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1 An Ice Age JWST inventory of dense molecular cloud 2 ices

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46 **ABSTRACT**

47 **Icy grain mantles are the main reservoir of the volatile elements that link chemical processes in dark, interstellar clouds with the formation of planets and composition of their atmospheres. The initial ice composition is set in the cold, dense parts of molecular clouds, prior to the onset of star formation. With the exquisite sensitivity of JWST, this critical stage of ice evolution is now accessible for detailed study. Here we show the first results of the Early Release Science program “Ice Age” that reveal the rich composition of these dense cloud ices. Weak ices, including, $^{13}\text{CO}_2$, OCN^- , ^{13}CO , OCS , and COMs functional groups are now detected along two pre-stellar lines of sight. The $^{12}\text{CO}_2$ ice profile indicates modest growth of the icy grains. Column densities of the major and minor ice species indicate that ices contribute between 2 and 19% of the bulk budgets of the key C, O, N, and S elements. Our results suggest that the formation of simple and complex molecules could begin early in a water-ice rich environment.**

48 In molecular clouds, the volatile elements that make up life as we know it (carbon, hydrogen, oxygen,
49 nitrogen, and sulfur, i.e. CHONS) are locked up in ices on the surfaces of dust grains. Vibrational modes
50 of these molecular ices are observed in absorption against the near- and mid-infrared continuum provided
51 by field stars located behind clouds. Fully-resolved absorption bands have logarithmic depths directly
52 proportional to the ice column density along the line of sight, allowing model-independent assessment of
53 relative ice abundances within the same beam. At low extinctions in the outer regions of clouds, a mixture
54 of water (H_2O), methane (CH_4), and ammonia (NH_3) ice forms initially through accretion of atomic H in
55 combination with atomic O^{1,2}, C^{3,4}, and N^{5,6} onto silicate/carbon-rich dust grains. Carbon dioxide (CO_2)
56 also forms efficiently in this water ice layer. In the densest and coldest cloud cores, carbon monoxide
57 (CO) freeze-out forms a CO-dominated ice phase^{7,8}, where CO_2 and other simple ice species continue
58 to form. CO and its reaction products can be hydrogenated to produce methanol (CH_3OH)⁹ or have a
59 hydrogen atom abstracted¹⁰, and subsequent radical-radical reactions can also lead to the formation of
60 other complex organic molecules (COMs). These simple ices and methanol should provide the feedstock
61 for more complex COMs, such as the biomolecule glycine that is seen in comets¹¹, some of which are also
62 capable of forming under pre-stellar core conditions¹². Ground-based telescopes and space observatories,
63 like the *Infrared Space Observatory (ISO)*¹³, *Spitzer*¹⁴, and *Akari*¹⁵, have probed ice chemical evolution
64 along sightlines through the envelopes of nascent protostars. However, chemical assays of cloud ice have
65 been limited to regions with visual extinctions below $A_V \sim 50$ magnitudes, due to the faintness of field
66 stars seen at larger A_V ^{16,17}.

67 Here we report the first observations of pristine cloud ices at $A_V > 50$ towards two background
68 stars, NIR38 (11:06:25.57 -77:23:15.87, J2000) and SSTSL2J110621.63-772354.1 (hereafter "J110621",
69 11:06:21.64 -77:23:54.12, J2000), using the James Webb Space Telescope (JWST). These stars probe
70 dense lines of sight just outside the infalling envelope of a Class 0 protostar, Cha MMS1¹⁸ in the low-
71 mass star forming region Chameleon I (192 pc,¹⁹). Initial calculations of their extinction based on the
72 intrinsic colors of K and G giant stars and mid-infrared photometry suggest values of $A_V \sim 60$ and
73 $A_V \sim 95$, respectively (see section 3.4 in²⁰), or $N_{\text{H}}=1.1 \times 10^{23} \text{ cm}^{-2}$ and $1.7 \times 10^{23} \text{ cm}^{-2}$, respectively.
74 The observations presented here were obtained with NIRSpec²¹ Fixed Slit (FS) mode ($R \sim 2600$, 2.7–5.3
75 μm), NIRCам²² Wide Field Slitless Spectrograph (WFSS) mode ($R \sim 1600$, 2.4–5.0 μm), and MIRI²³
76 Low Resolution Spectrograph (LRS) FS mode ($R \sim 100$, 5–14 μm) (see Methods section for more details),
77 in order to cover all five major simple ice species, H_2O , CO_2 , CO , CH_4 , and NH_3 , and the simplest COM,
78 CH_3OH .

79 The full, multi-instrument 2.5–13 μm spectra towards both high- A_V background stars are presented
80 in the top panel of Figure 1, with major solid-state features labeled. The identifications of features that
81 we detect, tentatively detect, and do not detect are presented in Table 1. The spectra obtained from each

82 instrument are compared in Figure 2; NIR38 is detected in the continuum at $3.97 \mu\text{m}$ by NIRSpec FS
83 with $547.1 \pm 2.6 \mu\text{Jy}$ ($S/N \sim 207$) and NIRCам WFSS with $551.2 \mu\text{Jy}$, while its flux at $7.5 \mu\text{m}$ with MIRI
84 LRS is $310.7 \pm 0.6 \mu\text{Jy}$ ($S/N \sim 499$). J110621 was detected at $3.97 \mu\text{m}$ by NIRSpec FS with $54.4 \pm 0.4 \mu\text{Jy}$
85 ($S/N \sim 145$) and by MIRI LRS at $7.5 \mu\text{m}$ with a flux of $39.7 \pm 0.2 \mu\text{Jy}$ ($S/N \sim 208$). This high sensitivity
86 allows us to detect both the expected strong absorption features of abundant ice species, as well as a
87 number of weak absorption features that are now detectable through quiescent molecular cloud lines of
88 sight (Figure 1, bottom, and Figure 3). For these spectra we fit a global continuum to specific continuum
89 regions (see Methods and Figure 1 caption) to calculate optical depths for these ices.

90 We report column densities and abundances relative to water of the different ice species in Figure 4
91 and Table 2, as determined from both global and local fitting of laboratory data (Table 3) to the optical
92 depths over the whole wavelength range (see Methods and fits given by Extended Data Figures 1-3) and to
93 individual ice features (see Supplementary Data Figures). We also consider the shape of the ice bands,
94 which depends on the local environment, in particular whether the ice is mixed with water or not.

95 Results

96 **Ice inventory and new features** - Both spectra in Figure 1 display all of the deep features that we
97 expect to be associated with the main icy grain constituents: H_2O ice, the main isotopolog of both major
98 C-bearing ices, $^{12}\text{CO}_2$ and ^{12}CO , and rocky silicates. The column density of water ice increases from
99 $N_{\text{H}_2\text{O}} \sim 7 \times 10^{18} \text{cm}^{-2}$ to $N_{\text{H}_2\text{O}} \sim 13 \times 10^{18} \text{cm}^{-2}$, respectively, between NIR38 and J110621, while CO_2
100 and CO are present at 10-20% and 20-40% of H_2O ice. Additionally, the sensitivity and spectral resolution
101 of NIRSpec also allow us to detect a number of new features that probe the structure of these main ices, as
102 well as the chemical diversity of additional small molecules in the ice.

103 Inorganic O- and C-ices - In these simple ice species, we see structure in the $^{12}\text{CO}_2$ stretching feature
104 at $4.27 \mu\text{m}$, with both an excess emission over the continuum in the blue wing at $4.2 \mu\text{m}$ and a strong
105 absorbing red wing that extends to at least $4.35 \mu\text{m}$. While the continuum shape may change slightly
106 with future photospheric model fits, there is no physically motivated fit that could locally change the
107 continuum enough to erase the warped profile. A similar asymmetric profile is theoretically expected to
108 result from ice mantle growth²⁴. An analogous scattering profile is tentatively seen in the CO band at 4.7
109 μm , where there is red-shifted absorption below the continuum. However, the blue-shifted CO excess
110 requires confirmation, as it overlaps other absorption features. We also detect both the combination mode
111 of $^{12}\text{CO}_2$ at $2.7 \mu\text{m}$ and perhaps the dangling O-H mode of H_2O at $2.74 \mu\text{m}$ (see Extended Data Figure 1,
112 panel b inset), the latter of which would signify that some fraction of the water ice is porous or mixed with
113 other species. The ^{13}C isotopologs of CO_2 and CO are both detected (see Extended Data Figures 4 and
114 5, respectively), superimposed over the $4.6\text{--}5.0 \mu\text{m}$ CO ro-vibrational gas phase lines originating in the
115 stellar photospheres of these background stars. The $^{12}\text{CO}_2/^{13}\text{CO}_2$ ratio ranges from 69-87 towards these
116 two lines of sight, while the $^{12}\text{CO}/^{13}\text{CO}$ ratio ranges from 99-169.

117 N-rich ices - We detect the main N-carrying ice, NH_3 , in isolation at $9.1 \mu\text{m}$ after the removal of the
118 broad $10 \mu\text{m}$ silicate feature profile from the optical depth spectrum (see Extended Data Figure 6), along
119 with a blended ammonium (NH_4^+) feature at $6.85 \mu\text{m}$, which have both been seen before towards dense
120 cores. However, with JWST we are now able to detect the cyanate anion (OCN^-) at $4.62 \mu\text{m}$, where it
121 overlaps with the blue scattering wing of ^{12}CO (Extended Data Figure 7). Ammonium (NH_4^+), a potential
122 counter ion, is also detected, securing the identification of OCN^- . In contrast, we do not detect other small
123 nitriles, such as CN , HCN , and CH_3CN (see Methods). The upper limits to these ice column densities
124 range from 0.7 to 2% of H_2O in our spectra. This limit is similar to the 0.1-1% level of HCN seen in
125 comets²⁵.

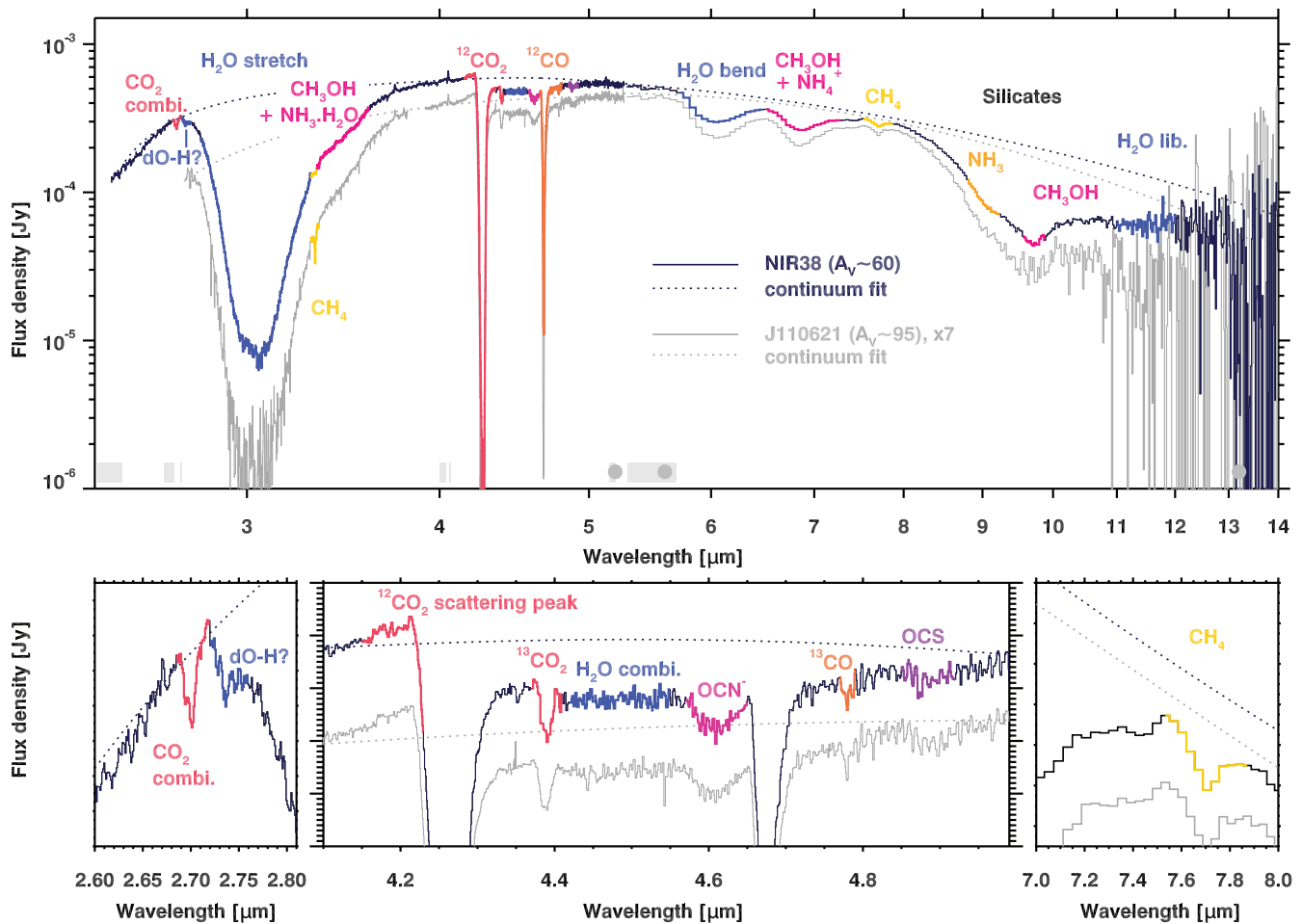


Figure 1. NIRSpec FS [NIRCam WFSS] and MIRI LRS spectra of NIR38 and J110621. Top: Full NIRSpec FS and MIRI LRS spectra of NIR38 ($A_V \sim 60$, solid navy line) and J110621 ($A_V \sim 95$, solid light gray line), with associated continuum fits (dotted lines).

For NIR38, a preliminary NIRCam WFSS spectrum has been scaled to the NIRSpec spectrum at $3.8 \mu\text{m}$ and spliced in to cover the NIRSpec FS gap from $3.85\text{--}3.9 \mu\text{m}$ and extend the spectrum to $2.5 \mu\text{m}$. Ice absorption features are color-coded according to species and labelled in the NIR38 spectrum. Wavelength regions used for the continuum fit are indicated by light gray bars (NIRSpec) and dark gray filled circles (MIRI) at the bottom of the top panel. Bottom: Zoom in on the weaker ice features and structure revealed by JWST. The potential dangling O-H feature is indicated by "dO-H", and the combination modes of CO_2 and H_2O by "combi."

