a dust-to-gas ratio of \(\sim 10^{-3}\), appropriate when considering grain growth and particle drift\(^{20}\)).

We constrain the inventory of CO in gas and solids in the protoplanetary disks considered here (Table 1). Our results are consistent with an initial CO abundance in these systems that is similar to the interstellar ratio (which we take to be \(10^{-4}\) by ref. \(^{23}\)). The partitioning of the CO mass inventory depends on the disk diffusive parameter, \(t_{\text{age}}/t_{\text{diff}}\) where \(t_{\text{age}}\) is the age of the system and \(t_{\text{diff}}\) is the diffusion timescale (Methods). When the diffusive parameter is very small, as is the case for the disk around HD 163296, most of the initial CO mass remains in the gas phase in the outer disk, where it is being converted to CO ice as described in the first step in Supplementary Fig. 1. As the diffusive parameter increases, the ice formation process continues and most of the initial CO mass will be located in solid ice in the outer disk, as is the case for the disk around DM Tau. At larger diffusive parameters, the ice particles that have depleted the gaseous CO in the outer disk have drifted inwards past the CO ice line, where they desorb their volatile materials (steps 2–4 in Supplementary Fig. 1). Thus, disks with larger diffusive parameters either have a roughly equal amount of their initial CO mass located in gas in the inner disk and lost to accretion, such as the disk around TW Hya, or have lost a majority of their initial CO mass to accretion, such as the disk around IM Lup. We note that the age of protoplanetary disks is uncertain and that literature estimates can vary by a few million years for a given system. In our modelling, the age of the system is degenerate with the level of diffusive mixing we derive such that an older, less-diffusive disk such as HD 163296 can have similar levels of observed depletion to a substantially younger, more-diffusive disk such as DM Tau, though the corresponding

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**Fig. 3** | The amount of CO gas depletion depends on the disk diffusion timescale. The average CO depletion (unitless, Fig. 2) exterior to the midplane ice line is a function of the current disk age divided by the disk diffusion timescale. The amount of gaseous CO depletion increases with time (coloured lines indicate depletion evolution).

**Fig. 4** | Surface-energy-regulated ice formation can describe CO gas abundances for a variety of observed disks. **a**–**d**, For each system, we compare our model results (coloured lines and crosses indicating the beam-size-convolved value) with the quantity reported in the observational literature (black solid lines or crosses indicating the half-beam separation). The literature-reported quantity is either CO surface density (\(\Sigma_{\text{CO}}\)) or CO depletion, and we have presented our results to be consistent with the original reported quantity (Fig. 2). The initial CO gas distribution is also shown (black dashed lines). The CO emission that arises from the grey shaded regions is probably optically thick throughout the vertical extent of the disk for all commonly observed CO isotopologues, unless clearing occurs by gas–planet interactions, which are not considered in this model. For a detailed discussion of our model–data comparisons, see Methods. Systems shown are DM Tau\(^{6,22}\) (a), IM Lup\(^{6}\) (b), TW Hya\(^{7}\) (c) and HD 163296 (d); disk-averaged values indicate a lack of CO depletion while higher spatial resolution data show some features\(^{70,71}\).
distribution of CO mass throughout the disk will vary between these two cases.

Our results demonstrate that the abundance of the gaseous and solid material in protoplanetary disks in the planet-forming regions changes as a function of time and disk semi-major axis. For solid material, the fraction of ice relative to refractory solids in the outer disk is a function of time and particle size. At late times probed by observations, the total mass of CO-ice-free grains is roughly an order of magnitude larger than the total mass of CO ice particles due to inward drift of large CO ice grains. At early times, however, the bulk-ice-to-refractory ratio is larger due to an ice fraction on large particles that is much higher than the bulk-ice-to-refractory ratio. Large bodies that form in protoplanetary disks at early times via the processes of streaming instability or pebble accretion, which preferentially accrete the largest particles in the distributions presented in this work, are likely to have compositions with substantial volatile components.

A prediction of this model is that the about-micrometre-sized particles in evolved disks are not likely to have a stable coating of CO ice (Fig. 1a). The population of small CO-ice-free grains that is abundant throughout the vertical and radial extent of the disk is likely to dominate the reflected light flux and possess scattering properties different from those of larger CO-rich particles. Future observational studies, using James Webb Space Telescope and other facilities, of the lack of infrared CO ice features or CO-ice-rich reflective properties contributed from small grains could validate this prediction (Methods).

A similar process of depletion should occur for the other volatile species in disks, such as H₂O and CO₂, meaning that future modeling can constrain the abundance ratios in disks. The abundance ratios of different elements, such as the C/O ratio, can be used to determine a planet’s formation region via comparing the abundances of a planet with the abundance ratios as a function of radius in protoplanetary disks. Exterior to the CO ice line, we expect that the bulk composition of the ice particles at the midplane will be a stellar abundance and similarly, the bulk composition of the ice particles between the CO₂ and CO ice lines should be substellar in C/O as predicted in ref. 2. This is because our modelling indicates that the ice formation of volatile species in these regions is regulated by the same vertical diffusion timescale, even though these species have different ice formation efficiencies. Because giant planets that form via core-accretion are thought to obtain the majority of their metallicity primarily from solid material, the compositions of young, giant planets that span this region should see a corresponding change in C/O ratios. Indications of this trend are emerging for the planets in the HR 8799 planetary system, where the two planets in the outer solar system (b and c) may have stellar C/O ratios. While the C/O ratios of the two inner planets are not as well constrained, there have been some indications of substellar C/O ratios, which agrees with these predictions. The C/O ratios should deviate from those predicted in ref. 2 interior to the CO₂ ice line. Qualitatively, this will occur because the radial transport rates of solid CO₂ and gaseous CO will differ, though further work is needed to robustly constrain abundance ratios in the inner disk.

