An inherited complex organic molecule reservoir in a warm planet-hosting disk

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Quantifying the composition of the material in protoplanetary disks is essential to determining the potential for exoplanetary systems to produce and support habitable environments. When considering potential habitability, complex organic molecules are relevant, key among which is methanol (CH$_3$OH). Methanol primarily forms at low temperatures via the hydrogenation of CO ice on the surface of icy dust grains and is a necessary basis for the formation of more complex species such as amino acids and proteins. We report the detection of CH$_3$OH in a disk around a young, luminous A-type star, HD 100546. This disk is warm and therefore does not host an abundant reservoir of CO ice. We argue that the CH$_3$OH cannot form in situ, and hence that this disk has probably inherited complex-organic-molecule-rich ice from an earlier cold dark cloud phase. This is strong evidence that at least some interstellar organic material survives the disk-formation process and can then be incorporated into forming planets, moons and comets. Therefore, crucial pre-biotic chemical evolution already takes place in dark star-forming clouds.

Young stars are surrounded by a disk of dust, gas and ice that will ultimately form an exoplanetary system composed of planets, moons, asteroids and comets. The potential for these exoplanetary systems to produce and support habitable environments is set by the composition of the material in the parent protoplanetary disk. So far, the Earth is the only environment in the Solar System within which life is known to have begun and thrived. Comet impacts are thought to have played a key role in this by delivering volatile organic-rich material, thus seeding the surface of the proto-Earth with the basic ingredients for life1. Biologically important molecules for life, for example, glycine, and the precursors methyamine and ethylamine, have been detected in comet 67P/Churyumov-Gerasimenko2. The icy moons that orbit Jupiter and Saturn have been earmarked as potential habitats for extraterrestrial life due to the presence of sub-surface liquid oceans3. Also, the New Horizons mission revealed that Kuiper Belt Object (KBO) 486598 (Arrokoth) has a surface rich in organic material including methanol (CH$_3$OH)4.

Assessing the potential habitability of forming extraterrestrial planetary systems remains challenging. One way to assess this is by measuring the inventory of organic material present during planet formation. Complex organic molecules (COMs) bridge the gap in complexity between the two- or three-atom molecules that are typically found in space and those molecules that are needed for life, such as amino acids and proteins. COMs are found to be ubiquitous in the warm surroundings of forming stars where they are seen in the gas phase, after sublimation following formation in CO-ice-rich ice in cold dark clouds5. However, it is still uncertain whether this organic ice reservoir survives the assembly of the protoplanetary disk6. Recently, observations of cold disks with the Atacama Large Millimeter/submillimeter Array (ALMA) have resulted in the first detections of simple members of some key functional groups in organic chemistry: acetonitrile (CH$_3$CN, a simple nitrile)6,7, methanol (CH$_3$OH, an alcohol)8 and formic acid (HCOOH, a carboxylic acid)9. These detections demonstrate that relatively complex molecules are present at the epoch of planet formation, but do not yet provide firm constraints on their origin: in situ formation versus inheritance from the cold cloud phase.

One COM of particular significance is CH$_3$OH. This COM is only formed efficiently on the surfaces of very cold dust grains ($\lesssim$20 K) via the hydrogenation of CO ice10. Laboratory experiments have revealed CH$_3$OH as a feedstock for building molecules of higher complexity, including simple esters, ketones and aldehydes11. Hence, the presence of gas-phase CH$_3$OH is a key indicator that larger, more complex molecules could also be present. The temperature structures of protoplanetary disks strongly depend on the luminosity of the host star. The typical luminosities of Herbig Ae stars are of the order of 10–100 solar luminosities compared with the 0.01–10.0 solar luminosities for their lower-mass counterparts, T Tauri stars12,13. Thus, disks around intermediate-mass Herbig Ae/Be stars will have a substantially lower fraction of disk mass at the coldest temperatures ($\lesssim$20 K) than their cooler Sun-like (T Tauri) counterparts. Oxygen-bearing COMs have so far only been detected in disks around T Tauri stars. This means that disks around Herbig Ae/Be stars are expected to be poor in CH$_3$OH. This theory is supported by the non-detection of CH$_3$OH with deep ALMA observations towards the otherwise molecule-rich Herbig Ae/Be disks around HD 163296 and MWC 480 (refs.14,15) as well as detailed astrochemical models that predict a negligible reservoir of CO ice in these systems16,17.