126 S-rich ices - In these spectra, we detect the S-bearing ice species carbonyl sulfide (OCS) around 4.9
 127 μm , superimposed on the stellar photospheric CO absorption features (Extended Data Figure 8). The
 128 simultaneous detection of OCS and CO ice is consistent with a solid-state formation mechanism of $\text{CO} +$
 129 $\text{S} \rightarrow \text{OCS}$ ²⁶, but constraining the intimate chemical environment of OCS would require careful removal of
 130 the photospheric features. There are hints of another S-bearing ice, SO_2 , at $7.6 \mu\text{m}$ in the blue shoulder of
 131 the CH_4 feature, with detection limits of 0.1-0.3% with respect to water. The source of sulfur for OCS and
 132 potentially SO_2 could be from gas-phase depletion into the ice²⁷, as well as from minerals, such as troilite
 133 (FeS)²⁸. However, the dominant S-bearing ice in comets, hydrogen sulfide (H_2S)²⁹, remains undetected
 134 at an upper limit of 0.6% of H_2O , as the $3.92 \mu\text{m}$ feature is not detected towards NIR38. This limit is
 135 comparable to the 1% level of H_2S seen in comets²⁵.

136 Organic ices - We detect both bands of the simple organic ice CH_4 for the first time in background

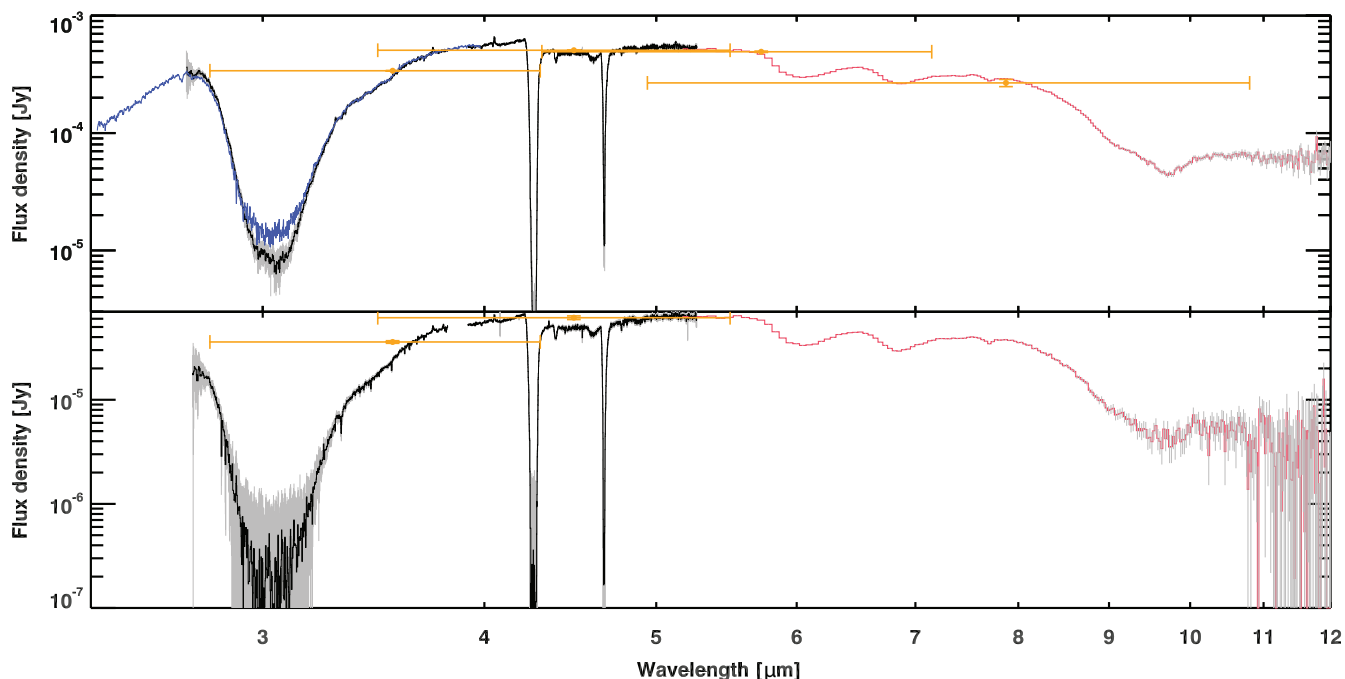


Figure 2. Data quality comparison for NIR38 and J110621. (Top panel) Comparison of the NIRCcam WFSS (blue), NIRSpec FS (black), and MIRI LRS FS (red) spectra of the $A_V = 60$ background star. Error bars (gray) are 3σ , and in some regions are smaller than the thickness of the lines.

Spitzer IRAC photometry (gold points) from the IPAC SEIP catalog is given for reference, with error bars and bandpass indicated. (Bottom panel) Comparison of NIRSpec FS and MIRI LRS FS data for the $A_V = 95$ star. Colors are the same as in the top panel.

stars, at 3.32 and 7.6 μm . Another low-contrast feature appears from 3.35–3.6 μm in the red wing of the water ice band. This feature has been detected before towards background stars, but we detect it here with a S/N of 150 and 70 in the $A_V=60$ and 95 sources, respectively. At this sensitivity, the feature separates into four distinct peaks that are reproducible between the NIR38 NIRCcam and NIRSpec spectra, as well as between NIR38 and J110621 (see Methods). These features are consistent with a blend between the C-H stretch of CH_3OH and a broad component centered at 3.47 μm (Extended Data Figure 9). Ammonia hydrates ($\text{NH}_3 \cdot \text{H}_2\text{O}$) are considered to be the primary contender for this broad component³⁰, but the sensitivity of our observations will enable a differential diagnosis in a future work. As seen in previous dense cloud spectra, methanol ice is detected additionally in isolation at 9.7 μm and blended with the NH_4^+ feature at 6.85 μm . There is excellent agreement between the column densities derived from both methanol features ((See Supplementary Figure 2)). Although the 6 and 6.85 μm features appear smooth at $R \sim 100$ in both sources, there are weak but robust absorption excesses at 6.94, 7.06, 7.24, and 7.43 μm , (see Figure 3), attributable to the functional group in COMs caused by the asymmetric deformation mode of CH_3 ³¹, which has been tentatively detected with *Spitzer*¹⁴ and *JWST*³². These two bands are seen in the IR spectra of acetone (CH_3COCH_3)³³, ethanol ($\text{CH}_3\text{CH}_2\text{OH}$)³¹, and acetaldehyde (CH_3CHO)³¹. These background stars will require the higher spectral resolution of MIRI MRS to confirm these identifications, determine the COMs chemical environment, and the degree to which complex chemistry has begun along the J110621 sightline.

155

Stable ice chemical environment from $A_V \sim 20$ to 95 - The absolute column densities of most ice species are slightly larger towards J110621, as expected from the increase to $A_V \sim 95$. However, the ice inventory is very similar towards both sightlines, suggesting that although the total amount of ice

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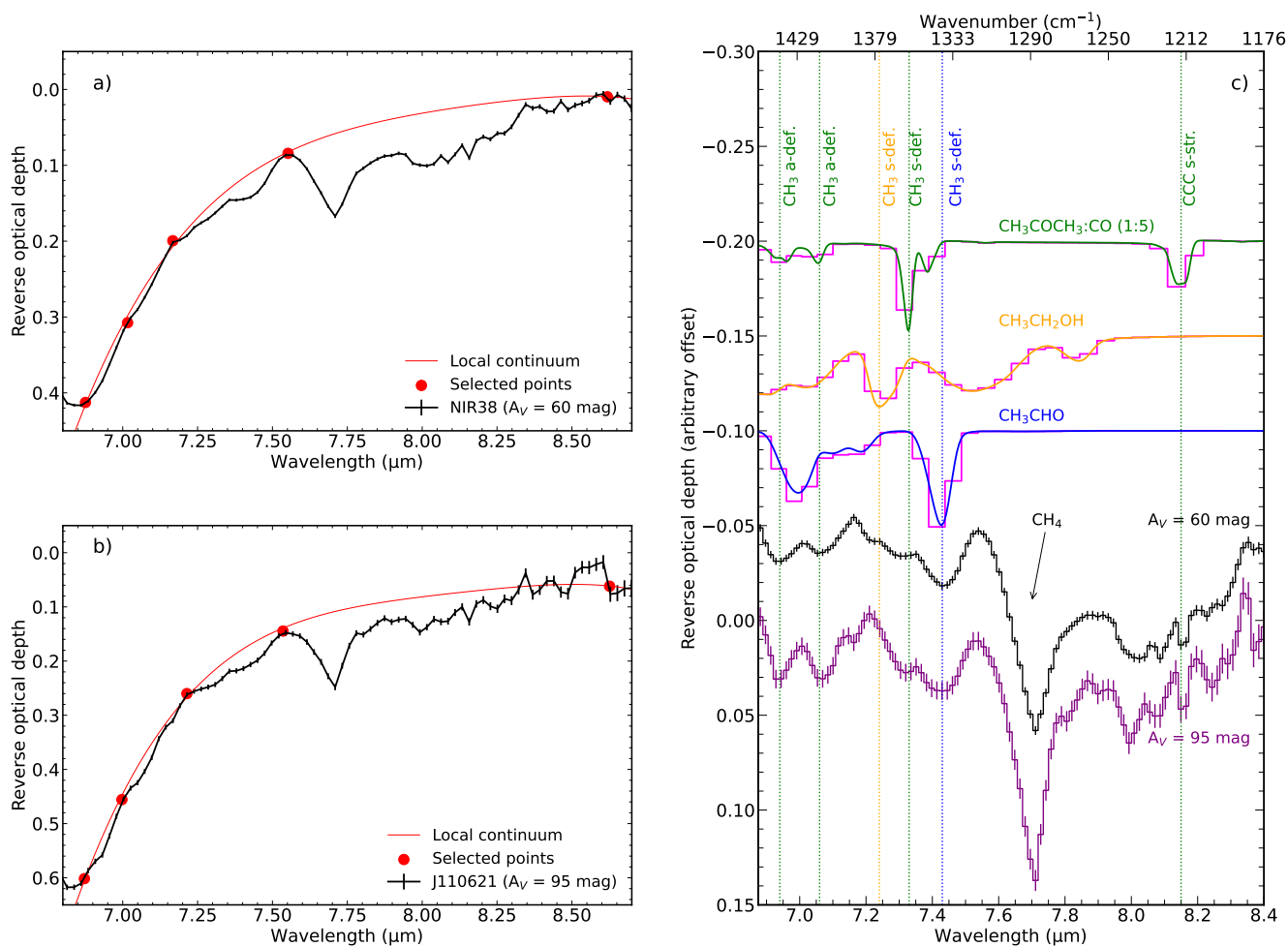


Figure 3. Detections of complex organic molecule (COMs) functional groups. Panels (a) and (b): Local continuum over the optical depth spectra of NIR38 ($A_V = 60$ mag) and J110621 ($A_V = 95$ mag) in the range between 6.9 and 8.6 μm . Panel (c): Local continuum subtracted spectra of NIR38 ($A_V = 60$ mag) and J110621 ($A_V = 95$ mag) compared to laboratory IR spectrum of COMs (CH_3CHO - green line³¹, $\text{CH}_3\text{CH}_2\text{OH}$ - orange line³¹, and $\text{CH}_3\text{COCH}_3:\text{CO}$ - blue line³³) in the solid phase. The magenta line shows the laboratory spectra degraded to a resolving power of 150. The vertical lines indicate the match of the experimental data with the observations. The vibrational modes of the experimental data are indicated.

159 increases, the ice composition is set at a lower A_V . In fact, the relative column densities of the simple ices
 160 from $60 < A_V < 95$ are broadly consistent with the ice evolution sequence proposed on the basis of *Spitzer*
 161 observations from $20 < A_V < 50$ ¹⁶, as exemplified by the comparison with the background star Elias 16
 162 ($A_V \sim 19$) in Figure 4 well as laboratory data and chemical modeling of this dense cloud region²⁰. These
 163 results could suggest that, although CO ice is the second most abundant species detected in our spectra,
 164 the local cloud gas density may be less than the limit of $n_H \sim 10^5 \text{cm}^{-3}$ required for CO to catastrophically
 165 freeze out via collisions^{7,8}. Supporting this, initial modeling of the ^{12}CO ice profiles (Extended Data
 166 Figures 1 and 2) suggests that they may be dominated by a pure component, with two additional weaker
 167 components mixed with methanol or CO_2 ¹⁶. In contrast, the local $^{13}\text{CO}_2$ ice profiles of both stars suggest
 168 that CO_2 is dominated by an intimate mixture with H_2O , with a lesser contribution from a CO-rich mixture
 169 (Methods and Extended Data Figure 4). Additionally, based on comparisons between laboratory data and
 170 the profiles of the ^{12}CO and 9.7 μm methanol bands, methanol seems to reside in environments containing
 171 both H_2O and CO (see Methods, Extended Data Figures 1 and 2). The amount of methanol appears to
 172 be approximately the same in both sources, based on both the 3.53 μm and 9.7 μm features. In contrast,
 173 there are constant or increasing column densities of the simple hydrides, NH_3 and CH_4 .