Including surface energy effects in ice nucleation and condensation in future disk models will be important for understanding the composition of solids of different sizes, particularly at later times once particle drift is efficient. This is because species with larger surface energies will more readily form on larger particles that are more susceptible to drift, which could lead to a solid abundance that varies with particle size and disk semi-major axis. Once gas has been depleted on a vertical diffusion timescale, the gas composition will be set by the saturation vapour pressures of the various gas species and should differ significantly from stellar abundance ratios, though the overall gas metallicity will be greatly reduced. Our work provides new constraints on the environment of planet formation and sheds light on the variation in the bulk composition of planetary bodies and their building blocks with orbital distance and formation timescale.

**Methods**

We model the formation of CO ice in a series of vertical one-dimensional (1D) columns for a discrete set of disk semi-major axes. Each vertical disk model starts with an initial population of small grains that are allowed to grow via coagulation and the nucleation and condensation of CO ice. The model is then coupled with a global model of gaseous diffusion and radial dust grain aerodynamics. In particular, we account for accretion onto the star from the disk as well as the release of gaseous CO due to the influx of icy pebbles from the disk’s outer regions into its hotter inner regions.

The primary inputs to our modelling are the total gaseous surface density of the protoplanetary disk, the midplane temperature structure, the age of the system and the diffusion coefficient that describes the mixing in the system. The diffusion coefficient is treated as a free parameter, as it is not well constrained from observations. As noted in the main text, our derived values are consistent with existing estimates and within the range of reasonably expected values.

**Non-equilibrium ice formation and particle evolution**

We model a series of 1D vertical columns separated by 10 au and exterior to the midplane CO ice line with an additional vertical column immediately radially exterior to the midplane ice line. The results presented in this work do not change when the radial resolution of the models is doubled. At each vertical column, we sample the disk density and midplane temperature (for values see the "Disk parameters" section) at that location and use these values as inputs in our modelling of vertical particle evolution.

The primary quantities of interest from the modelling of CO ice formation are the extent to which gas can be vertically depleted in the column at a given semi-major axis, the solid-ice-to-gas ratio and the resulting size distribution of the particles at that location. To derive these quantities, it is essential to treat ice formation as a non-equilibrium process and to fully resolve the size distribution of particles.

We modify the 1D Community Aerosol and Radiation Model for Atmospheres (CARMA) to simulate the formation of CO ice in the diffuse outer regions of protoplanetary disks. CARMA computes the vertical and size distributions of ice particles by solving the discretized aerosol continuity equation, taking into account particle nucleation (homogeneous and heterogeneous), condensation, evaporation and coagulation. CARMA uses bins to resolve the particle size distribution, allowing for multiple particle modes to be simulated simultaneously and avoiding the need to parameterize the size distribution using an analytical function. We refer the reader to ref. 22 and the appendix of ref. 2 for an additional detailed description of CARMA and its history. We do not consider particle fragmentation or the photodesorption of CO ice. For the regions of the disk where the formation of CO ice occurs (typically beyond ~10 au), the process of fragmentation is not likely to contribute to the shaping of the particle size distribution assuming reasonable levels of disk size.
turbulence and particle compositions. We do not include the photodesorption of CO ice as all of the ice-covered particles in our modelling evaporate quickly once they reach the heated surface layers, which are often several au deeper in the disk than the region that is optically thin to UV photons. We approximate the UV optical depth using the method described in equation (7) in ref. 2. For each column, we begin with an initial ISM abundance (dust-to-gas mass ratio of 10$^{-3}$) of small, 10 au, cm-grains. This initial grain size is smaller than the ~0.1 μm size of a typical ISM grain, though this assumption does not affect the resulting particle size distribution. These particles are allowed to coagulate and grow to larger sizes (see appendix A.3 of ref. 3 for details of the coagulation scheme) as well as grow via the nucleation and condensation of CO ice. The particle size grid in our modelling is discretized into 72 bins with a mass ratio between successive bins equal to 2.

The total solid surface density in a vertical column decreases with time because particles drift radially inward due to gas drag. As we do not have a two-dimensional microphysical model, we approximate the time evolution of the column’s solid surface density analytically. At early times, the huge influx of particles from the outer disk may lead to a particle surface density given by ref. 2. However, at late times relevant to current observations of disks, we are in a regime where particle growth is limited by drift throughout the radial extent of the disk such that the maximum particle size present at each radial location is given by ref. 3:

$$a_{\text{max}}(r, t_{\text{disk}}) = \frac{2r_{\text{disk}}}{5k_{\text{disk}} \rho_{\text{gas}}},$$

(1)

where $r_{\text{disk}}$ is the disk surface density, which varies with semi-major axis; $t_{\text{disk}}$ is the current age of the system; $r_{\text{disk}}$ approximately corresponds to the maximum drift velocity and is defined as $v_{\text{drift}} = c_{\text{s}} \theta_{\text{sat}}$, where $c_{\text{s}}$ is the local Keplerian velocity and $c_{\text{drift}}$ is the local sound speed; $r_{\text{drift}}$ is the inner particle density; and $r$ is the orbital distance in the disk. When particles grow larger than the size given in equation (1), we remove them from the column, reflecting the fact that they have drifted inwards.