We report the detection of this key COM, CH$_3$OH, in a disk around the Herbig Ae/Be star, HD 100546. HD 100546 is an intermediate-aged (4.79$^{+1.82}_{-0.22}$ Myr) Herbig Be star (2.18$^{+0.02}_{-0.02}$ $M_\odot$; $T_{\text{eff}}$ = 10,000 K) at a distance of 360 lightyr (110$^{+4}_{-3}$ pc)18. The disk around HD 100546 is warm and gas-rich and has been well observed at multiple wavelengths with compelling evidence for two giant planets embedded in the disk at $\sim$10 and $\sim$60 au (refs.19,20). Our data uncover a reservoir of circumstellar COMs and show that
disks around Herbig Ae/Be stars are at least as chemically complex as their Sun-like counterparts. As Herbig Ae/Be disks are warm and cannot form CH$_3$OH in situ, the detection of this COM provides strong evidence for inheritance.

**Results**

The integrated intensity maps and radial profiles for the CH$_3$OH lines detected in the HD 100546 disk are presented in Fig. 1. Most of the CH$_3$OH emission is spatially compact (that is, it lies within the observing beam of 1.40 arcsec × 1.11 arcsec) and therefore originates from the inner ≤ 60 au (half of the beam minor axis) of the disk. For reference, Pluto’s orbit ranges from ~30 to ~50 au from the Sun. There is also some diffuse emission in the outer disk, hinting at a ring of CH$_3$OH coincident with an outer emission ring at ~200 au (ref. 20) arising from millimetre-sized dust. Formaldehyde, H$_2$CO, which is chemically related to CH$_3$OH, is also detected in our data (Supplementary Fig. 1). The H$_2$CO emission shows a centrally peaked component of emission and a well-detected outer ring at ~200 au. Also shown in Fig. 1 are the spectra extracted using both a mask that follows the expected Keplerian pattern of emission with a radius of 400 au and an elliptical (grey) mask. The line profile velocities ($V$) on the $x$-axis have been corrected for the velocity of the source ($V_{LSR}$). The grey-shaded region is the $p$-H$_2$CO 4$_{2,3}$–3$_{2,2}$ transition where the flux is multiplied by 0.5 to allow for a qualitative comparison between the two species.‘Blend’ refers to two CH$_3$OH lines that are blended. These are the 6$_{2,5}$–5$_{2,4}$ and 6$_{2,4}$–5$_{2,3}$ transitions, see Supplementary Table 1 for further details.
The degree of chemical processing of organic ices that may have happened in the protoplanetary disk during disk formation and evolution can be estimated from these data. Chemical models show that the abundance ratio of CH$_3$OH to H$_2$CO is a useful diagnostic of such processing, showing an increase in this ratio with time$^{29}$. This is because H$_2$CO is also formed via the hydrogenation of CO ice, en route to the formation of CH$_3$OH. All the detected lines of CH$_3$OH and H$_2$CO are optically thin and so the column density ratio of CH$_3$OH to H$_2$CO can be determined (see the Supplementary Information for full details). If the inner disk emission is more compact than the observing beam then the observations may suffer from beam dilution and this would result in higher column densities. This disk-averaged ratio is shown in Fig. 2 alongside the values reported for the disks around TW Hya (a Sun-like star), HD 163296 (a Herbig Ae star) and IRAS 04302+2247 (a young, <1-Myr-old Sun-like star)$^{26,27}$. The CH$_3$OH-to-H$_2$CO abundance ratio in the HD 100546 disk is consistent with, or up to 80% higher than, the value reported for the TW Hya disk, at least 7 times larger than the upper limit in HD 163296 and distinctly higher than the value for IRAS 04302+2247.

This same column density calculation strategy was applied to the radial emission profile of the single unblended CH$_3$OH emission line to calculate the column density of CH$_3$OH as a function of radius. The radial CH$_3$OH-to-H$_2$CO ratio is also shown in Fig. 2, alongside the reported disk-averaged values for the disks of IRAS 04302+2247, TW Hya and HD 163296. In the outer disk, HD 100546 has a TW Hya-like ratio, showing that the species potentially have the same chemical origin in both disks. In the inner disk the ratio is much higher, and is more similar to the values inferred in various young stellar objects$^{26–28}$. This highlights HD 100546 as host to a more chemically complex protoplanetary disk in terms of oxygen-bearing COMs than the other sources observed to date.