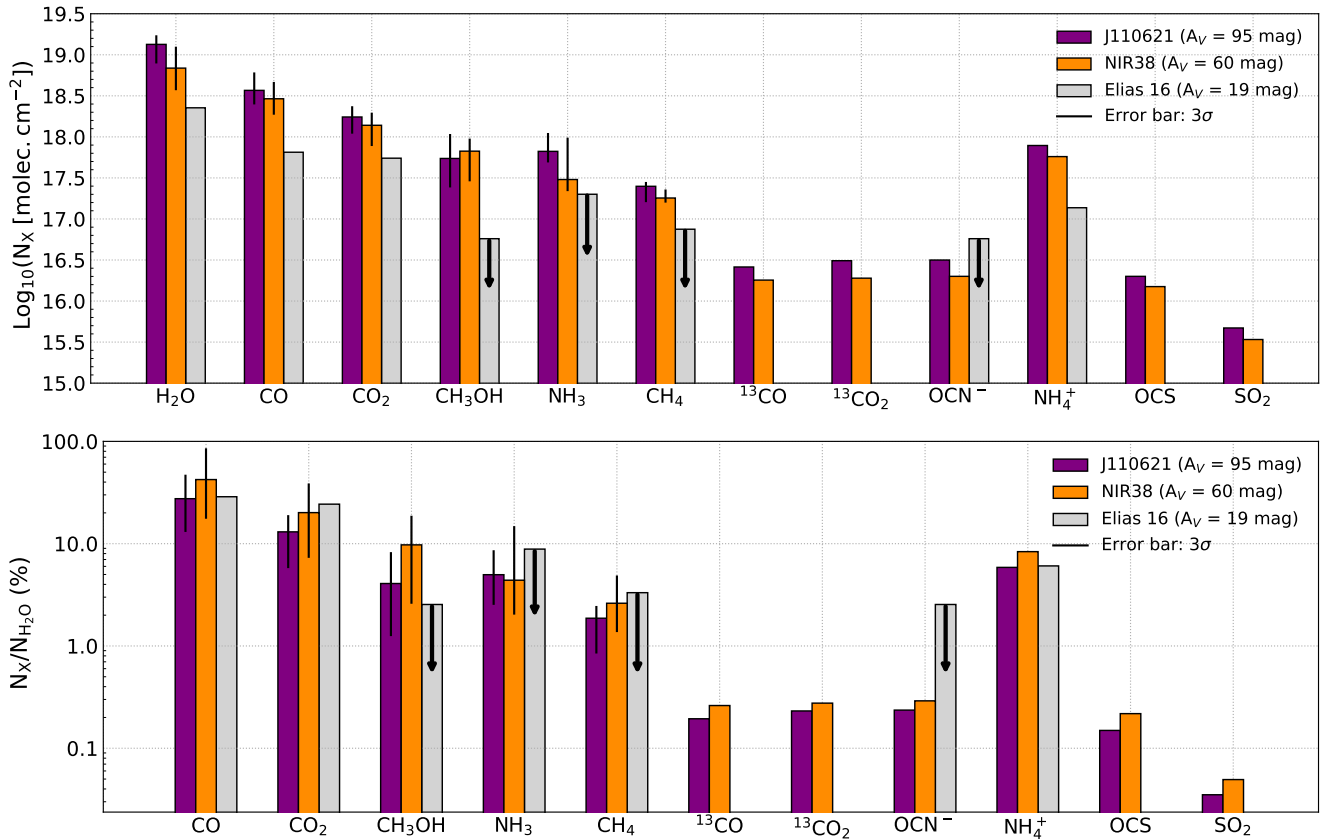


Figure 4. Barplots showing the derived ice column density for different species towards NIR38 ($A_V \sim 60$ mag) and J110621 ($A_V \sim 95$ mag). (Top) Column densities of the ice species identified in this work, compared to the literature values of Elias 16 ($A_V \sim 19$ mag)³⁴. The column densities of the major ice components are from the global ENIIGMA fit (best of $n=112$ models), and we use the values from the local fits for the minor ice components. Black arrows indicate upper limits and error bars are taken from the 3σ confidence intervals. (Bottom) Relative column densities of the detected ices, normalized to H₂O ice. For the major ice components, we use the values from the global ENIIGMA fit, and for the minor ice components, we use the values from the local fits. Black arrows indicate upper limits and error bars are taken from the 3σ confidence intervals.

174 Discussion

175 The sum of the column densities for both CO isotopolog ices and their potential reaction products is
 176 less than the expected total CO column density from A_V for each line of sight, suggesting that at most
 177 46% and 33% of the available CO gas has frozen out into ices towards NIR38 and J110621, respectively.
 178 Although NIR38 samples a smaller total column of dust, its line of sight appears to pass closer to the
 179 Class 0 protostar (see Extended Data Figure 10). If this region contains locally denser or colder dust, it
 180 could explain the larger fraction of total CO that is frozen out onto the grains. These results imply that the
 181 rich variety of ices that we see likely formed early, prior to catastrophic CO freeze-out, rather than later
 182 through purely CO hydrogenation pathways.

183 The other ice column density results are also consistent with efficient, early formation of CO₂, NH₃,
 184 and CH₄ in water-rich ices through H-addition and abstraction^{3,6,35,36}, followed by a small amount of the
 185 subsequent CO-based chemistry that we would expect to see at these high extinctions. While methanol was
 186 traditionally thought to form efficiently via successive CO hydrogenation, with H₂CO as an intermediate⁹,
 187 it can also form earlier and more slowly in the H₂O-rich ice phase^{37,38}. Our fit to the feature at 9.7 μ m
 188 suggests that both formation pathways may operate in these ices. This conclusion is supported by the
 189 detection of functional groups of COMs at 7-7.5 μ m towards pre-stellar sources that lie outside of the
 190 coldest cores in this region, suggesting their early formation in the water rich phase¹⁰. Models predict

191 only ethanol at $N \sim 6\text{-}15 \times 10^{16} \text{ cm}^{-2}$,²⁰ which is broadly consistent with the optical depths at $7.2 \mu\text{m}$ in
192 both spectra, but not the other potential COMs species that could produce the other absorption features
193 seen at 6.94 , 7.06 , and $7.34 \mu\text{m}$. Our detections of COM functional groups in these pre-stellar ices hint at
194 the non-energetic complexity achieved in ices already before the formation of a hot protostellar core.

195 Accounting for the amount of C, O, N, and S in the ices is critical to determine the bulk volatile budget
196 of the stellar and planetary systems that will form within this molecular cloud. Comparing the column
197 densities of the detected ices for both NIR38 and J110621 with the expected cosmic abundances for C, O,
198 N, and S, we see at most 19% of the total O- and C-, 13% of the total N-budget, and 1% of the S-budget
199 in this dense cloud (see Methods). These numbers are similar to what has been previously reported for
200 protostars¹⁶, but now we are able to trace the budgets of these elements back to their initial conditions in
201 dense clouds. Most of the remaining budgets will be made up of refractory species, including silicates and
202 amorphous carbons, or other ices like N_2 that do not show spectral features at these wavelengths. Some of
203 the budget may additionally be accounted for in COMs that we cannot yet identify conclusively with the
204 MIRI LRS spectral resolution.

205 The profile distortions of the deepest ice bands show that the increase in H_2O , CO_2 , and CO is
206 accompanied by an increase in the size of these icy grains. The enhanced, red-shifted absorption wing,
207 as seen in H_2O and CO_2 (e.g.³⁹), in addition to the blue-shifted emission wing described earlier for the
208 $^{12}CO_2$ and possibly ^{12}CO ice features²⁴, are associated with scattering effects resulting from icy grain
209 growth to sizes on the order of the wave vector at which they are detected, i.e. a few microns. Whereas
210 red wing extinction due to scattering is a rather robust effect produced by larger grains, the intensity of the
211 blue emission excess can be highly variable. Its strength is highly sensitive to specific local changes in the
212 optical constants of the grains' core and mantle materials. The profiles of our observed CO_2 ice features
213 imply growth to sizes of around $1 \mu\text{m}$, as predicted by some grain growth models (e.g.^{40,41}). Despite
214 this relatively modest increase in maximum grain size, the observed growth occurs at the expense of the
215 smaller grains, which are depleted. Our observed change in icy dust grain size distribution would not only
216 influence the visual extinction but also reduce the total grain surface available for reactions in such dense
217 regions. However, our tentative detection of the OH dangling mode of H_2O near $2.7 \mu\text{m}$ could suggest
218 that the water in these large grains is porous or mixed with other ices. In that event, the pore surfaces may
219 also provide space for additional reactions.

220 Detailed modelling to quantify the maximum grain size, shape, and porosity of these ices will be
221 presented in a future work. Further analysis of the reaction pathways and relative ice abundances requires
222 both chemical modeling and future observations of molecular clouds at both low and high A_V s to confirm
223 when the simple hydrides are formed in relation to CO freeze-out. Complementary molecular gas phase
224 observations will also confirm the extent to which CO has frozen out in this region. Such work will in part
225 continue through another component of the Ice Age ERS program, in which we have obtained hundreds of
226 ice spectra in the same Chameleon I region with the new multi-object capabilities of NIRCcam WFSS. By
227 combining these datasets, the superlative sensitivity, spectral resolution, and wavelength coverage with
228 JWST now enable us to fully probe the initial conditions of all of the major ices in molecular cloud cores
229 just prior to their collapse to form protostars. These new capabilities open the door to understanding the
230 formation and inheritance of these key CHONS-species through the star- and planet-formation process
231 and, ultimately, address what role they will play in shaping the chemistry on emerging planets.

232

233 Methods

234 Observations and data reduction

235
236 **NIRSpec:** NIRSpec Fixed Slit (FS)²¹ observations of the targets NIR38 ($A_V = 60$) and SSTSL2J110621.63-
237 772354.1 ($A_V = 95$) were taken on July 6, 2022 and July 8, 2022, respectively, using the G395H grating,
238 combined with F290LP blocking filter. Target acquisition was achieved using the Wide Aperture Target
239 Acquisition (WATA) method and the SUB2048 subarray with the CLEAR filter and a readout pattern
240 of NRSRAPID6 with an exposure time of 14.5 seconds for both sources. Spectra of the two stars were
241 obtained using the ALLSLITS subarray at four dither positions, spaced along the S200A2 slit. Each
242 integration was composed of 57 groups and 265 groups using the NRSRAPID readout pattern, for total
243 on-source exposure times of 1274.7 seconds and 5845.7 seconds, respectively.

244 The JWST calibration pipeline was used for detector level 1 processing to calculate rate files
245 from the uncalibrated ramps using version 1.7.1, Calibration Reference Data System (CRDS) context
246 `jwst_0948.pmap`, and the PUB CRDS server. The two-dimensional rate spectra were distortion
247 corrected using a second-order trace function derived from a commissioning observation of the standard
248 star TYC 4433-1800-1, observed as part of program PID 1128. The two-dimensional spectral dithers were
249 pairwise differenced to efficiently remove the background, and a one-dimensional spectrum from each
250 dither was then optimally extracted⁴² using a cross-dispersion profile calculated by median-collapsing each
251 dither in the spectral direction. An uncalibrated spectrum was then derived using a median for the four
252 separate dithers to remove most cosmic rays. Note that the observation of SSTSL2J110621.63-772354.1
253 used very long integrations (>1000 s), and suffers from large numbers of cosmic ray hits, not all of which
254 could be fully corrected. To flux calibrate the spectra, we extracted spectra from the identically-processed
255 level 1 rate files of the standard star observation of TYC 4433-1800-1 using the same grating and slit. By
256 dividing with the standard star spectrum, and multiplying by a model spectrum of the standard star, scaled
257 to $K_S = 11.584$ mag, we arrive at the final, calibrated spectra. This yielded excellent results, although the
258 direct use of the standard star leave a small number of artifacts from uncorrected hydrogen absorption lines
259 in the standard star spectrum. Note that this process does not rely on pipeline flat fields or calibrations,
260 which are not yet available. However, the wavelength calibration does use the solution from the pipeline.
261 Errors were formally propagated from pixel errors estimated by the ramps-to-slopes fits from the level 1
262 processing.

263
264 **NIRCam:** NIRCam Wide-field Slitless Spectroscopic (WFSS)²² grism observations of the Cha-MMS 1
265 field were taken on July 3, 2022 with the F322W2 filter (2.5-4.0 μm) using Grism C with NIR38 (A_V
266 = 60) residing in module A. We obtained 24 individual integrations of the field with a total exposure
267 time of 1.7 hours. We followed a data reduction routine similar to that in⁴³. We first reduced the grism
268 spectroscopic data with the standard JWST calibration pipeline v1.6.2 to the level of Stage-1, using the
269 default CRDS setup with JWST OPS and no modifications, i.e. CRDS context 0953, and then performed
270 2D sky-background subtraction using the sigma-clipped median images that were constructed from the
271 obtained WFSS data. Flat-field correction was also applied using the imaging flat data obtained with
272 the same filter. We then extracted the spectra of the two background stars using the optimal extraction
273 method⁴² from each individual integration, and co-added them together using the SpectRes package⁴⁴.
274 The wavelength and flux calibrations were performed using the in-flight measurements obtained with
275 JWST Commissioning Program #1076. At this stage, it is important to note that the current background
276 subtraction method has not been fully optimised, so small systematic offsets may exist within data. Addi-
277 tionally, the optimal extraction method reduces, but may not entirely eliminate, potential flux contamination

278 from other nearby sources. Therefore we may be marginally overestimating the flux for our $A_V = 60$ source.

279

280 **MIRI LRS:** MIRI Low Resolution Spectrograph (LRS) Fixed Slit (FS)²³ observations of the targets
281 NIR38 ($A_V = 60$) and SSTS2J110621.63-772354.1 ($A_V = 95$) were taken on July 4, 2022 and July 11,
282 2022, respectively. Target acquisition was achieved using the F560W filter with a FAST readout pattern
283 with 4 groups per integration for an exposure time of 11.1 seconds for both sources. These two targets
284 used observations with 40 groups per integration and 104 groups per integration, respectively, with 5
285 integrations per exposure with a two-nod dither pattern along the slit, for a total of 10 total integrations per
286 source and total exposure times of 1132.2 seconds and 2908.2 seconds, respectively. The FASTR1 readout
287 pattern was used.

288 We reduced the data with the same procedure for the two sources. We used the STScI JWST
289 pipeline (<https://jwst-pipeline.readthedocs.io>) version 1.8.2, the PUB CRDS server, and CRDS context
290 `jwst_0986.pmap` to obtain the Stage 1 and Stage 2 products. We started from the uncalibrated data
291 (Level1b, ‘uncal’ files). We ran the Detector1Pipeline with default parameters and the Spec2Pipeline step
292 by step. We used each dither position as a background image for the other and subtracted the background
293 pixel-wise. From the calibrated images (‘cal’ files), we extracted a one-dimensional spectrum from each
294 dither position using the optimal extraction method⁴² where a cross-dispersion profile is calculated by
295 median-collapsing the 2D spectral trace in the spectral direction. The spectra from both dither positions
296 were averaged to obtain a final spectrum. As a comparison, we extracted a spectrum using the JWST
297 Spec3Pipeline. We combined the two dither positions into a single image using the ‘resample_spec’
298 step and extracted the 1D spectrum using the ‘extract_1d’ step. We defined the extraction region in
299 a custom reference file and disabled the offset that accounts for the expected location of the source
300 (‘use_source_posn’ set to ‘False’). This ensured that the aperture was centered on the source. We also
301 extracted spectra from the ‘cal’ files using a simple aperture method (not relying on ‘extract_1d’) and
302 from the resampled image using the optimal extraction method. All these spectra are in good agreement
303 but the optimal extraction method applied on the ‘cal’ files provides a smoother spectrum, which we
304 kept for scientific interpretation. The CRDS context `jwst_0986.pmap` uses a wavelength calibration
305 that has been updated for MIRI LRS Fixed Slit after an initial mismatch that was found between the
306 flight calibration and the first extracted science spectra. This new wavelength calibration (encoded in the
307 ‘jwst_miri_specwcs_0005.fits’ reference file) is in good match with the known spectral features detected
308 in our spectra.