In addition to removing particles due to drift, we also account for the influx of smaller particles due to particle drift from larger orbital distances at each time step (Δt). After particles have grown large enough to experience drift, we calculate the flux of particles into a bin as $F_{\text{drift}} = 2\pi a \rho_{\text{gas}} r_{\text{disk}}$, where $a_{\text{max}} = 2r/5k_{\text{disk}} \rho_{\text{gas}}$, is the particle drift velocity (in the relevant Epstein drag regime) that was used to derive equation (1) and $f_{\text{disk}}$ is the solid-to-gas mass ratio (including both refractories and ice) defined just exterior to the radius of interest (r+1 au) and is calculated analytically based on a treatment of particle growth following equation (8) in ref. 2. We have validated this approximation for $f_{\text{disk}}$ is appropriate given that the dust-to-gas ratio calculated using CARMA at each orbital distance closely matches the analytic expression for dust-to-gas ratio described in ref. 2 as coagulation is the dominant mode of large particle growth in all of our models. The mass of particles that move inwards due to drift is calculated as $F_{\text{drift}} \Delta t$. This additional mass is added to the particle bin that is smaller than the maximum particle size bin at that time. We assume that the composition of the drifting particles is equivalent to particles of that size at the given radius.

In each column, the nucleation and condensation of CO are calculated. To adapt CARMA to the diffuse outer regions of protoplanetary disks, we make several common choices for nucleation and condensation following classical nucleation theory, which has been shown to be useful in understanding experiments of the nucleation of CO ice in the diffuse regions of Mars’s atmosphere as well as the formation of water ice on Earth (for example, refs. 33–35; for a more detailed discussion of classical heterogeneous nucleation modelling see chapter 9 in ref. 4). The heterogeneous nucleation process is the dominant pathway for CO ice formation as CO cannot undergo efficient homogeneous nucleation at the low pressures found in the outer regions of protoplanetary disks. Thus, once the initial population of CO-ice-free small grains grows to sizes large enough such that nucleation is stable and ice formation can occur, CO nucleates heterogeneously.

We treat a particle that has accreted CO as an ice particle unless it evaporates and releases the CO ice back to the gas phase. CARMA tracks the ice fraction of each particle throughout its evolution, which enables us to self-consistently calculate mass conservation in our model.

We follow ref. 3 (appendix A.1) to calculate the heterogeneous nucleation of CO ice on seed grains using classical nucleation theory. This prescription is the most fundamental lens of viewing heterogeneous nucleation as derived from surface energy effects. While this model is based on the formation of a liquid nucleation germ, it also serves as the basis for the heterogeneous nucleation of solids$.^2$ In this formulation, which includes the Kelvin effect, CO molecules diffuse over a seed particle’s surface after impinging upon it until a sufficiently large number of molecules can congregate into a critical germ cluster, resulting in nucleation. We assume that the nonisothermal coefficient that accounts for the released heat of sublimation during ice growth is unity as the close contact of the gas and an ice particle increases the efficiency of heat partition for particle seeds larger than a critical cluster size (often ~10$^{-3}$ cm in our simulations$^3$). We also assume that the mean jumping distance of a CO molecule is 0.4 nm (due to a lack of experimental measurements, we take the value for CO$_2$ in ref. 3). We further assume that the density of the seed grain is the density of CO$_2$ (p$_{\text{CO}} = 1.5$ g cm$^{-3}$), which is likely to form the initial ice mantle given the classically assumed condensation sequence in disks (for example, ref. 4).

While the Kelvin effect determines whether nucleation will occur by setting the size of the critical ice cluster that forms supraspherically, a key component that determines the efficiency of heterogeneous nucleation is the geometric shape factor for ice formation, which reduces the nucleation energy of germ formation as compared with the case of homogeneous nucleation. The shape factor appears in the exponential term of the heterogeneous nucleation rate equation and is given by$^2$:

$$f(m, x, \theta) = 0.5 \left[1 + \frac{1 - 3x}{\sqrt{1 - 2mx}}\right] + 3x^2(2 - 3k^2 + k^4) + 3m^2(1 - k^2),$$

(2)

where $x$ is the ratio of the radius of the ice condensation nucleus to the critical germ radius, $m = \eta_{\text{cof}}$ is the cosine of the contact angle, $\theta$ (valued between 0° and 180°), between the ice condensate and the condensation nucleus, which is a measure of their surface and interfacial energies, and $k = x - m/\sqrt{\Phi}$ and $\Phi = \sqrt{1 - 2mx + x^2}$ are geometric factors. The use of contact angles to describe the interaction of the ice germ and the solid substrate assumes that the ice germ is a spherical cap$^3$ and that there is direct vapour deposition (page 341 in ref. 4). We note that nucleated ice germs may have crystalline structures as may be the case for water ice (for example, ref. 4, page 473) such that it may be difficult to define a contact angle (although ice germs may be so small that a simple geometric description is insufficient). Furthermore, experiments demonstrate that the nucleation of water ice in cosmic crystals is too small in specific locations (active sites) on the surface of a condensation nucleus such that specific surface features may play a dominant role in this process (for example, refs. 36–38). However, the statistical model described above is still appropriate if the preferred sites for ice germ growth can be considered equal and randomly distributed$^4$ and this prescription remains the dominant theoretical tool to interpret laboratory experiments (for example, refs. 39–41). Additionally, recent laboratory experiments are consistent with the predictions of classical heterogeneous nucleation theory (for example, ref. 40). For example, the accretion rate of H$_2$O and CO$_2$ ices on grains with different sizes (and thus curvatures) can be reduced by an order of magnitude for the small grain sizes relevant for protoplanetary disks in comparison with much larger particles (~10,000 μm) and further depends on the composition of the ice nucleus. Furthermore, ice formation is strongly inhibited for small, highly curved grains regardless of the composition of the ice condensation nucleus. Results such as these that indicate a dependence of size and composition on the nucleation efficiency are to be expected under the picture of classical heterogeneous nucleation theory.