Chemical models of protoplanetary disks predict a much larger mass reservoir of CH$_3$OH ice than CH$_3$OH gas in the outer disk, on the order of 10$^6$ times more massive$^{29}$. To investigate the chemical origin of gas-phase CH$_3$OH in the HD 100546 disk, we ran a gas–grain chemical model using a physical structure specific to HD 100546 with initial dark cloud molecular ice- and gas-phase abundances (see Methods for full details). This ice is initially CH$_3$OH rich. The resulting column densities of CH$_3$OH gas and ice at different times in the model are shown in Fig. 3. We find high abundances of gas-phase CH$_3$OH only in the inner disk (<50 au), located at the edge of the known dust cavity (~13 au). Here the dust is warm enough to thermally sublimate the ices formed in the cold phase$^{28}$. The radial distribution is consistent with the observations (Fig. 1). Methanol is destroyed via reactions with cations (for example, H$_3$O$^+$) with time and has not reached steady state by 5 Myr. This is because CH$_3$OH cannot reform efficiently in the gas phase, as also shown in previous work$^{30}$. The average column density in the model at 5 Myr (the approximate age of the source) is ~100 times less than the column derived from the observations within 50 au (2.0×10$^{14}$ cm$^{-2}$; see Supplementary Fig. 2). However, the column at earlier times better matches that derived from the observations. At 2 Myr it is only around two times less than observed. This potentially indicates an earlier phase of chemical and physical evolution that we have not accounted for in our static model. It has been shown that dust dynamics and grain growth will also have an effect on the gas and ice chemistry by continuously enriching the inner disk with CH$_3$OH-rich ices$^{31}$. To further investigate the formation and destruction pathways of CH$_3$OH in the disk, we ran models with initial atomic abundances, mimicking total reset of chemistry in the disk due to, for example, shocks, to test whether the CH$_3$OH is able to form in situ (see Methods for further details). We found that under these atomic initial conditions, CH$_3$OH cannot form efficiently within 1 Myr and is ~10$^8$ lower than in our inherited model at the same timestep. In the inner disk, the inherited gas-phase CH$_3$OH can be sustained for 1 Myr via the same gas-phase reactions that are important in hot-core chemistry$^{11}$. In the outer disk, no net CH$_3$OH is formed and over time the CH$_3$OH ice abundance continually decreases. This is primarily because the dust temperature is >20 K and therefore there is little CO ice present for hydrogenation reactions to proceed to replenish CH$_3$OH ice lost through non-thermal desorption$^{14}$.

Fig. 2 | A comparison of the HD 100546 CH$_3$OH-to-H$_2$CO ratio with other sources. Left: disk-averaged CH$_3$OH-to-H$_2$CO column density ratios for four disks. The vertical bars show the error on the ratio and the arrow for HD 163296 denotes an upper limit. Right: the CH$_3$OH-to-H$_2$CO ratio as a function of radius for the HD 100546 disk. The shaded region highlights the error propagated from the radial profiles shown in Fig. 1 and Supplementary Fig. 3. The dashed lines mark the average ratios for other objects (data from refs. $^{10,16,25–28}$).

Fig. 3 | Model gas- and ice-phase CH$_3$OH column density in the HD 100546 disk as a function of disk radius and time. Gas-phase (solid coloured lines) and ice-phase (dashed coloured lines) column densities ($\Sigma_{\text{CH}_3\text{OH}}$) are shown for the times indicated. The vertical black dashed line is the edge of the dust cavity. The vertical black solid line marks where the x axis changes from linear to log scale.
Figure 4 | Cartoon of the HD 100546 disk structure. The regions where CH$_3$OH is detected in the disk are shown, as well as the different physical and chemical mechanisms that we propose are taking place. The grey region of the disk illustrates where CH$_3$OH is in the ice phase and the blue region where the CH$_3$OH is in the gas phase. The purple circles represent the locations of the inferred planets in the disk.