309

310 **Data quality:** The spectra from all three instruments are shown in Figure 2 for the $A_V=60$ star. The
311 flux calibration of these data is such that they match each other within their respective 3σ error bars. The
312 differences in the signal at the bottom of the $3\ \mu\text{m}$ H_2O feature are due to the increased sensitivity of
313 NIRSPEC FS relative to NIRCAM WFSS, but are within the error bars. Both stars are saturated in the 4.3
314 μm $^{12}\text{CO}_2$ ice bands and we lose the signal at the bottom of these features, which occurs as well in the 3
315 μm band of the $A_V=95$ star. The reproducibility of the spectral features between NIRCAM and NIRSPEC is
316 excellent, and the spectra are broadly consistent with the *Spitzer* IRAC photometry of this source given in
317 the SEIP Source List server (<https://irsa.ipac.caltech.edu/cgi-bin/Gator/nph-dd>), taking into account the
318 lack of convolution with the IRAC filter and the assumed color correction.

319

320 **Global continuum fit:** The continuum shape of background stars, which is physically limited to be a
321 stellar Rayleigh Jeans tail with ices superimposed on it, is fitted either with detailed stellar photosphere
322 models or simple piece-wise polynomial continua to each star⁴⁶. We do not yet have photospheric models
323 for these stars, so we use polynomial fits: in our case, one over the NIRSPEC range and another over the

324 MIRI range. For NIR38 ($A_V=60$) we fit the continuum using a fifth order polynomial with continuum
325 points of 2.4-2.49 μm , 2.65-2.69 μm , 2.715-2.720 μm , 4.0-4.04 μm , 4.06-4.07 μm , 5.15-5.2 μm , 5.3-5.7
326 μm . For J110621 ($A_V=95$), we fit the following continuum points: 2.74-2.78 μm , 3.98-4.01 μm , and
327 5.4-5.7 μm . The continuum determination in the MIRI LRS range is not straightforward due to the
328 broad ice and silicate features. We determine the continuum on the MIRI LRS range (5.2–13 μm)
329 using a second-order polynomial function. We set the continuum points at 5.2, 5.6, and 13.2 μm for
330 NIR38 and J110621. Then we combine the two continua in a piece-wise fashion, with the cutoff between
331 them taken at 5.1 μm . The continuum shape may change slightly when the more detail stellar model is
332 applied. However, our initial steps in stellar modeling (not discussed here) show good agreement with the
333 polynomial continuum fit found here. We estimate that the uncertainty introduced by the continuum is
334 within the uncertainty in the A -values used to derive the column densities.

335 The silicate absorption band is removed by a synthetic silicate spectrum composed of amorphous
336 pyroxene⁴⁵ ($\text{Mg}_{0.7}\text{Fe}_{0.3}\text{SiO}_3$) and olivine⁴⁵ (MgFeSiO_4), as previously used in the literature⁴⁶ for back-
337 ground stars (see Extended Data Figure 6). We used the optool code⁴⁷ to create a synthetic spectrum
338 assuming grains of 1 μm . We aim at matching the spectral ranges between 8.3 and 8.7 μm and between
339 10.1 and 10.4 μm . In both sources, the absorption of pyroxene dominates over olivine at 9.8 μm . For the
340 $A_V = 60$ mag star, pyroxene and olivine corresponds to 60% and 40%, respectively, whereas for the the
341 $A_V = 95$ mag star, the absorptions are 70% due to pyroxene and 30% due to olivine.

342
343 **ENIIGMA global fitting and local fits:** We used the ENIIGMA fitting tool^{2,49} to simultaneously fit
344 multiple features across the NIRSpc and MIRI/LRS range by scaling laboratory ice spectra to match
345 the optical depths in Figure 1. A full list with data used in this paper is shown in Table 3. It is worth
346 mentioning that these laboratory data are previously baseline corrected and noise smoothed at relevant
347 bands. No further processing is performed during the fitting procedure. In the fits, we assume saturated
348 bands at 3 μm and 4.27 μm because of negative fluxes. At these two bands, the fit is not limited by the
349 peak of the band. This is an important assumption to make to avoid underestimating column densities of
350 the molecules contributing to the absorption of these bands. ENIIGMA searched for the best combination
351 of experimental data measured at temperatures of 15 K or below. Motivated by previous works, we
352 explored combinations with ice mixtures composed of $\text{CO}:\text{CO}_2$ ⁵¹, $\text{CO}:\text{CH}_3\text{OH}$ ⁵², $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ ⁵³ and
353 $\text{H}_2\text{O}:\text{NH}_3$ ³⁰, $\text{H}_2\text{O}:\text{CO}_2:\text{CH}_4$ ⁵⁶, and pure CO ⁵⁵. In addition to these data, ENIIGMA tested other IR spectra
354 measured at temperatures below 16 K. We did not include the spectrum of the ammonium ion (NH_4^+)
355 in the global fits because it is not a consensus that the 6.85 μm is attributed to this chemical species. A
356 dedicated study of this spectral feature will be performed in a follow-up paper by considering different
357 chemical environments where NH_4^+ . Additionally, since NH_4^+ is formed by a chemical reaction between
358 other molecules (e.g., NH_3 , HNCO) induced by temperature (warm-up) or radiation (e.g., ultraviolet,
359 X-rays, cosmic rays), the spectrum shows other products that have to be taken into account when making
360 assignments of the IR bands. Overall, ENIIGMA provides a good global fit of the major ice components
361 in the observations, which are used to derive the ice column densities (see Table 2). They are calculated by
362 $N_X = \int \tau_\nu d\nu / A$, where $\int \tau_\nu d\nu$ is the integrated optical depth of a specific band, A is the band strength,
363 and X is the chemical species. The uncertainties are derived from 3σ confidence intervals based on
364 correlation plots shown in Extended Data Figure 3. Additional sources of uncertainties are not considered
365 in these values. ENIIGMA does not fit entirely the isotope bands of $^{13}\text{CO}_2$ and ^{13}CO at 4.38 μm and
366 4.78 μm , respectively. First, this is because the global fit limits the amount of the isotopes by the strong
367 $^{12}\text{CO}_2$ and ^{12}CO bands. Second, the isotope abundances in the gases used to make the ice samples in
368 the laboratory may not be the same as found in these astronomical targets. By performing local fits, the
369 chemistry of the isotope bands is better constrained (see Extended Data Figure 4). Nevertheless, the ice

370 column densities are similar to the values obtained with the global fits as seen in Table 2.

371 Local fits are also used to calculate the ice column densities of the major components (see Figure
372 1 of the Supplementary Data). For the H₂O ice, we scale the pure H₂O ice IR spectrum at 15 K⁵⁴ to
373 match the ranges around 2.85–2.95 μm and 3.17–3.23 μm because of the saturation of the bands. The
374 broadband between 5 and 8 μm are fitted by NH₄⁺ and H₂O as scaled to the 3 μm band. Independently of
375 the global fit, the NH₄⁺ spectrum can be locally scaled to the astronomical data since this method does not
376 take into account the contribution of the chemical specie at other wavelengths. The goal of the local fits is
377 to estimate the highest amount of a specific component to the absorption band including or not blending
378 effects with other molecules. Since the contribution of CH₃OH absorption is minimal at 6.85 μm (see
379 Extended Data Figures 1 and 2), we do not include methanol in the local fit of this band. In the cases of
380 CO₂, CO, CH₄, SO₂, NH₃ and CH₃OH, we adopted Gaussian profiles to fit the A_V=60 mag and A_V=95
381 mag spectra, and calculate the ice column densities. Around 4.67 μm and 7.7 μm, we adopted more than
382 one sub-component to fit the observations, following the previous studies of these two bands^{55,56}. For
383 CH₃OH, we also perform a local fit analysis around 3.5 μm, and the column densities are similar to both
384 local and global fits at 9.8 μm. The local column densities are compared with the global column densities
385 in the Supplementary Information to validate the global fits.

386 The ice column densities derived from the global and local fit are collated in Table 2. In Figure 4,
387 we show the column densities of the major ice species derived from the global fits and the minor species
388 derived from the local fits. Additionally, we show a comparison with the column densities derived for a
389 background star with A_V = 19 mag³⁴. These column densities are normalized to H₂O ice in the bottom
390 panel of Figure 4. In the Supplementary Information, all the values from global and local fits, and from
391 the ranges reported in the literature are compared. A caveat in the ENIGMA methodology, is that it does
392 not perform grain shape correction of the ice bands. Such a correction comes with a level of discussion
393 beyond the scope of this paper, for example, which grain shape better reproduces the observations, and
394 what are the size distributions. These geometry effects will be explored in a subsequent study.

395
396 **Local continuum fit for weak features:** To separate the weaker features from the wing of the water
397 stretch and combination bands, we also fit a local continuum to both spectra. The continuum points
398 were set to the following ranges: 3.215-3.231 μm, 3.252-3.263 μm, 3.289-3.295 μm, 3.306-3.311 μm,
399 3.610-3.626 μm, 3.686-3.693 μm, 3.711-3.727 μm, and 3.759-3.795 μm. We calculated a fifth-order
400 polynomial to these regions and took the local optical depths with respect to this continuum. For ¹³CO,
401 CH₃OH, OCN⁻, and OCS we scaled laboratory data of simple ice mixtures to match the feature profiles.
402 The profile of the best fitting scaled laboratory mixture and band strengths were used to determine local
403 column densities, as described below.

404
405 **3.4 - 3.6 μm blended absorption (CH₃OH and NH₃ · H₂O):** The absorption feature between ~3.35 - 3.6
406 μm is likely caused by a combination of different ices and grain properties. However there is a distinct
407 peak at 3.53 μm for both sources indicating the presence of CH₃OH ice (C-H stretching mode).¹⁶ In order
408 to constrain the CH₃OH ice abundance, we used the fifth order polynomial local baseline described above
409 to obtain the optical depths for this feature. Previous studies have fit a simple Gaussian to CH₃OH along
410 lines of sight toward background stars but this underestimates the red wing in the feature for both lines
411 of sight in this study.^{46,67} We therefore scaled laboratory spectra of pure CH₃OH ice at 15K³¹ to fit the
412 region and minimize the residuals between 3.53 and 3.65 μm. We did not fit the laboratory data to shorter
413 wavelengths because the use of a local baseline instead of a global baseline cuts off some of the CH₃OH
414 ice profile. Additional absorbing species and scattering signatures may contribute to this absorption
415 feature. The column densities are calculated by integrating the scaled laboratory optical depths using a

416 band strength $A_{\text{CH}_3\text{OH}} = 1.6 \times 10^{-16} \text{ cm molec}^{-1}$ over the 2.778-3.704 μm regime⁵⁸ and represent upper
417 limits to the amount of methanol present, due to the potential for additional absorption described above.
418 These results are presented in Table 2 as upper limits, and the fits for both sources are shown in Extended
419 Data Figure 9.

420 The peak near $\sim 3.47 \mu\text{m}$ has been previously attributed to the $\text{NH}_3 \cdot \text{H}_2\text{O}$ hydrates but this is still up
421 for debate.^{30,68} Nonetheless, we model the feature using a simple Gaussian at this time with a FWHM
422 of 0.1 μm and a central peak at 3.47 μm to understand how much this overlapping feature may reduce
423 the column density of the CH_3OH . We model the Gaussian and lab data simultaneously and minimize
424 the residuals of the sum of both fits between 3.4 - 3.65 μm (Extended Data Figure 9). When doing
425 this we find that the column densities for CH_3OH are lower by $\sim 20 - 30\%$ ($N = 4.1 \times 10^{17} \text{ cm}^{-2}$ and
426 $N = 4.5 \times 10^{17} \text{ cm}^{-2}$ for the $A_V = 60$ and $A_V = 95$ sources, respectively). These column densities agree
427 with those found by using the ENIIGMA fits to the globally determined optical depths. Further follow-up
428 studies will model the full 3.4 - 3.6 μm absorption feature and constrain the column densities not only for
429 CH_3OH , but also the other possible absorbing species.

430
431 **$^{13}\text{CO}_2$:** Extended Data Figure 4 shows the observed $^{13}\text{CO}_2$ feature, around 4.39 μm , compared with
432 laboratory spectra of CO_2 in different ice mixtures, which peak at slightly different wavelengths depending
433 on the ice mixture. The peak of each laboratory spectrum is scaled to the observed $^{13}\text{CO}_2$ feature at the
434 wavelength corresponding to the peak of the laboratory data. Overall, the band of $^{13}\text{CO}_2$ in H_2O -rich
435 ice reproduces the peak and width of the observed feature. A weak blue shoulder around 4.384 μm is
436 also noticeable and could possibly be due to a fraction of $^{13}\text{CO}_2$ mixed in CO . A detailed study of the
437 components that contribute to the 4.39 μm feature, combined with an analysis of the CO_2 bands, can
438 provide more insights about the formation and chemical environment of solid CO_2 and its ^{13}C isotopologue,
439 and it will be the focus of a future work. In this work, we provide an estimate of the $^{13}\text{CO}_2$ column density
440 assuming that the 4.39 μm band can be modeled using the laboratory spectrum of a $\text{CO}_2:\text{H}_2\text{O}(1:10)$ ice at
441 10 K. The column density of $^{13}\text{CO}_2$ is derived by scaling the laboratory spectrum to the optical depth of
442 the 4.39 μm feature. A band strength of $A = 7.8 \times 10^{-17} \text{ cm molec}^{-1}$ ⁵⁷ is assumed for $^{13}\text{CO}_2$ asymmetric
443 stretching. The laboratory data used for the comparison are taken from^{69,70}. In these laboratory ices,
444 $^{13}\text{CO}_2$ is set at ratios of $^{12}\text{CO}_2/^{13}\text{CO}_2 \sim 90$, which need not be the same ratio in the astronomical targets.
445 To calculate this ratio from the astronomical data, we divide the column densities derived with ENIIGMA
446 for the $^{12}\text{CO}_2$ feature by those derived here for the $^{13}\text{CO}_2$ feature, yielding a ratio of $^{12}\text{CO}_2/^{13}\text{CO}_2 \sim$
447 69-87 ratio for these two targets.