Given these considerations, the important parameter of the contact angle of CO ice germs on CO$_2$ ice must be determined empirically via experiments in the laboratory. Due to a lack of such experiments, we assume that the contact angle between the seed particle and the forming ice is an intermediate value of 90° such that nucleation is neither prohibited nor highly efficient. This assumed value may indicate that CO is heterogeneously nucleating onto a surface where it does not preferentially form a strong bond, which may be the case for CO forming on a CO$_2$ surface as indicated from laboratory experiments$^{42,43}$. We note that when we reduce the shape factor by an order of magnitude, we initially nucleate more small particles; however, nucleation remains less efficient than condensational growth such that we ultimately derive very similar particle size distributions and the same resultant gas distributions as our nominal case. Thus, while the modelling of heterogeneous nucleation is uncertain because this process is at the limit of current theoretical knowledge, this formulation is within the range of uncertainty and can be used in this modelling due to the large separations of scale between global gaseous diffusion and hyper-local ice formation.

Once CO has heterogeneously nucleated onto a seed grain, the ice particle can grow by coagulation and/or condensation. The ice particle can also evaporate, be lofted and/or settle to the midplane. In the scheme treated in this work, once particles coagulate, they are treated as compact grains. While the aggregate or compact nature of grains is unknown, this assumption is reasonable, particularly if condensation processes increase the compactification of particles that form as aggregates. During coagulation, when an ice particle coagulates with a seed grain, the resultant particle is treated as an ice particle.

We use a formulation of particle condensation that is applicable in the diffuse outer regions of protoplanetary disks where molecules do not diffuse along a path but instead interact collisionally, such that the change in mass of a particle with time is given by

$$\frac{dm_{\text{ice}}}{dt} = \frac{n_{\text{ice}} v_{\text{sub}}}{\sqrt{2\pi m_{\text{ice}} k_{\text{sub}}}} \left[1 - \frac{1}{S_{\text{sat}}} \right],$$

(3)

where $m_{\text{ice}}$ is the mass of the ice particle, $a$ is the radius of the ice particle, $n$ is the number density of condensable molecules, $m$ is the mass of a vapour molecule, $v_{\text{sub}} = (8\pi/3)^{1/2}$ is the thermal velocity and $S_{\text{sat}}$ is the saturation ratio over a curved particle surface given by

$$S_{\text{sat}} = \frac{P_{\text{CO}}}{P_{\text{eq}}(\delta/\bar{r})}.$$

(4)
The partial pressure of the CO gas, \( P_{\text{CO}} \), changes with time and altitude as the system evolves. The equilibrium condensate saturation vapour pressure depends on the size of the grain facilitating the phase change, as given by

\[
P_{\text{sat}}(a, T) = \exp \left( \frac{2 \gamma T}{a \pi R} \right) P_{\text{sat}}(T),
\]

where \( P_{\text{sat}}(a, T) \) is the saturation vapour pressure over a curved surface, \( P_{\text{sat}}(T) \) is the saturation vapour pressure over a flat surface, \( \sigma \) is the surface energy of the condensable species, \( R \) is the volume per mole of the species in the condensable phase, \( T \) is the universal gas constant, \( s \) is the radius of the particle facilitating the phase transition and \( T \) is the temperature of the particle. The saturation vapour pressure for CO is taken from ref. \( 16 \).

The growth processes in equation (5) thus include the Kelvin effect through the supersaturation term. This formulation is consistent with the Hertzsprung–Knudsen model for particle growth \( g \). This formula is valid for a broad range of sizes, where a few simplifying assumptions. In particular, we take the condensation and evaporation constants to be unity such that all molecules impinging on the ice particle are incorporated into the ice and evaporation is set purely by theoretical arguments and not explicitly benchmarked to laboratory data. We further assume that the ice temperature and background disk temperature are in equilibrium. For a discussion of this formulation and the simplifying assumptions we make, see ref. \( 16 \).

The Kelvin effect and particle size distributions. The inclusion of the Kelvin effect and other surface energy effects in this work substantially alters the size distribution of ice particles from the classic view of ice formation accepted in the field. We provide a short overview of the key physical differences here and note that a more in-depth discussion will be the focus of future study.

The Kelvin effect, a well-known effect in atmospheric sciences that is important in evaluating rates of nucleation and condensation \( 5 \), including in meteorological processes on Earth \( 1 \), acts as an added barrier to ice formation on particles with high curvatures where ice coatings are unstable. This barrier is particularly stringent in the case of nucleation, which requires either the presence of large condensation nuclei or sufficient supersaturations of the condensable gas. While the Kelvin effect is important in regulating both nucleation and condensational growth, the most critical factor in our modelling is the barrier to nucleation. In our modelling, nucleation occurs substantially only at early times when CO gas is abundant in the ice-forming regions of the disk. For example, in our modelling, the nucleation rate decreases by 16 orders of magnitude for the same particle size when the supersaturation decreases by a factor of 5 (from \( S = 2,000 \) to \( S = 400 \)).