Discussion

Disks around Herbig Ae/Be stars have been thought to be COM-poor when compared with their T Tauri counterparts due to their warmer midplane temperatures and higher levels of ultraviolet irradiation. Chemical models support this, showing different CO ice reservoirs between T Tauri and Herbig Ae/Be disks with very little CO freeze-out in the latter$^{19,20}$. This is also consistent with ref. 19, which showed on average, from the current source sample, that there is less H$_2$CO observed in Herbig Ae/Be disks than T Tauri disks. In the T Tauri source TW Hya the gas-phase CH$_3$OH traces the CO ice reservoir, whereas the disk around HD 100546 is too warm to host a reservoir of CO ice$^{21}$. The detection of CH$_3$OH in the HD 100546 disk is therefore surprising, and we sought to understand its origin.

In protoplanetary disks, CH$_3$OH can only be observed once released from the ice into the gas phase, either via thermal sublimation (desorption) in hot regions ($\geq$100 K) or via non-thermal desorption triggered by, for example, UV photons, in cooler regions ($\leq$100 K). In the TW Hya disk, the CH$_3$OH is distributed in a ring where the outer radius is at the edge of the millimetre dust disk and the inner edge is at the CO snowline$^{22,23}$. At these low temperatures, non-thermal processes are most likely responsible for the occurrence of the gas-phase CH$_3$OH. The observed abundance in the TW Hya disk is much lower than initially predicted by chemical models$^{24}$. This is because the outer disk is too cold for thermal desorption and the CH$_3$OH primarily fragments during the process of non-thermal desorption$^{25}$. In comparison, the bulk of the CH$_3$OH emission in the HD 100546 disk originates from the warmer inner disk (Fig. 4). Hence, it is likely to be a thermally desorbed reservoir of CH$_3$OH that originates from the edge of the dust cavity that is exposed to radiation from the central star. Direct evidence for the high dust temperature at the cavity edge for the HD 100546 disk comes from the detection of crystalline silicates$^{10}$. The unique chemistry of transition disks has been predicted from models$^{26}$ but our data provide evidence for warm and rich complex organic chemistry due to thermal sublimation in a class II disk. Both TW Hya and HD 163296 lack large (>5 au) inner cavities and therefore, in both cases, the non-detections of an inner warm CH$_3$OH component like that seen in HD 100546 may be attributed to optically thick dust at millimetre wavelengths. Any gas-phase CH$_3$OH in the outer disk of HD 100546 probably has the same chemical origin as in TW Hya—that is, non-thermal desorption from the ice coated dust grains.

Methanol has gone undetected towards both class I and class II disks where H$_2$CO is detected robustly, aside from in TW Hya and IRAS 04302+2247 (refs 19,27). The low CH$_3$OH/H$_2$CO ratios observed in these class I/II sources have been interpreted as evidence for chemical processing of material as it is accreted onto the disk, but temperature can also be responsible for the lack of emission$^{28}$. Our detection of CH$_3$OH in the HD 100546 disk shows that complete chemical reset/reprocessing of ice during disk formation may not occur. Owing to the nature of the HD 100546 disk, a disk with a central cavity, we have been able to detect a thermally desorbed reservoir of CH$_3$OH. This means that our gas-phase abundances should be more representative of the total CH$_3$OH ice in the system. The lack of a similar warm CH$_3$OH reservoir in the inner disk of other sources is probably due to the high optical depth of the dust, which masks any thermally desorbed CH$_3$OH emission. The current upper limits on CH$_3$OH abundances probably probe the cold outer disk, where most of the CH$_3$OH is on the icy grains. Our observations also cover CH$_3$OH transitions with higher upper energy levels and therefore lines that are more sensitive to warm gas.