448
449 **OCN^- :** In our analysis of the XCN band a single component fit is used and plotted in Extended Data Fig-
450 ure 7. This is a Gaussian function with peak center at 2165.9 cm^{-1} and $\text{FWHM} = 23 \text{ cm}^{-1}$ previously used
451 to reproduce laboratory spectra of OCN^- ⁷¹ and the XCN band of embedded young stellar objects.^{17,60,72,73}
452 Only data points on the blue wing of the XCN band are considered to avoid any contributions from the
453 CO -ice band to the fit. The Gaussian profile reproduces the red wing and the component of the XCN
454 band of both targets. In addition, the residuals are negligible, justifying the use of a single component.
455 OCN^- ice column densities were estimated by integrating over the fitted Gaussian function and scaling
456 with a band strength A_{OCN^-} of $1.3 \times 10^{-16} \text{ cm molec}^{-1}$ ⁷¹. The resulting column densities are listed in
457 Table 2, and they are in good agreement with values obtained for quiescent lines of sight in nearby clouds.⁶⁰

458
459 **^{13}CO :** The region around 4.779 μm shows a weak feature that can be associated with ^{13}CO (Extended
460 Data Figure 5). This feature is contaminated by the presence of photospheric absorption lines, which
461 makes the feature difficult to integrate cleanly. For this reason, the laboratory spectrum of pure CO ice at

462 15 K^{74} was scaled to the astronomical data to derive the maximum abundance of this species in the spectra
463 of both background stars. The band strength value is $A = 1.3 \times 10^{-17} \text{ cm molec}^{-1}$.⁵⁷

464
465 **OCS:** The region around $4.90 \mu\text{m}$ shows tentative detection that can be associated with the CO stretching
466 vibration of the OCS molecule (Extended Data Figure 8). A comparison with laboratory infrared spectra
467 of OCS-containing ices shows that this band in pure OCS ice is too broad compared to the feature seen
468 toward the background stars. Previous studies showed that this absorption band is better modeled by
469 $\text{CH}_3\text{OH}:\text{OCS}$ -containing ices^{75,76}. The column densities for OCS were derived using the profile of the
470 OCS mixed in H_2O and a band strength value of $A = 1.18 \times 10^{-16} \text{ cm molec}^{-1}$.⁶²

471
472 **Non-detections and upper-limits:** With these high S/N data, we have placed strong constraints on
473 several ice species, including HDO, HCN, CH_3CN , H_2CO , and H_2S . H_2CO may still be present at low
474 levels in these spectra, but with the lower resolving power ($R \sim 100$) of MIRI LRS FS, it is not possible
475 to separate it from the blue wing of the H_2O bending mode at $6 \mu\text{m}$. In contrast, it was clearly detected
476 in a protostar with JWST's MIRI MRS mode ($R \sim 3000$)³². HDO was tentatively detected with AKARI
477 at $\sim 4.1 \mu\text{m}$ with an abundance of 2-10% relative to H_2O towards several protostars and disks¹⁵. We
478 do not see an obvious feature there in these spectra, although reliable upper limits can only be obtained
479 after correction for the $^{12}\text{CO}_2$ blue scattering emission wing. Upper limits for the H_2S , CH_3CN , and
480 HCN abundances are estimated considering the noise level in the region where the strongest vibrational
481 feature of these molecules absorb. Here, the regions around $3.92 \mu\text{m}$, $4.44 \mu\text{m}$, and $4.76 \mu\text{m}$ for H_2S ,
482 CH_3CN , and HCN, respectively. The upper limits are calculated from the root mean squared (RMS) as
483 $N = \text{RMS} \times \text{FWHM}/A$, where FWHM and A are the full width at half maximum and band strength of
484 the absorption feature in the pure ice, respectively. The resulting 1σ upper limits in the abundances w.r.t.
485 H_2O ice is less than 1 % for H_2S in NIR38. Data covering this region is not yet available for J110621. For
486 HCN the upper limits w.r.t. H_2O ice is less than 1% for both sources. For CH_3CN the value is less than
487 2% for both sources. The FWHM and band strengths for the pure ices are taken from^{62,65,66}.

488
489 **The location of the background stars in their larger scale environments:** Complementary information
490 about the larger scale environment is critical when interpreting the column densities inferred from the
491 ice observations. Extended Data Figure 10 shows a map of the H_2 column density maps extracted from
492 the larger scale Chamaeleon maps⁷⁷ created based on far-infrared data 70 to $500 \mu\text{m}$ from the *Herschel*
493 Space Observatory's Gould Belt survey⁷⁸. The maps clearly show the decrease of the column density
494 from the peak near the Class 0 protostar ChamI-MMS with a more extended structure encompassing also
495 the clump Cha1-C2¹⁸. The $A_V \approx 95$ star at a projected distance of 6600 au is located in the direction of
496 this core, while the $A_V \approx 60$ star at a projected distance of 5600 au is located in a direction orthogonal
497 to this structure from the Class 0 protostar²⁰. The H_2 column densities toward the two background stars
498 are similar within $\approx 10\%$, suggesting that the local conditions are similar, despite the difference in A_V .
499 The A_V we use was derived from average giant star colors²⁰; from these JWST spectra, a more detailed
500 fit taking into account the spectral type of these background stars will soon be possible, which may
501 reduce the difference in A_V . If the discrepancy remains, the difference in A_V could represent local radial
502 extensions of the cloud along the line of sight or a superposition of additional clouds along the line of sight.
503 Complementary observations, e.g. of gas-phase line tracers, are needed to assess whether there are dif-
504 ferences in the densities, and thereby, e.g., the time-scales for freeze-out, toward the two differ significantly.

505
506 **Calculation of the icy C, O, N, and S budgets:** The column of molecular hydrogen is calculated for
507 each line of sight as $N_{\text{H}_2} \sim 1.0 \times 10^{21} \text{ cm}^{-2} A_V$ ⁷⁹. Assuming cosmic abundances for the combined volatile

508 and refractory abundances in the interstellar medium (ISM)⁸⁰, the molecular hydrogen column can be
509 converted into expected bulk budgets of C, O, N, and S. To determine what fraction of these budgets our
510 ices represent, we summed the column densities of all C-bearing, O-bearing, N-bearing, and S-bearing ice
511 species. For the O-bearing species, we doubled the column densities of $^{12}\text{CO}_2$, $^{13}\text{CO}_2$, and SO_2 to account
512 for the two oxygen atoms. For both NIR38 and J110621, we see only 19% of the total O-budget, 19%
513 and 14%, respectively, of the C-budget, and 13% of the N-budget and 1% of the S-budget for both. If we
514 assume the $N_{\text{H}_2}/N_{\text{CO}}$ conversion for molecular clouds⁷⁹, then the expected amount of total CO towards
515 NIR38 and J110621 are $1.08 \times 10^{19} \text{ cm}^{-2}$ and $1.71 \times 10^{19} \text{ cm}^{-2}$, respectively.

516 Data Availability

517 Our raw data are available at the STScI MAST JWST archive, and our enhanced spectra are available as part
518 of our ERS science enabling product deliverables at the following Zenodo DOI: 10.5281/zenodo.7501239

519 Code Availability

520 The ENIIGMA global fitting tool⁴⁹ is publicly available on GitHub at the following URL: <https://github.com/willastro/E>
521 fitting-tool

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550 **Author contributions**

551 MKM originated the proposal, designed the observations, co-managed the team, determined the feature
552 optical depths and wrote much of the main text. WR performed global and local fitting to determine the
553 column densities, including the error analysis, and wrote part of the Methods section. KP contributed to
554 the observational design, reduced and optimized the NIRSpec data, wrote part of the Methods section, and
555 commented on the draft. NC reduced and optimized the MIRI LRS data to allow for the global fitting
556 and wrote part of the Methods section. LEUC performed the local fitting of the methanol + hydrates
557 band, wrote part of the Methods section, and commented on the draft. ED wrote part of the discussion
558 and made suggestions for the analysis. TL wrote portions of the results section and reorganized the draft.
559 JAN contributed to the original proposal, wrote portions of results section, and made suggestions for the
560 analysis. YJP managed the Overleaf file, wrote part of the results section, and made suggestions for the
561 local fitting. GP locally fit the OCN^- feature, wrote part of the Methods section, and commented on the
562 draft. DQ managed the Overleaf file and suggested parts of the results and discussion sections. MGR
563 did the local fitting of the $^{13}\text{CO}_2$, ^{13}CO and OCS features, determined the upper limits, and wrote part of
564 the Methods section. ZLS and FS reduced the NIRCам data, with contributions to the reduction scripts
565 from HD, and wrote part of the Methods section. TB benchmarked the NIRSpec spectra to validate them.
566 ACAB helped to design the original program, co-managed the team, organized the NIRCам analysis, and
567 commented on the draft. WAB, PC, SBC, HC, MND, EE, JE, HF, RTG, DH, SI, IJS, MJ, JKJ, LEK, DCL,
568 MRSM, BAM, GJM, KIO, MEP, TS, JAS, EFvD, and HL commented on the draft. ZS, FS, EE, JE, HF,
569 and TS also contributed to the observational design and analysis of the NIRCам data. HL helped motivate
570 the original proposal, co-managed the team, and organized the laboratory data used for the analysis. All
571 authors participated in discussion of the observations, analysis and interpretation of the results.

572 **Competing Interests**

573 The authors declare no competing financial interests.

574

Table 1. Absorption features of molecules in ices and dust features observed towards NIR38 ($A_V \sim 60$) and J110621 ($A_V \sim 95$).

λ (μm)	ν (cm^{-1})	Species	Identification ^a	Detection	
				NIR 38	J110621
2.69	3708	CO ₂	combination	✓	...
2.73	3664	H ₂ O	O–H dangling bond	✓	...
3.0	3330	H ₂ O	O–H stretch	✓	✓
3.24	3249	CH ₃ OH	O–H stretch	✓	✓
3.32	3012	CH ₄	C–H stretch	✓	✓
3.47	2881	Ammonia hydrate	NH ₃ · H ₂ O	!	!
3.32–3.64	3012–2890	CH ₃ OH	C–H asym. str. + overt.	✓	✓
3.92	2548	H ₂ S	S–H	✗	...
4.07	2457	HDO	O–D str.	✗	✗
4.17–4.77	2400–2100	H ₂ O	combination	✓	✓
4.27	2340	¹² CO ₂	C–O str.	✓	✓
4.38	2280	¹³ CO ₂	C–O str.	✓	✓
4.44	2252	CH ₃ CN	C–N str.	✗	✗
4.59	2175	OCN [−]	C–N str.	✓	✓
4.67	2140	¹² CO	C–O str.	✓	✓
4.76	2100	HCN	C≡N str.	✗	✗
4.78	2090	¹³ CO	C–O str.	✓	✓
4.90	2040	OCS	C–O str.	✓	✓
6.0	1666	H ₂ O	bending	✓	✓
6.85	1459	CH ₃ OH	CH ₃ def.	✓	✓
6.85	1459	NH ₄ ⁺	N–H str.	✓	✓
6.9–7.5	1449–1333	Unidentified absorption	COMs functional groups?	✓	✓
7.24	1384	CH ₃ CH ₂ OH?	CH ₃ def.	!	!
7.43	1362	CH ₃ CHO?	CH ₃ def. + CH wag.	!	!
7.60	1318	SO ₂	S–O str.	!	!
7.71	1300	CH ₄	C–H str.	✓	✓
8.86	1131	CH ₃ OH	CH ₃ rock	✓	✓
9.01	1110	NH ₃	umbrella	✓	✓
9.74	1025	CH ₃ OH	C–O str.	✓	✓
9.80	1020	Silicate	Si–O str.	✓	✓
11.0	910	H ₂ O	libration wing	✓	✓

^aSymbol legend: ✓ - observed, ✗ - not observed, ! - possibly observed, ... - insufficient data

Table 2. Integrated optical depths and column densities of molecules in ices observed towards AV60 and AV95 sources.

Species	ν (cm ⁻¹)	A (cm molec ⁻¹)	$\int \tau_{\nu} d\nu$ ^a		$N_{\text{ice}} [\times 10^{18} \text{ cm}^{-2}]$ ^b	
			A _{V=60}	A _{V=95}	A _{V=60}	A _{V=95}
H ₂ O	3330	2×10^{-16} [ref. ⁵⁷]	1376.07	2676.12	$6.88_{3.70}^{12.5}$ (6.93)	$13.38_{7.83}^{17.27}$ (13.17)
¹² CO	2140	1.1×10^{-17} [ref. ⁵⁷]	32.56	40.48	$2.96_{1.86}^{4.66}$ (3.22)	$3.68_{2.48}^{5.46}$ (3.94)
¹³ CO	2090	1.0×10^{-17} [ref. ⁵⁷]	0.32	0.31	$0.03_{0.02}^{0.04}$ (0.02)	$0.02_{0.01}^{0.03}$ (0.02)
¹² CO ₂	2340	1.1×10^{-16} [ref. ⁵⁷]	151.8	191.4	$1.38_{0.77}^{1.97}$ (1.36)	$1.74_{1.09}^{2.36}$ (1.62)
¹³ CO ₂	2280	7.1×10^{-17} [ref. ⁵⁷]	1.42	2.30	$0.02_{0.01}^{0.03}$ (0.03)	$0.02_{0.02}^{0.04}$ (0.03)
CH ₃ OH ^c	2830	1.3×10^{-16} [ref. ⁵⁸]	53.3 {68.9}	58.5 {84.5}	0.41 {0.53}	0.45 {0.65}
CH ₃ OH	1025	1.8×10^{-17} [ref. ⁵⁹]	10.98	9.18	$0.61_{0.28}^{0.95}$ (0.54)	$0.51_{0.24}^{1.08}$ (0.49)
NH ₃	1110	2.1×10^{-17} [ref. ⁵⁹]	6.31	13.86	$0.30_{0.21}^{0.97}$ (0.41)	$0.66_{0.48}^{1.11}$ (0.68)
CH ₄	1303	8.4×10^{-18} [ref. ⁵⁹]	1.51	2.11	$0.18_{0.14}^{0.23}$ (0.16)	$0.25_{0.16}^{0.28}$ (0.28)
OCN ⁻	2175	1.3×10^{-16} [ref. ⁶⁰]	2.58 ^d	4.11 ^d	0.02	0.03
NH ₄ ⁺	1459	4.4×10^{-17} [ref. ⁶¹]	25.08 ^d	34.32 ^d	0.57	0.78
OCS	2040	1.2×10^{-16} [ref. ⁶²]	1.18 ^d	2.36 ^d	0.01	0.02
SO ₂	1310	3.4×10^{-17} [ref. ⁶⁴]	0.11 ^d	0.16 ^d	0.0034	0.0047
1σ upper limits						
H ₂ S	2548	1.7×10^{-17} [ref. ⁶²]	0.64 ^e	...	0.04	...
HCN	2100	1.0×10^{-17} [ref. ⁶⁵]	0.66 ^e	0.88 ^e	0.06	0.09
CH ₃ CN	2252	1.9×10^{-18} [ref. ⁶⁶]	0.26 ^e	0.35 ^e	0.14	0.19

^aWhen not indicated, these values are based on the global fit.

^bUpper and lower values are from 3 σ confidence intervals. Values inside the parenthesis are calculated from local fits.

See [Supplementary Information](#).

^cCalculations performed on optical depth data after local continuum extraction around 3.5 μm . See Extended Data Figure 9. Values in the curly brackets are obtained excluding the ammonia hydrate effect.

^dValues from the local fits (see [Supplementary Information](#)).

^e $\int \tau_{\nu} d\nu = \text{RMS} \times \text{FWHM}$.

Table 3. Laboratory data tested in the global fit performed with ENIGMA.