To illustrate the importance of the Kelvin effect, we modelled the same nominal disk entirely without the Kelvin effect, without the Kelvin effect in the nucleation process and without the Kelvin effect in the process of condensational growth.

The ice particle size distributions for the three cases discussed here are shown in Supplementary Fig. 2. When we do not consider the Kelvin effect at all in our modelling, we uncover a broad distribution of ice particles where the \( \approx 0.1 \mu m \) grains are particularly favoured sites of ice formation (Supplementary Fig. 2a). This outcome is expected and can be seen in studies of the ISM (for example, refs. \( 5, 57 \)) and previous studies of protoplanetary disks (for example, refs. \( 12, 13 \)). In these works, the rate of ice formation on grains (and as such, rates of gas–grain chemistry) is preferentially enhanced on the grains with the largest cumulative surface area (that is, the grain size with the largest number density multiplied by its surface area). Under the assumption of an ISM-like particle size distribution, the size typically quoted is \( \approx 0.1 \mu m \), which are particles that are large enough such that they are not readily raised to sublimation temperatures and small enough such that they have large number densities. These small grains are readily lofted to higher altitudes in the disk where they lose their volatile material back to the gas phase such that CO gas is not as strongly depleted as in the nominal case where the Kelvin effect is considered.

When we do not include the Kelvin effect in the process of nucleation, we derive a bimodal size distribution with a mode at \( \approx 0.1 \mu m \) caused by the continuous nucleation of small grains and an extended mode at larger sizes due to condensational growth (Supplementary Fig. 2b). The abundant nucleation of small ice particles in this model leads to a similar outcome as the model completely devoid of the Kelvin effect where CO gas is not depleted as substantially as in our nominal case.

Finally, when we do not include the Kelvin effect in the growth process but do include the effect in nucleation, we uncover a similar outcome to our nominal case, where ice is preferentially located on the largest grains in the particle size distribution (Supplementary Fig. 2c). One notable difference between this case and our nominal case is that growth occurs marginally more efficiently such that there are fewer ice grains located in the system at later times as more of them are lost to particle drift due to their enhanced size via efficient condensational growth.

It is worth noting that even with an abundant supply of background gas, the Kelvin effect causes the largest particles in a size distribution to form stable ice coatings more efficiently than smaller grains. This effect is further exacerbated when the supply of condensable gas is diffusion-limited, as is the case in the models presented in this work. In the diffusion limit of particle growth via condensation, large particles with the lowest barrier to ice formation preferentially form ice \( 1 \) even with their lower overall surface areas due to the smaller total number of large particles (which dominate the mass distribution of grains while small particles dominate the number density). We note that the relative inefficiency of heterogeneous nucleation as compared with condensational growth is important for atmospheric processes on Earth, and is probably relevant for CO ice formation on Mars \( 35 \) and for water ice in protoplanetary disks (for example, ref. \( 8 \)).

Radial diffusion and accretion. We couple our microphysical model of non-equilibrium ice formation to a global model of gaseous diffusion. We make several simplifying assumptions in the absence of a spatially two-dimensional microphysical model that is the subject of future work. We assume that the vertical and radial diffusion coefficients are the same across the midplane of the disk. The diffusion coefficient, \( D \), is set by \( D = a \pi H \tau \). The parameter \( a \) is a parameter of ignorance \( 30 \). The sound speed and disk scale height, \( H \), are defined locally at the disk midplane. We divide the disks into 200 radial bins with an even, linear spacing. We note that simulations with double the number of radial bins produce the same results.

As can be seen in Fig. 1b, CO gas is only abundant in the warm upper layers of the disk, which are also the regions accessible to observations \( 3 \). We thus model the radial diffusion of CO gas in the warm layers using the 1D diffusion equation in cylindrical coordinates including radial transport due to accretion. We use a modified forward Euler scheme such that at each grid cell the mass-mixing ratio of CO is set by

\[
u_{\text{in}} = \frac{g}{\ln(1 + (1 - g) e^{-\tau_{vert, diff}})} + \frac{g}{\ln(1 + (1 - g) e^{-\tau_{vert, diff}})}
\]

where \( g \) is the mass-mixing ratio of CO gas at a given point in our time grid and radial distance grid \( i \) and \( j \) and \( \tau_{vert, diff} \), which is the fraction of the local vertical diffusion timescale that has occurred over a given time step. The vertical diffusion timescale is defined as \( \tau_{vert, diff} = 3H/D \), where \( H \) is defined at the disk midplane (Supplementary Fig. 3). This treatment of vertical diffusion is validated using our vertical column microphysical modelling.

While both diffusion and accretion are viscous processes that are dictated by the amount of diffusion in the system, we treat them separately because CO gas is diffusively mixed to reduce concentration gradients while also accreting following the accretion flux of the background H gas. To calculate the terms \( u_{\text{solar}} \) and \( u_{\text{vert, solar}} \) we thus determine the local accretion fluxes of H gas and then multiply these fluxes by the local CO abundance to determine the flux in and out of each radial grid cell. Each of our H2 gas surface density profiles are similarity solutions such that we can calculate the flux from accretion through each orbital distance grid cell using the analytic prescription described in equation (21) in ref. \( 3 \), which is appropriate for disk surface density profiles of this form. The outer disk boundary condition is set to be a zero radial condensation gradient while the inner disk boundary condition is set to be a zero disk surface density. We note that the boundary condition in the diffusion equation at the inner edge of the disk does not have an effect on our results. To accurately account for the reservoir of solid CO as a function of time, we determine the dust-to-gas ratio and ice-to-dust ratio as a function of time from our microphysical modelling of ice formation and linearly interpolate these values along our radial grid.