We used models to investigate the chemical origin of the CH$_3$OH in the HD 100546 disk and, in particular, whether CH$_3$OH can be formed in situ. We found that with the current observationally constrained HD 100546 disk model, it is not possible for CH$_3$OH to be synthesized in non-negligible abundances anywhere in the disk when beginning with atomic initial conditions (chemical reset). This means that the disk either inherited CH$_3$OH-rich ices from an earlier dark cloud phase, or earlier in the evolution of the disk there was a substantial cold (<20 K) reservoir in the outer disk that would allow for in situ formation. However, recent studies of the temperature structure of class I disks show that young disks are warm and thus probably cool with age (for example, ref. 29). The bulk volatile carbon abundance in the disk is also consistent with an interstellar medium abundance$^{30}$. This means that there has been very little in situ CO freeze-out in this disk, unlike in other sources, such as HD 163296 and TW Hya$^{31,32}$. All of the above is very strong evidence for interstellar inheritance of CH$_3$OH-rich ice in a disk. This allows us to make a clear argument, as, for example, the observations of CH$_3$CN in TW Hya can be explained by in situ chemistry$^{33}$. Our models also show that the CH$_3$OH column density does not reach steady state in the inner disk and declines steadily after 1 Myr. Therefore, it is possible that the inner disk is being replenished with CH$_3$OH ice from the outer disk. This could be achieved via radial transport (for example, ref. 34), for which there is evidence that this is ongoing in this disk$^{35}$.

Disks around Herbig Ae/Be stars often present numerous direct and indirect signatures of forming gas giant planets$^{36,37}$. We have shown that these disks can host a substantial chemically complex reservoir that is inherited from an earlier cold phase. Therefore, the forming cores of planets and moons in these systems will be able to accrete icy, organic-rich material, and, the building blocks of pre-biotic molecules are present at the epoch of planet formation.
two transitions was overlapping in the line wings between the two rest frequencies. These measurements sets were therefore combined using concat. The CH$_3$OH(E) $6_{1,3} - 5_{1,2}$, and $6_{1,3} - 5_{0,2}$ transitions were covered in the same spectral window and were also blended with their rest frequencies $\sim$0.4 km s$^{-1}$ apart. This means that the frequency resolution of the observations was not sufficient to distinguish between the emission attributed to the individual transitions.

All of the molecular lines were imaged with iCLEAN using a 400 au Keplerian mask (approximately the same size as the $^{12}$CO molecular disk) and natural weighting. The resulting m.s. peak line flux and integrated flux for each line are listed in Supplementary Table 1 along with the respective beam sizes. The $^{12}$CO and $^{13}$CO lines were clearly detected at the native spectral resolution of the data whereas the CH$_3$OH(E) data needed to be rebinned to 1 km s$^{-1}$ to make a clear (≥5σ) detection. The CH$_3$OH(A) $6_{1,3} - 5_{0,2}$ transition was not detected at 1 km s$^{-1}$ nor when using a matched filter analysis$^{46}$. This line has a slightly higher upper energy level and lower transition probability than the detected CH$_3$OH lines (these values for all transitions covered are in listed Supplementary Table 1), and because the signal-to-noise ratio for the detected lines is low, the non-detection of this line is not unreasonable. The channel maps of all CH$_3$OH lines with the Keplerian masks overlaid are shown in Supplementary Fig. 3.

The CH$_3$OH integrated intensity maps shown in Fig. 1 were generated with Keplarian masks. These were then deprojected and azimuthally averaged assuming a disk inclination of 44° and position angle of 146° (ref. 20). The resulting radial Keplerian masks. These were then deprojected and azimuthally averaged assuming $k$ is the excitation temperature of the gas and $o$ is the opacity at the line centre. This can be calculated via $\tau = c_0 n_o \Delta v \rho (\nu/kT_o - 1)$, where $\Delta v$ is the rest frequency of the line. The Doppler linewidth is given by $\Delta v = \sqrt{\left(2 k T_o / m_g \right) + \left(2 k T_{ic} / m_{ic} \right)}$, where $m_g$ is the molecular mass (either for H$_2$CO or CH$_3$OH), $m_{ic}$ is the mass of hydrogen, $\mu = 2.37$, $t_{ic}$ is the turbulent component (assumed to be 0.01), $T_{ic}$ is the excitation temperature of the gas and $k_B$ is the Boltzmann constant. The average Doppler linewidth calculated between a rotational temperature $T_{rot}$ of 30 and 60 K was in the calculations (0.17 km s$^{-1}$). The linewidth / full-width at half-maximum of the line is then $\sqrt{\ln(2) \times \Delta V}$. The total column density, $N_{\text{tot}}$, can finally be calculated from relating equation (3) to the Boltzmann equation resulting in,

$$\ln N_{\text{tot}} = \ln C_r + \ln N_T - \ln Q(T_{rot}) - \frac{E_u}{k_B T_{rot}}.$$  

(5)

where $C_r$ is the degeneracy of the corresponding upper state level, $Q$ is the partition function and $E_u$ is the upper state level energy. We then created a likelihood function from equation (5) and used emcee$^{51}$ to retrieve posterior distributions for $N_{\text{tot}}$, $T_{rot}$ and $r$.