Label/Temp.	Temperature (K)	Database/Reference
H ₂ O	15 K	LIDA ⁵⁴
NH ₃	10 K	LIDA ⁸¹
CH ₄	10 K	LIDA ³³
CO	12 K	LIDA ⁷¹
CO ₂	12 K	LIDA ⁷¹
CH ₃ OH	10 K	LIDA ³¹
NH ₃ :CH ₃ OH (1:1)	12 K	UNIVAP ⁴⁹
H ₂ O:NH ₃ (10:1.6)	10 K	...
H ₂ O:CO ₂ (10:1)	10 K	LIDA ⁶⁹
H ₂ O:CO ₂ (1:10)	10 K	LIDA ⁶⁹
H ₂ O:CO ₂ (1:6)	10 K	LIDA ⁶⁹
H ₂ O:CO ₂ (1:1)	10 K	LIDA ⁶⁹
H ₂ O:CO (20:1)	16 K	NASA/Ames ⁶³
H ₂ O:CH ₄ (20:1)	15 K	NASA/Ames ⁶³
H ₂ O:CO ₂ :CH ₄ (10:1:1)	12 K	UNIVAP ⁴⁸
H ₂ O:CH ₃ OH:CO ₂ :CH ₄ (0.6:0.7:1:0.1)	10 K	LIDA ⁷⁰
H ₂ O:CH ₃ OH:CO ₂ (9:1:2)	10 K	LIDA ⁷⁰
H ₂ O:CH ₃ OH:CO:NH ₃ (100:50:1:1)	10 K	NASA/Ames ⁵⁸
H ₂ O:CH ₃ OH (10:0.8)	10 K	...
CO ₂ :CH ₃ OH (1:1)	10 K	LIDA ⁶⁹
CO:CO ₂ (1:1)	15 K	LIDA ⁷¹
CO:CH ₃ OH (4:1)	15 K	LIDA ⁵²

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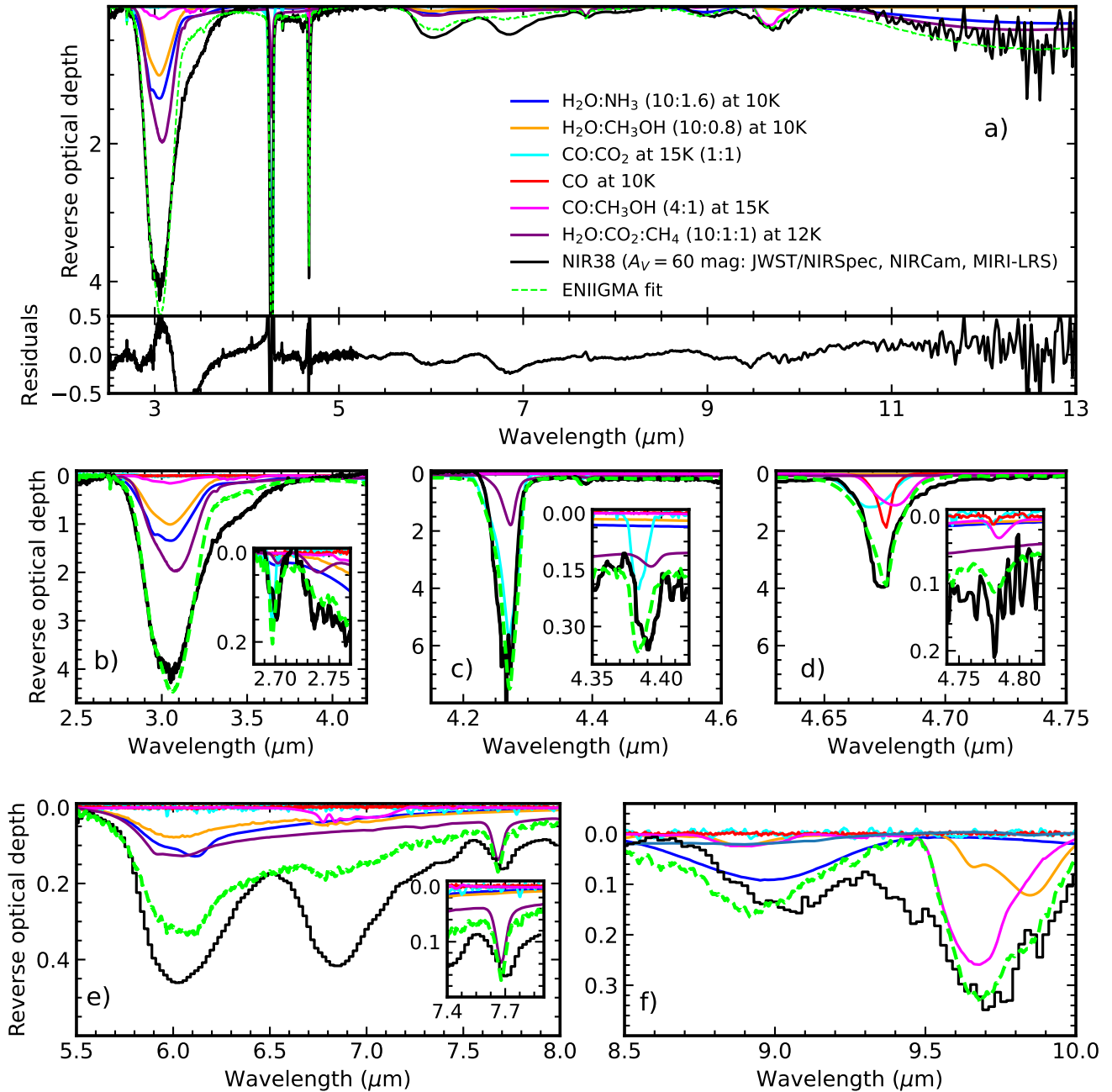
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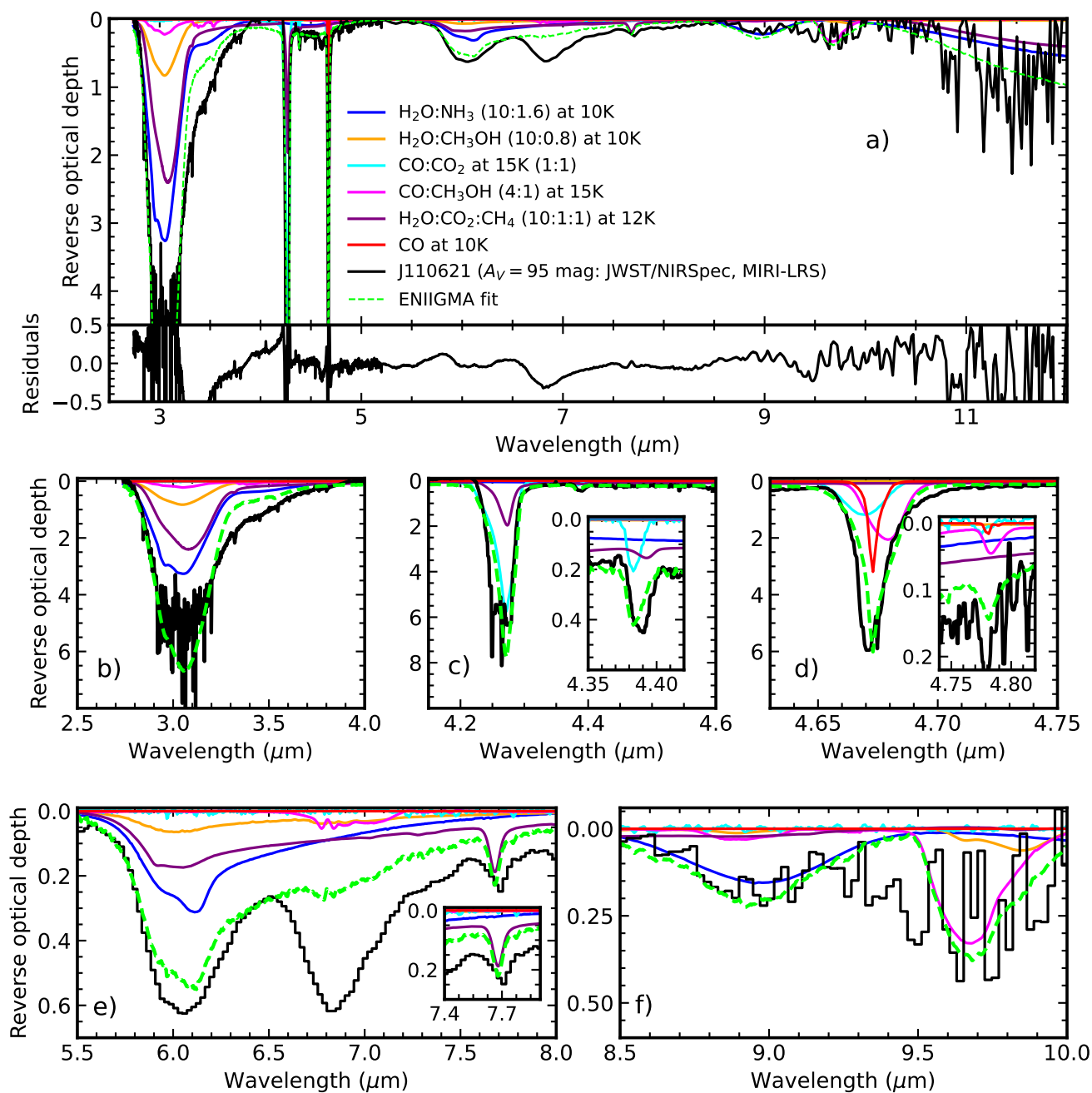
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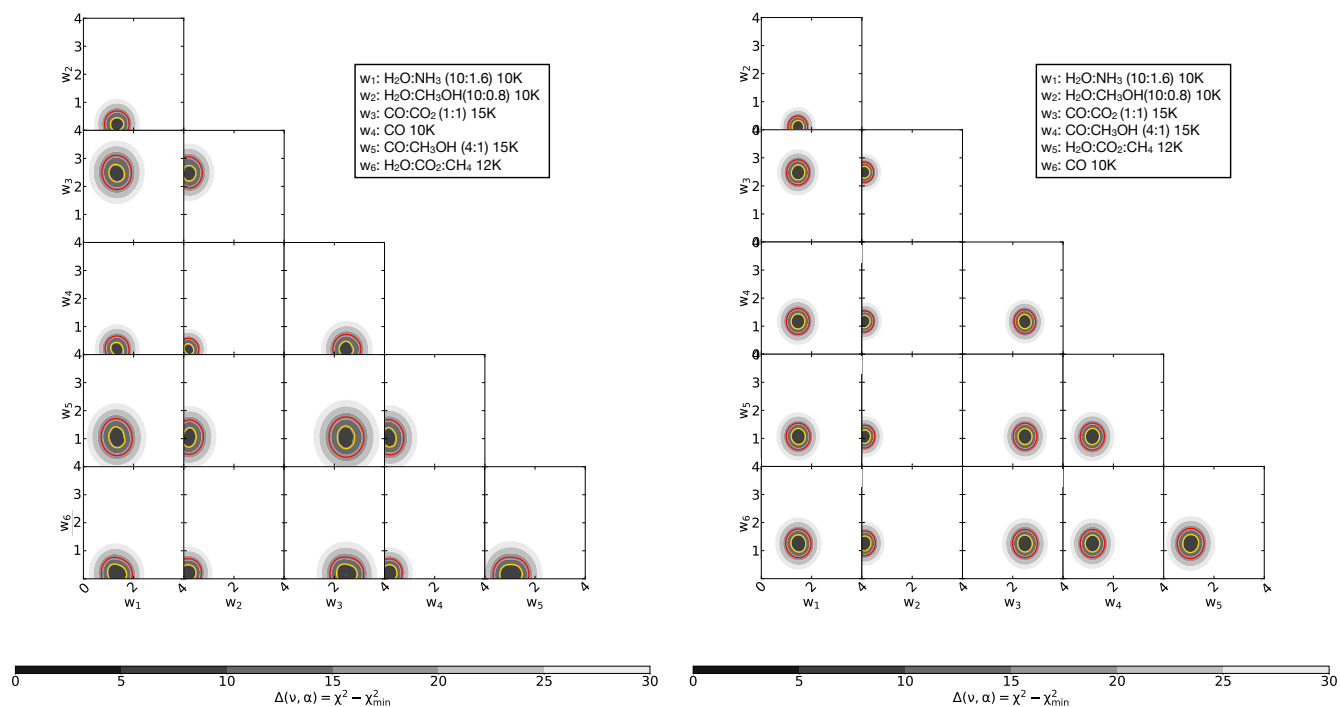
1 Extended Data



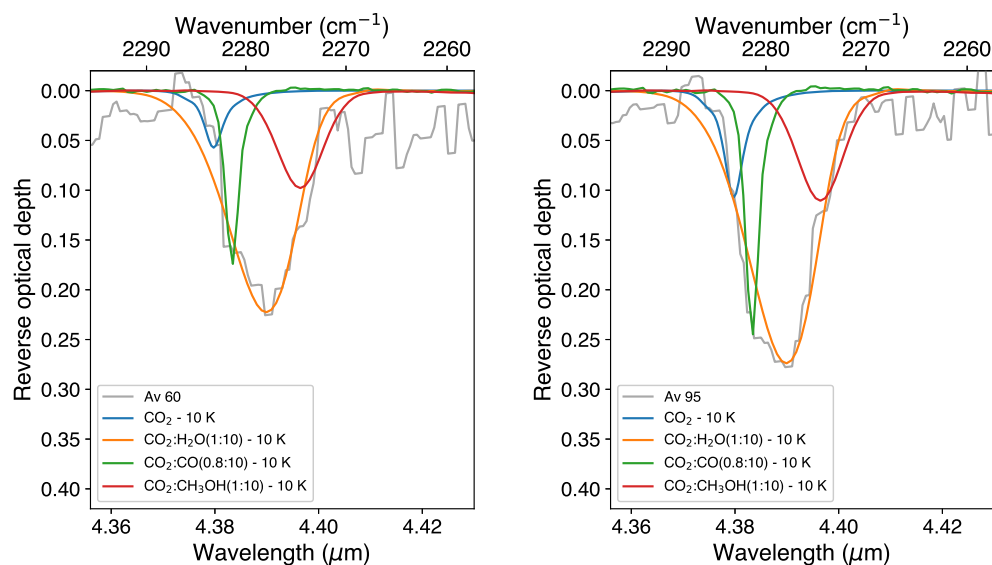
Extended Data Figure 1. Global fit of the combined spectrum for NIR38. Combined NIRSpec and MIRI/LRS spectrum of the NIR38 source (black), with the ENIIGMA fitting tool model (green). Each component in the fit is colour-coded. Panel *a* shows the entire range between 2.5 and 13 μm and the residuals of the fit. Panels *b-f* show a zoom-in of selected ranges corresponding to the major ice components. Small insets show the fit of $^{12}\text{CO}_2$ (Panel *b*), $^{13}\text{CO}_2$ (Panel *c*), ^{13}CO (panel *d*) and CH_4 (panel *e*).