Around the midplane CO ice line, we must additionally treat the formation and drift of ice as we radially evolve the gas present in the system because there is substantial cycling of particles and gas around this region \( 36 \). We calculate the location of the midplane ice line as the hottest radial location in the disk where the nominal saturation ratio over a flat surface is equal to unity, that is, the radial where \( \text{f}_{\text{H}}(\rho, \theta, D, t) = 1 \) in the midplane. Particles that drift across the midplane CO ice line quickly lose their ice mantles at a radial region just interior to the midplane ice line due to their small particle sizes \( 37 \). Cycling occurs because of the increased abundance of CO gas interior to the ice line will diffuse back outwards across the ice line, due to the steep radial condensation gradient. After gas diffuses across the midplane ice line, it is rapidly incorporated into solid ice due to the relatively short vertical diffusion timescale near the CO ice lines. Once more ice forms, there is again an increase in particle drift and the cycle repeats.

We model the surface density of CO ice immediately exterior to the midplane CO ice line following:

\[
\frac{\Sigma_{\text{CO}}}{\Sigma_{\text{H}}}(t) = \frac{f_{\text{H}}}{f_{\text{CO}}} + f_{\text{acc, CO}}
\]

where \( f_{\text{H}} \) is the analytic dust-to-gas mass ratio as a function of time and \( f_{\text{CO}} \) is the solid-ice fraction from the microphysical modelling, both described above. The term \( f_{\text{acc, CO}} \) accounts for the accumulation of CO ice to the radial cycling of solids and gas around the ice line. It is calculated as

\[
f_{\text{acc, CO}} = f_{\text{acc, CO}}(1 - \mu_{\text{in}}) \frac{\Sigma_{\text{CO}}}{\Sigma_{\text{H}}}
\]
density in ice that has condensed in the last time step, \( \Sigma \) is the disk surface density that is dominated by the surface density of the background hydrogen gas that evolves with time due to accretion and \( \Sigma_1 = 2\pi r_\text{midplane} \rho_\text{midplane} \) is the amount of the accumulated surface density that is lost at the last time step where \( r_\text{midplane} \) is the location of the midplane CO iceline. We assume that the majority of the total solid mass is located in the largest particles in the size distribution, which is well supported by the results from our microphysical modelling and from previous works of drift-limited particle growth. We calculate the inward flux of icy pebbles at the ice line as:

\[
F_{\text{ice}} = 2\pi r_\text{midplane} \rho_\text{midplane} \Delta v_\text{drift}.
\]

We add the mass of CO gas that drifts through the midplane ice line in a given time step, \( F_{\text{ice}} \), to the radial bin just interior to the midplane CO ice line. In our models, the cycling of material around the ice line leads to an ice-to-gas ratio immediately exterior to the ice line that is enhanced with time and a corresponding enhanced abundance of CO gas interior to the CO ice line, as found in previous works of drift-limited particle growth.

Our simulations differ from those presented in refs. \(^{67,68} \) as we include the accretion of gaseous CO onto the host star and allow the amount of diffusion present in the system to be a free parameter. We do not include chemical processing of CO, as we find that we are able to reproduce observed levels of depletion with CO ice formation alone.

**Disk parameters.** We derive the total gaseous surface densities for the disks around TW Hya and HD 163296 from previous modelling\(^2\) using observations of dust lines. We note that the mass estimates that we use for TW Hya are consistent with the lower limit of the range given in ref. \(^2\) though our models also take into account the mass of the inner disk. For the disk around DM Tau, which has a mass estimate from hydrogen deuteride observations of warm molecular hydrogen, which is one of the relatively direct indicators of disk mass, we normalize the surface density profile from ref. \(^1\) (see their table 4 and equation (1)) such that the total disk gas mass is equal to \( 4.7 \times 10^{-3} M_\odot \) (ref. \(^1\)) (the surface density normalization \( \Sigma_0 = 0.94 \) cm\(^{-2} \)). For the disk around IM Lup, which does not yet have observations of a robust tracer of total disk mass, we use the gas surface density profile parameters, namely the surface density index of the gas and the gas critical radius, from ref. \(^1\) (see their table 4 and equation (1)). We then choose a surface density profile normalization (\( \Sigma_0 = 15 \) cm\(^{-2} \)) such that the total disk mass falls in the range of masses described in ref. \(^1\), though we note that while this change produces a larger CO mass it has a minimal effect on the amount of depletion from the original CO abundance, which is primarily controlled by diffusion.