First the disk-integrated intensities of the H$_2$CO lines were used to calculate the disk-averaged H$_2$CO column density and excitation temperature including a 10% flux uncertainty. We then used this excitation temperature to calculate the H$_2$CO gas disk-averaged column density from the $6_{1,3} - 5_{2,2}$ lines. We did not use the $6_{1,3} - 5_{0,2}$ lines as both molecules are emitting from the same vertical and radial region in the disk. Because all lines were found to be optically thin and had a similar emission morphology, and may have a similar chemical origin, this is a reasonable assumption. However, given that there is evidence for radial transport in this disk, this may have redistributed methanol ice and gas through the disk relative to H$_2$CO gas. Higher-angular-resolution data would be needed to confirm this.

The upper state degeneracy and energy, Einstein A coefficient, and frequency of each transition and partition functions were taken from CDMS for both H$_2$CO and CH$_3$OH$^{15}$. In this calculation, we did not distinguish between the ortho and para spin states of H$_2$CO for $F$ and $A$ types CH$_3$OH. The resulting disk-averaged H$_2$CO rotation diagram is shown in Supplementary Fig. 5, where the disk-averaged column density is $4.5 \times 10^{12}$ cm$^{-2}$ and the rotational temperature is $34 \pm 4$ K. The disk-averaged optical depth of the H$_2$CO transitions ranged from 0.004 to 0.013. For CH$_3$OH, the disk-averaged column density was $7.1 \times 10^{12}$ cm$^{-2}$ and $t_r$ was 0.008. The above error bars were propagated from a 10% uncertainty on the flux. Uncertainties are the 16th and 84th percentiles of the posterior distributions of the Markov chain Monte Carlo, corresponding to 1σ. If the excitation temperature of the CH$_3$OH is higher, then the inferred column density will also be higher. For example, at 100 K the column density of CH$_3$OH will increase by 1.7x and at 150 K by 2.5x. We could not constrain the CH$_3$OH excitation with our current data, but our inferred column densities are robust and realistic lower limits.

Because the molecular emission was radially resolved, we could extend the above analysis to derive N(H$_2$CO), N(CH$_3$OH) and $T_{rot}$ as a function of projected radius using the radial profiles shown in Fig. 1 and Supplementary Fig. 1. The resulting N(H$_2$CO) and $T_{rot}$ as a function of radius are shown in Supplementary Fig. 2. The radial temperature profile was then applied to the CH$_3$OH $6_{1,3} - 5_{2,2}$ radial profile and the resulting column densities are shown in Supplementary Fig. 2. Here the errors come from the errors in the radial emission profiles. The optical depth of the H$_2$CO lines reached a maximum of 0.026 in the inner disk and a maximum of 0.25 for CH$_3$OH. These radial column density profiles were then used to calculate the CH$_3$OH/CH$_2$DO ratio presented in Fig. 2. Noting that the CH$_3$OH/CH$_2$DO ratios are probably lower limits on the column density and line opacity in the inner disk due to beam dilution; however, the dilution factor is the same for CH$_3$OH and H$_2$CO if the emitting areas are the same. The column density ratio would therefore stay the same unless one transition becomes optically thin while the other does not.

Chemical modelling. To investigate the chemical origin of gas-phase CH$_3$OH in the HD 100546 disk, we ran a gas–grain chemical model over a physical structure specific to the HD 100546 disk. The aim of this calculation was not to make a model to reproduce the observations, but to explore where gas-phase CH$_3$OH is most likely to reside in the disk and whether the predicted location and column density are similar to the observations. The 2D disk physical model (Supplementary Fig. 6) is from ref. 41 and this includes $n_H$ (the number density of hydrogen nuclei), gas and dust temperatures, the UV radiation field and the X-ray ionization rate.