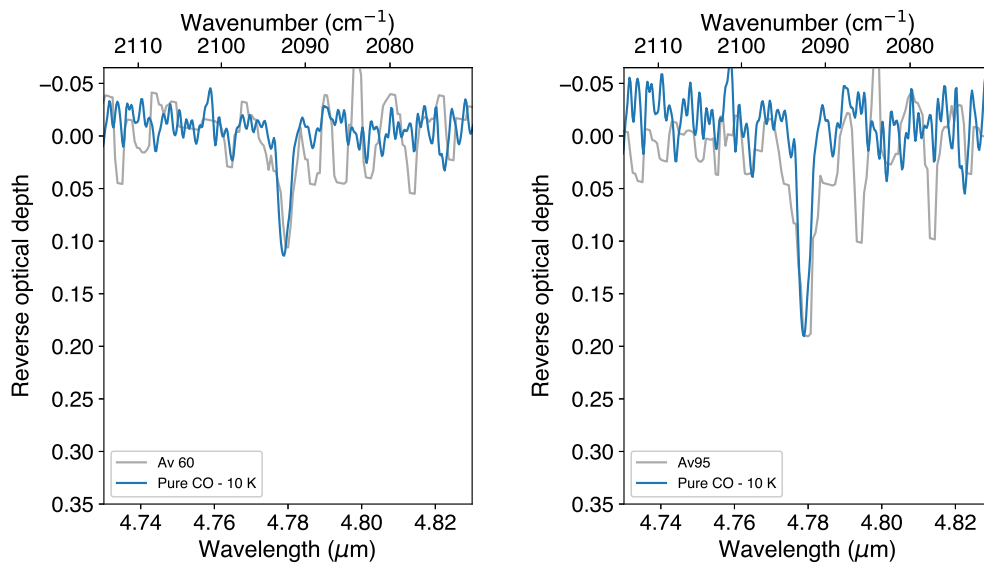
Extended Data Figure 2. Global fit of the combined spectrum for J110621. Combined NIRSpec and MIRI/LRS spectrum of the J110621 source (black), with the ENIIGMA fitting tool model (green). Each component in the fit is colour-coded. Panel *a* shows the entire range between 2.5 and 13 μm and the residuals of the fit. Panels *b-f* show a zoom-in of selected ranges corresponding to the major ice components. Small insets show the fit of ¹³CO₂ (Panel *c*), ¹³CO (panel *d*) and CH₄ (panel *e*).



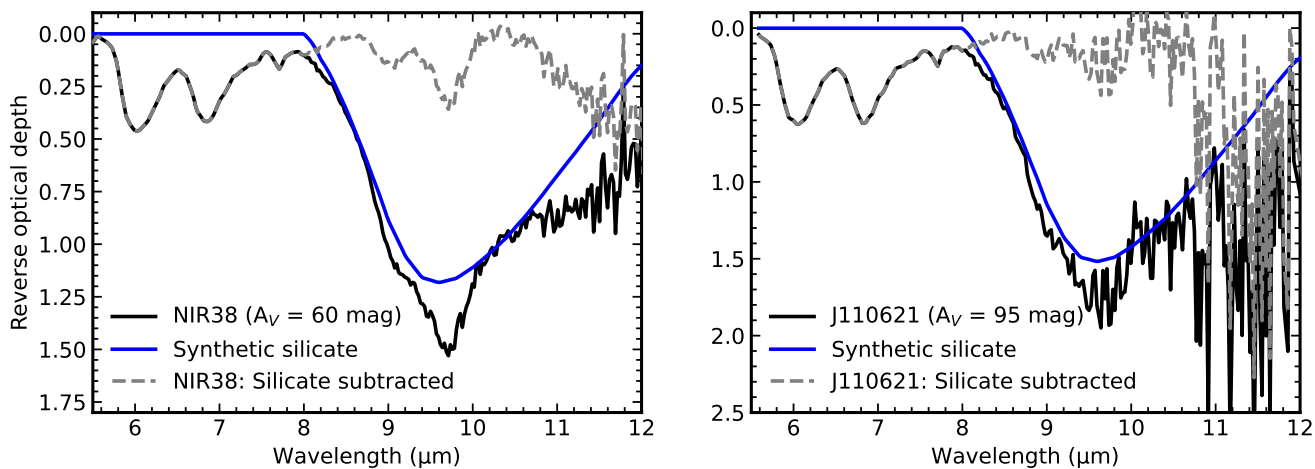
Extended Data Figure 3. Confidence interval analysis for the global fits to NIR38 and J110621. Corner plot showing the confidence interval analysis of the coefficients in the linear combination. The grey-scale contours show the differences in the χ^2 maps (Δ) which depends on the degree of freedom (ν) and the statistical significance (α). The yellow and red line contours indicate 2 and 3 σ confidence intervals. The *left* and *right* plots are for $A_V = 60$ and $A_V = 95$ sources, respectively. Note that the ice species assigned to w1-w6 is automatically determined and differs between the left and right panels.



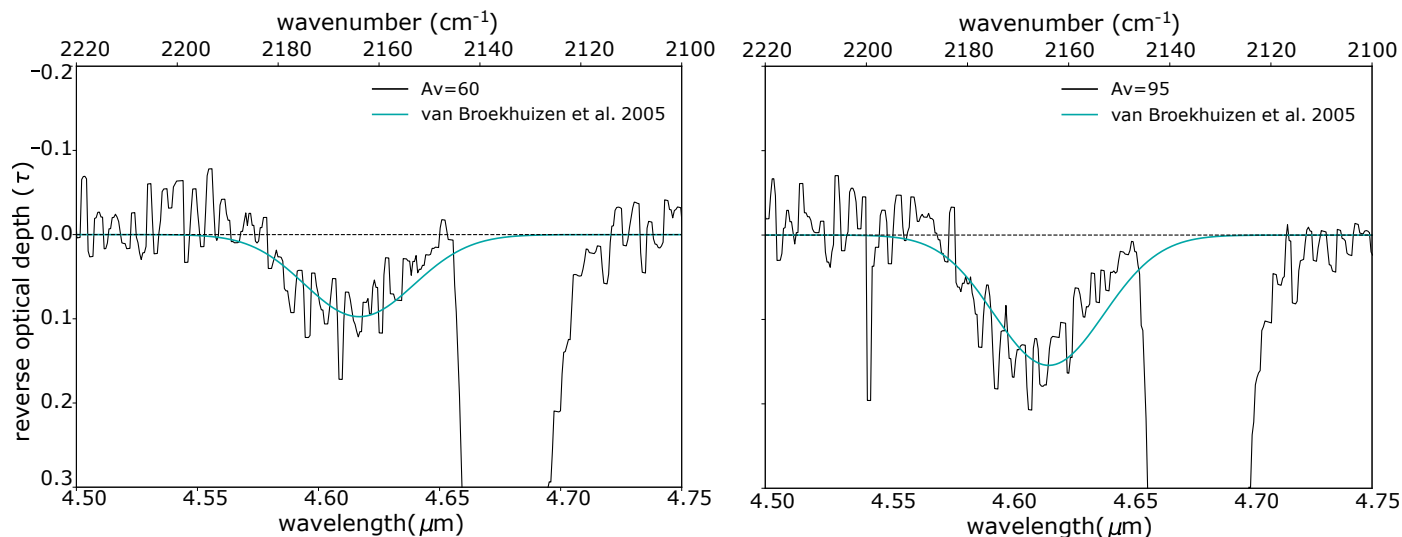
Extended Data Figure 4. Observed absorption profile of the $^{13}\text{CO}_2$ asymmetric stretching, around $4.39 \mu\text{m}$, in NIR38 (left panel) and J110621 (right panel). To demonstrate the ice chemical environment that best reproduces the observed feature peak, the colored curves show the scaled profiles of $^{13}\text{CO}_2$ in laboratory spectra of the following ice mixtures at 10 K: pure CO_2 (blue), $\text{H}_2\text{O}:\text{CO}_2$ (orange), $\text{CO}_2:\text{CO}$ (green), and $\text{CO}_2:\text{CH}_3\text{OH}$ (red). In all the ice mixtures, CO_2 is diluted in a ratio of $\sim 1:10$, with $^{12}\text{CO}_2/^{13}\text{CO}_2 \sim 90$.



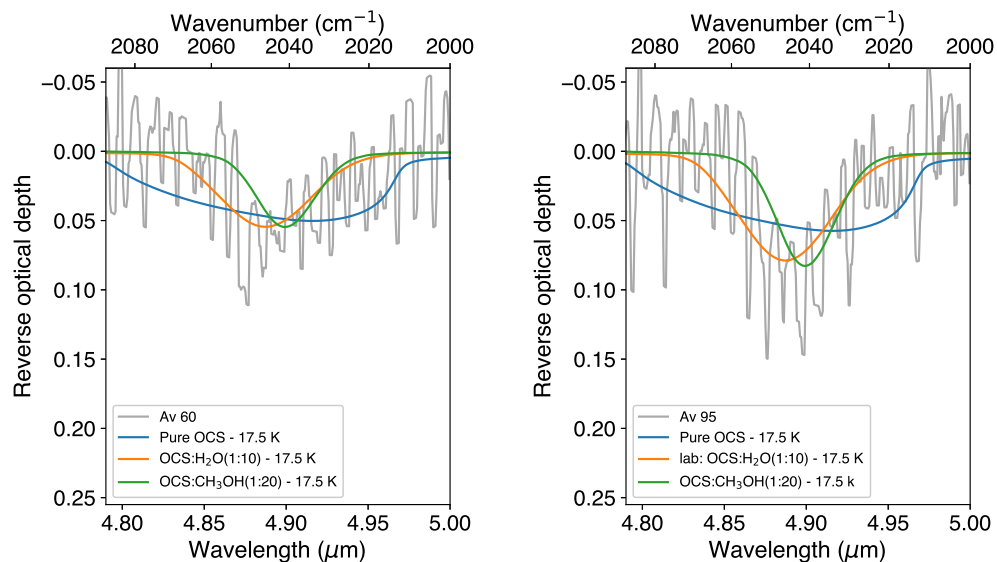
Extended Data Figure 5. Observed absorption profile of the ^{13}CO stretching, around $4.78\ \mu\text{m}$, in the $A_V = 60$ (left panel) and $A_V = 95$ (right panel) sources. The laboratory spectra of pure ^{13}CO ice at 10 K is also shown in blue.



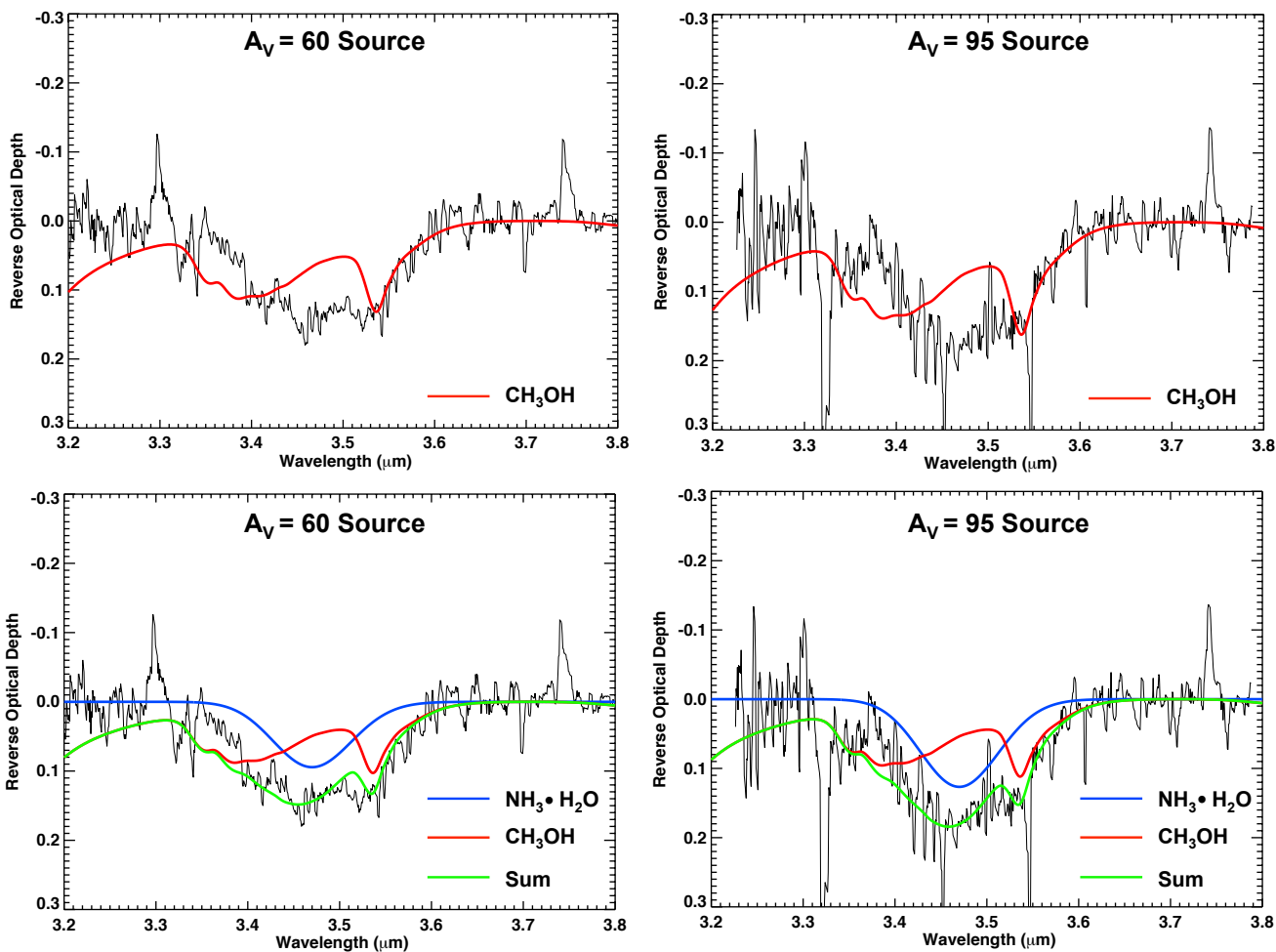
Extended Data Figure 6. Silicate subtraction during optical depth calculation for NIR38 and J110621. MIRI/LRS spectrum of the two background stars before (black) and after (blue) silicate subtraction. The grey dashed line is the synthetic silicate spectrum used to remove the silicate absorption toward the background stars.