We assume our fiducial disk temperature structures, particularly in the outer disk, are controlled by irradiation\(^2\) (see ref. \(^2\) for more details). Several scale heights above the ice line, the disk is heated by the surface heating to occur in the disk two scale heights above the midplane, such that the disk is isothermal within the first two scale heights \( T \approx T_\text{disk}(r) \). The temperature increases linearly within the third scale height of the disk until \( T \approx 3T_\text{disk}(r) \), and remains at this value beyond this height. This temperature structure is thus comparable to that used in refs. \(^{1,67,68}\). To simulate the additional radiative heating that occurs due to relatively large accretion luminosities from an early phase of active disk accretion, and simultaneously improve the numerical stability of our modelling, we increase the disk temperature by a factor of two and exponentially cool the disk to rapidly reach temperatures appropriate for present day. Our results are insensitive to the timescale over which this cooling occurs (100-year and 10,000-year cooling timescales reproduce identical model results) and this process numerically serves to avoid unphysically overshoot the amount of gas that is removed in the first time step. We note that the exact location of surface layer heating does not impact our results as long as the first scale height remains cool enough for ice formation to occur and the overall diffusion timescale from the observed upper layers to the disk midplane is not significantly affected. This is because the scale height of depletions in the disk sensitive to the saturation pressure at the disk midplane and thus the temperature at the disk midplane. The vertical density profile is in hydrostatic equilibrium calculated using these temperature profiles.

The parameters used for the disks modelled in this work are given in the Supplementary Information (Supplementary Table 1). As noted in the main text, the ages of protoplanetary disks are uncertain, and estimates vary in the literature by several million years for a given disk. The disk ages quoted in Supplementary Table 1 thus comprise a source of uncertainty in our modelling. We adopt these age estimates following the reasoning in ref. \(^1\) for the disks around HD 163296 and TW Hya. For IM Lup, the disk age is currently quoted to have a range of 1–Myr (for a detailed discussion, see ref. \(^1\)). The literature around DM Tau has a broad range of age estimates from ~1 to 5 Myr (refs. \(^{1,67}\)). We choose to adopt an age of 1 Myr for DM Tau, as much of the literature surrounding the rapid depletion of CO gas in observed systems quotes a young age for DM Tau and previous chemical models of this system were run for 1 Myr of evolution\(^1\). In our modelling, this younger age gives rise to higher levels of diffusion that are more consistent with those inferred from observations of gas kinematics in other systems and from previous works of drift-limited particle growth. We find that their relative ages are more likely to be robust\(^1\). As such, our chosen age estimates reflect that TW Hya and HD 163296 are probably significantly older than DM Tau and IM Lup.

The disk outer radii are primarily taken from ref. \(^7\) (see their fig. 8) but are also consistent with radii in ref. \(^1\). For TW Hya, we adopt the outer radius from observations of C/O and C/O of 100 au as we compare with results from ref. \(^1\), which observed significant emission out to ~80 au. We note that increasing the outer radius of TW Hya to 215 au, in line with estimates from C/O emission\(^1\), increases the CO abundance interior to ~5 au by a factor of ~2.5 due to a slightly increased rate of ice drift into the inner disk.

**Comparison with observations.** For DM Tau, we compare our beam-convolved model results (red crosses) with the shape of the depletion profile from ref. \(^1\) (black line), as shown in Fig. 4a. We also find agreement with the total level of CO depletion in our models, a factor of 3.7, and the level of depletion reported in ref. \(^1\) of a factor \( \leq 5 \). For IM Lup, we compare our beam-convolved model results (purple crosses) with the shape of the depletion profiles from ref. \(^1\) (black line), as shown in Fig. 4c.

For TW Hya, shown in Fig. 4b, we compare our beam-convolved modelling results (blue crosses) with observations from ref. \(^7\), who report the observed CO surface density (black crosses). Our results also agree with the similar CO column density profile presented in ref. \(^1\). We also compare the shape of the CO depletion profile with the shape of the gaseous CO depletion profile presented in ref. \(^1\) (see their fig. 8). We derive a similar profile shape with a dramatic increase in CO depletion at ~20 au and a slightly reduced level of depletion exterior to this radius until the background gas disk itself becomes diffused and truncated.

For HD 163296, shown in Fig. 4d, we compare our beam-convolved modelling results (green crosses) with observations from ref. \(^1\) (equivalent to the dashed black line). Our results show an overall lack of significant gas-phase CO depletion, though we do derive structures in the CO surface density profile. This is in agreement with the lack of disk-integrated gaseous CO depletion derived in ref. \(^7\) using C/O, a rare, optically thin CO isotope. Both ref. \(^1\) and ref. \(^7\) show a drop off in CO abundance at either ~150 au or ~70 au. Using our fiducial disk temperature profile, we find a drop off in CO abundance at ~80 au, although the exact location of the midplane ice line is sensitive to the disk midplane temperature structure. Our modelling for this disk is in agreement with results presented in ref. \(^1\), which show a dramatic decrease in CO abundance interior to the midplane ice line.

HD 163296, DM Tau and IM Lup are likely to have optically thick CO emission from the inner edge of the thick disk out to at least ~30 au for all commonly observed isotopologues of CO, such that the observed abundance or depletion factor in this region is uncertain. For IM Lup in particular, Bosman et al.\(^1\) demonstrate that the abundance of CO interior to 30 au is unknown as the emission from C/O falls off interior to this point. Their best-fit model results suggest that this is probably caused by a pileup of dust grains around this region. Our model predicts such a pileup of ice grains just exterior to the midplane ice line, located around 40 au in our microphysical temperature profile (Supplementary Table 1), which is particularly pronounced in the case of IM Lup due to high levels of diffusive mixing allowing for efficient radial redistribution of volatile CO near the ice line, which creates an enhancement in local ice formation. For TW Hya, gaseous CO becomes optically thick between a few and ~10 au, even for rare isotopologues such as C/O (ref. \(^1\)). In this region, the temperature structure is also uncertain, which causes the observed amount of CO in this region to be uncertain. We mark these uncertain regions in Fig. 4a–d in grey. However, while the majority of observations of CO gas in TW Hya are optically thick interior to ~20 au, we note that our results agree with the results derived from observations of an optically thin CO isotope in ref. \(^7\) from 5 to 21 au to within a factor of 3.