Following ref. 42, we assume a cosmic ray ionization rate of $5 \times 10^{-17}$ s$^{-1}$. We coupled this model with the gas–grain reaction network presented in refs. 35,43. The gas-phase chemistry network is based on the UMIST Database for Astrochemistry (Rate 12; ref. 44) that was first implemented into the code in ref. 45. The accretion and desorption rates are from ref. 39 and the grain surface reaction rates are from refs. 46,47. In the modelling framework, we also assume a gas-to-dust mass ratio of 100 at every point in the disk, with surface reactions assuming to occur on dust grains of radius 0.1 μm. The CH$_3$OH chemistry was recently updated$^{11}$ to include the fragmentation of CH$_3$OH upon non-thermal photo-desorption$^{48}$ and the surface chemistry network for CH$_3$OH was extended$^{49}$. This results in a total of 709 species with 9,441 reactions. The initial molecular abundances were determined by running a single-point dark cloud chemical model following initial conditions for 1 Myr. The gas and dust temperature was set to 10 K, and $n_H$ was $2.0 \times 10^{13}$ cm$^{-3}$ was assumed, and the cosmic ray ionization rate was set to $10^{-17}$ s$^{-1}$. The use of these initial abundances assumes the inheritance of the ice from an earlier cold phase. The initial fractional abundances of select ice species relative to $n_H$ were as follows: CH$_3$OH = 2.9 × 10$^{-4}$, H$_2$O = 1.5 × 10$^{-4}$,
CH$_3$OH ice or CH$_3$OH gas → CH$_3$O + H$_2$O

and

CH$_3$OH + H$_2$O $\rightarrow$ CH$_3$O$_2$ + H$_2$O.

The CH$_3$OH$_2$ ion primarily forms from proton transfer reactions with CH$_3$OH. These gas-phase reactions were originally found to be important in hot-core chemistry after the sublimation of CH$_3$OH ice.$^{33}$

In the reset model, the increase in CH$_3$OH at later times is also due to the above reaction, but after 10 Myr the abundance does not increase any further and is still $\lesssim$10% less than that required to match the observations. The increase in CH$_3$OH at starting 0.5 and up to 1.0 Myr is due to this barrierless ($\Delta G$=0 K) reaction:

CH$_3$OH + HCO $\rightarrow$ CH$_3$OH + CO

In the outer disk, at 220 au, no net CH$_3$OH is formed in either model and this is primarily because the dust temperature is >20 K and there is therefore no CO ice present for the hydrogenation reactions to succeed.$^{34}$

At early times there is some formation of CH$_3$OH in the grains via

OH$_3$ + CH$_3$OH$_{25}$ → CH$_3$OH$_{26}$ + H$_2$O,

and

OH$_3$ + CH$_3$OH$_{25}$ → CH$_3$O$_2$ + H$_2$O + CH$_3$OH$_{26}$ + H$_2$O.

but the destruction on the ice via reaction with H on the grain surfaces and proton transfer in the gas phase via

HCO$^+$ + CH$_3$OH → CH$_3$OH$^+$ + CO

are always dominant and the CH$_3$OH levels never increases above the initial inherited abundance.

Data availability

The data presented here are from the ongoing ALMA Cycle 7 Program 2019.1.00139.S (PI A.S.B.). The raw data will be made publicly available from 30 June 2021 via the ALMA archive. The scripts for self-calibration and imaging, and the reduced data (self-calibrated measurement sets) are available on request from the corresponding author. The final imaging products (channel maps) are available from VizieR.

Code availability

The HD 100546 disk physical structure model is publicly available at https://vizier.u-strasbg.fr/viz-bin/VizieR?source=1/A-A/592/A83. The chemical code is available on request from the corresponding author.

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Author contributions
A.S.B. reduced the data, ran the chemical models, analysed both the data and model output, and wrote the manuscript. C.W. contributed to the writing of the manuscript and provided the chemical model. J.T.v.S. provided analysis scripts for the data and contributed to the manuscript. J.E.F.V and J.D.I. contributed to the writing of the manuscript. M.K. provided the HD 100546 disk model and contributed to the manuscript.

Competing interests
The authors declare no competing interests.

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