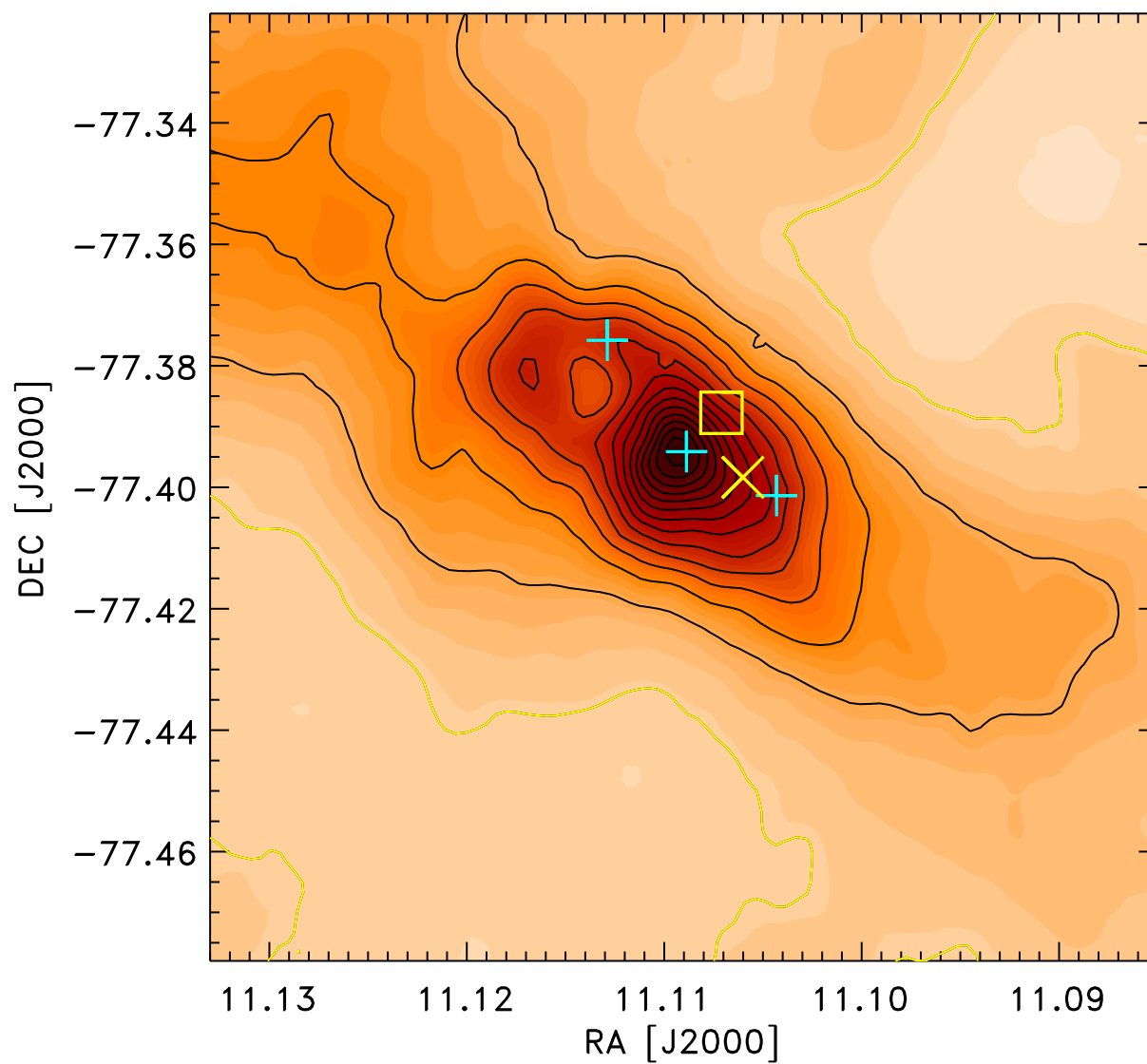
Extended Data Figure 7. Observed absorption profile of the OCN^- feature around $4.62 \mu\text{m}$, in the $A_v = 60$ (left panel) and $A_v = 95$ (right panel) sources. A gaussian fit using the parameters found in the literature² is also shown.



Extended Data Figure 8. Observed absorption profile of the C=O stretching of OCS, around $4.9 \mu\text{m}$, in the $A_v = 95$ source. The colored curves show the profile of the OCS in laboratory ice spectra of pure OCS (blue), H_2O :OCS (orange), and CH_3OH :OCS (green), all at 17.5 K.



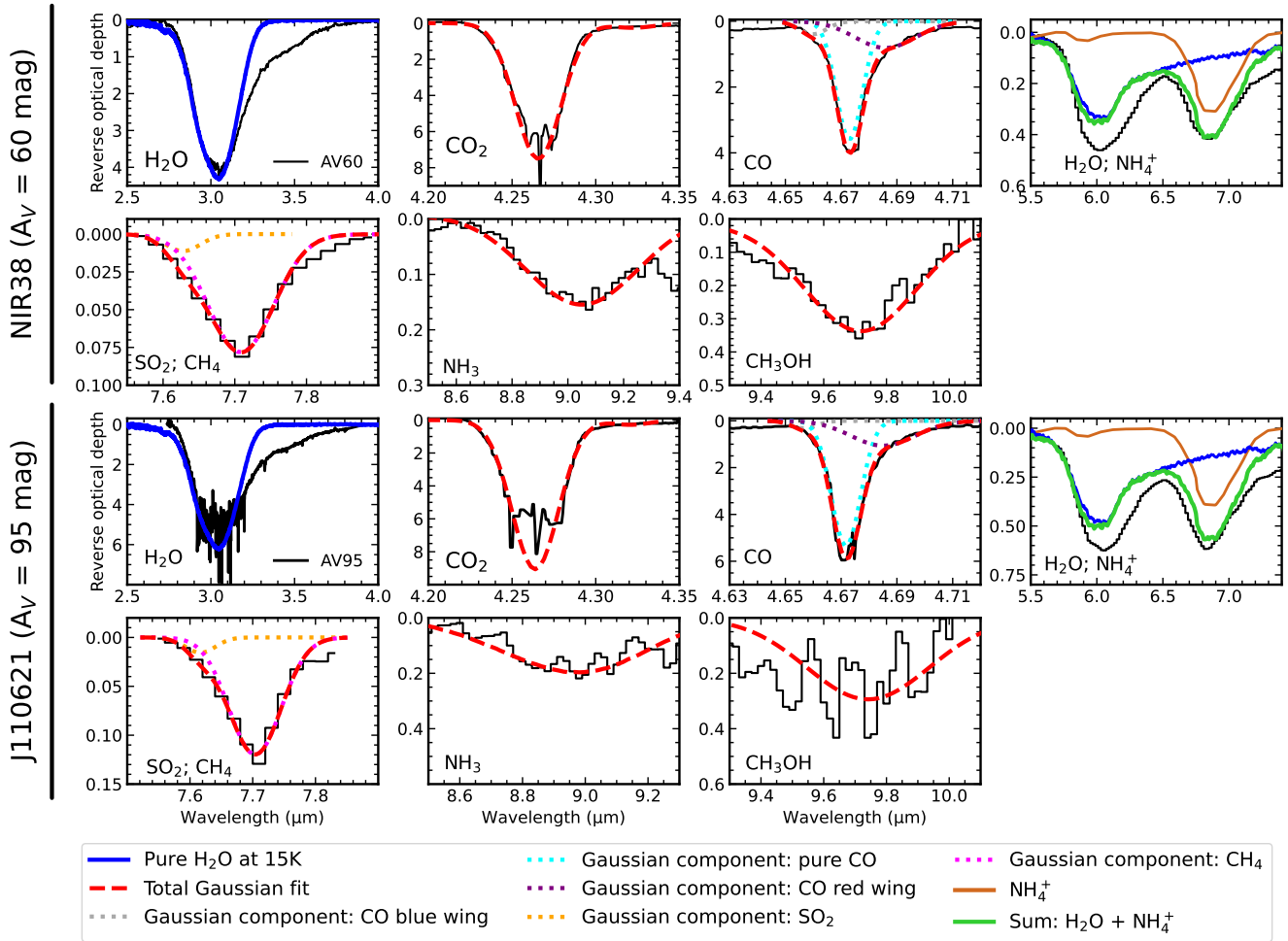
Extended Data Figure 9. Optical depths of the $A_V = 60$ (left) and $A_V = 95$ (right) background sources in the 3.2 - 3.8 μm ($3125 - 2631 \text{ cm}^{-1}$) region. Top: The red line shows the optical depths of CH_3OH laboratory data at 15K scaled for the C-H stretching band around the $3.53 \mu\text{m}$ feature. Bottom: The blue Gaussian represents the likely $\text{NH}_3 \cdot \text{H}_2\text{O}$ component centered at $3.47 \mu\text{m}$ and the red line again displays the CH_3OH laboratory data but both are simultaneously scaled so the sum (in green) fits the data from $3.40\text{-}3.65 \mu\text{m}$.



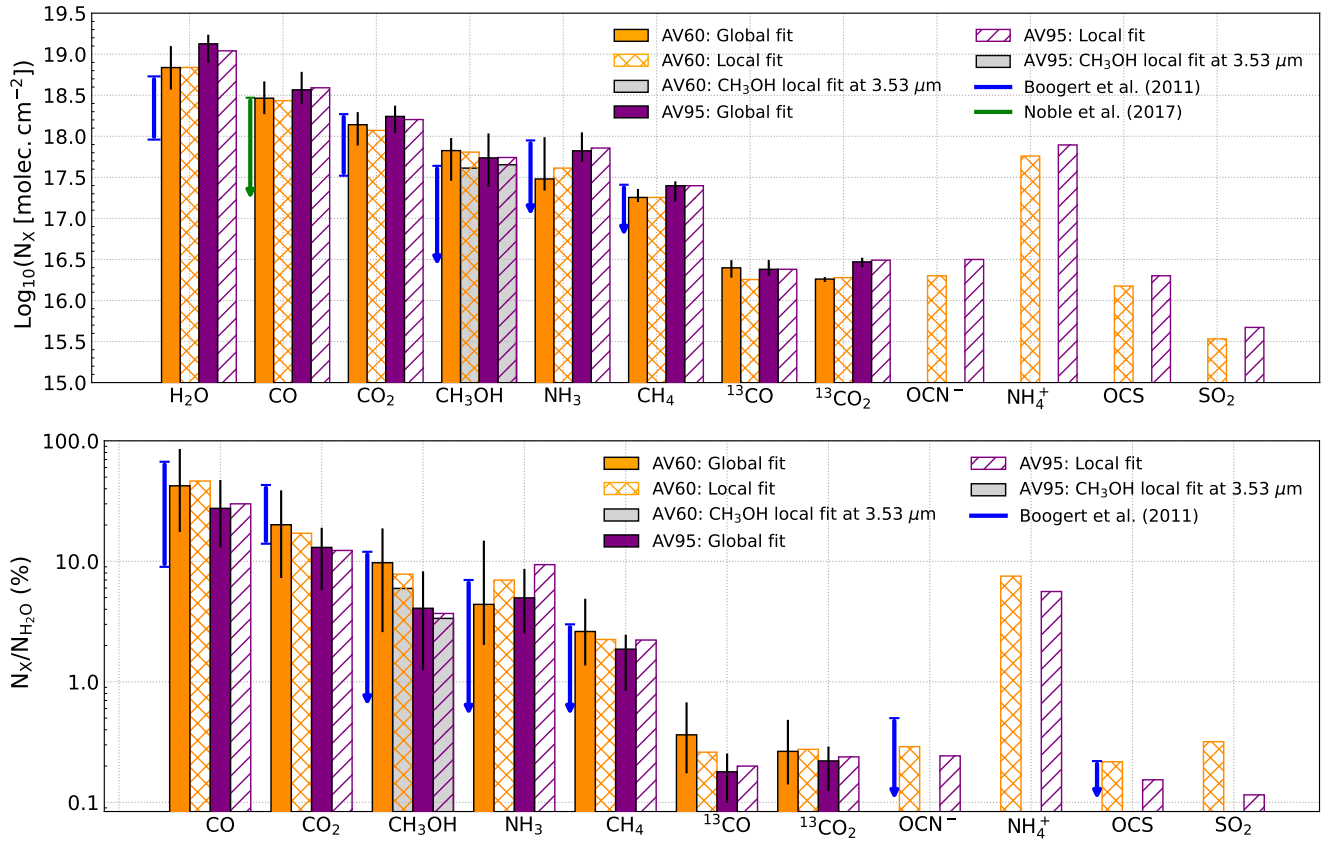
Extended Data Figure 10. Map of the column density distribution in the region inferred from the Herschel far-infrared maps from 70 to 500 μm . The cyan plus-signs indicate the locations of the Class I protostar Ced 110-IRS4, the Class 0 protostar ChamI-MMS and the clump ChaI-C2 going from the north-east (top-left) to south-west (bottom-right). The yellow box and cross indicate the location of the $A_V \approx 60$ and the $A_V \approx 95$ background stars, respectively. The contours indicate increasing H_2 column densities in steps of $5 \times 10^{21} \text{ cm}^{-2}$, starting at a value of $5 \times 10^{21} \text{ cm}^{-2}$ for the lowest contour (yellow line).

1 Supplementary Information

2 To validate the column densities derived from the global fitting using multiple features and mixed ice
 3 species, in Supplementary Figure 1 we show the local fits derived in the Main Text. In Supplementary
 4 Figure 2 we compare those results with the column densities determined from the local fits. The column
 5 densities from the local fits agree with those from the global fits to within the listed uncertainties.
 6



Supplementary Figure 1. Local fits of the major ice components in NIR38 and J110621. At 3 μm , we scale the H_2O ice spectrum at 15 K to match selected wavelengths that are not saturated (see Methods). Between 5.5 and 8.0 μm , we sum the NH_4^+ band and H_2O scaled to the 3 μm profile. For the other absorption bands, we perform a Gaussian fit. In the cases of CO and SO_2/CH_4 , more than one Gaussian profile is adopted.



Supplementary Figure 2. Barplot comparing individual column densities of ices derived from local fits to those derived from global fitting. (Top) Ice column densities towards NIR38 ($A_V = 60$ mag) and J110621 ($A_V = 95$ mag) derived from global (full bars, best of $n=112$ models) and local (hatched bars) fits. Blue and green lines indicate the range of values in the literature. Arrows are used for upper limits and error bars are from the 3σ confidence intervals. **(Bottom)** Relative column densities barplot of the detected ices, normalized to H₂O ice. Full and hatched bars are from global and local fits, respectively. Blue lines are from literature values, and arrows indicate upper limits. Error bars are from the 3σ confidence intervals.