In this work, we particularly focus on the radial regions of the disks probed by C/O and C/O emission, as these isotopologues are abundant and can serve as probes of CO column density. Emission from C/O is probably optically thick even in the outermost regions of disks\(^1\) such that it is relatively insensitive to even substantial changes in column density. We also note that the disk radial scale in C/O typically exceeds the radial scales observed in C/O, in which turn exceed the radial scales observed in C/O (for example, refs. \(^{71,72}\)). As shown in ref. \(^1\), the differences in radial scale for the different CO isotopologues may arise because the less abundant C/O and C/O have emission surfaces that are deeper in the disk. Thus, as the overall gas density decreases in the outer disk, C/O and C/O probe disk regions that are optically thin in CO, which in turn are optically thick in C/O and C/O, which are optically thick in C/O and C/O. For TW Hya, we adopt the outer radius of ~1 Myr (for a detailed discussion, see ref. \(^1\)). The literature around DM Tau has a broad range of age estimates from ~1 to 5 Myr (refs. \(^{1,67}\)). We choose to adopt an age of 1 Myr for DM Tau, as much of the literature surrounding the rapid depletion of CO gas in observed systems quotes a young age for DM Tau and previous chemical models of this system were run for 1 Myr of evolution\(^1\). In our modelling, this younger age gives rise to higher levels of diffusion that are more consistent with those inferred from observations of gas kinematics in other systems and from previous works of drift-limited particle growth. We find that their relative ages are more likely to be robust\(^1\). As such, our chosen age estimates reflect that TW Hya and HD 163296 are probably significantly older than DM Tau and IM Lup.
Model predictions. The primary prediction of this modelling is that –micrometre sized grains are not abundantly coated in CO ice in the outer regions of evolved protoplanetary disks. Furthermore, all grains are CO ice free at heights in the disk above the level where CO gas is no longer supersaturated, which is probably below the level where UV photodesorption is active (Fig. 1). The James Webb Space Telescope may be able to test these predictions using spatially resolved spectra of edge-on disks, which may have the sensitivity to detect CO ice features that arise from small CO-coated particles and constrain their vertical distribution. The detection of these features in an evolved disk would complicate the model presented here and would imply that either CO ice is abundantly present on small grains or perhaps that the CO ice forms as an aggregate with optical properties similar to small grains (for example, ref. 19).

The mechanism for CO depletion presented in this work requires both vertical and horizontal diffusion within the disk. Thus, for each disk we predict a parameter $c_{\text{obs}}/c_{\text{sec}}$ (Fig. 3) where $c_{\text{obs}}$ is the age of the system, $c_{\text{sec}} = r_{\text{acc}}/c_{\text{H}}$, $r_{\text{acc}}$ is the outer radius of the disk and both the sound speed and scale height are defined at $r_{\text{acc}}$. Thus, for a given disk temperature structure (which sets the sound speed and scale height), an assumed disk age implies a globally averaged $\alpha$ mixing parameter for each disk, given in Table 1. Observations of non-thermal CO gas motions using ALMA have been used to place constraints on turbulent mixing in the upper disk layers. Our results are broadly consistent with these studies, which find low upper limits for turbulent mixing in TW Hya and HD 163296. (that is, the turbulent mixing in these systems is below observable levels) and a detectable level of non-thermal motion in DM Tau, which implies a significant level of turbulent mixing. While a direct comparison between the globally averaged $\alpha$ parameter derived in this work and the level of mixing in the upper disk layers may not be appropriate in a one-to-one fashion, independent observational constraints of turbulent mixing may serve to better constrain the results of the modelling presented in this work.

Another prediction of this work is that the abundance of CO gas interior to the midplane ice line is enhanced compared with the CO abundance in the outer disk. The level of enhancement will vary from system to system and primarily depends on the amount of diffusive mixing that has occurred, which regulates the transport of solid CO as well as the transport and accretion of gaseous CO. We expect that future observations that constrain the CO abundance in the innermost disk regions will agree with this trend. Observations in the inner disk that point towards significant depletions comparable to those seen in the outer disk may instead point towards processes that alter solid CO into a more involatile form, such as processing via grain chemistry. We further expect that systems that have undergone significant accretion of an enhanced abundance of CO gas onto the host star, such as TW Hya and DM Tau, will have enhanced abundances of carbon relative to more refractory elements in the gas being accreted onto the host star. Studies of the UV spectrum of TW Hya indicate that gas-phase carbon is enhanced relative to silicon, possibly due to the accretion of carbon-rich material (for example, ref. 19). Future studies of the composition of the gas accreting onto disk host stars may thus serve as an additional test of the model presented in this work (for example, ref. 19).

Data availability
Observational CO data are published in refs. 81,146,145,5 (see Methods for more detail). Due to the large size of the data files, the full microphysical data generated by the simulations presented in this work are available from the corresponding author upon reasonable request.

Code availability
The numerical models used in this work are not public. However, they are available from the corresponding author upon reasonable request.

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