From Simple to Complex Molecules in Interstellar Ices

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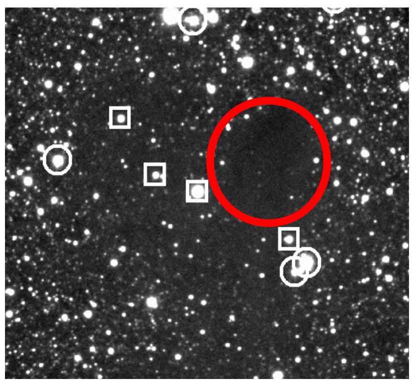
Topics

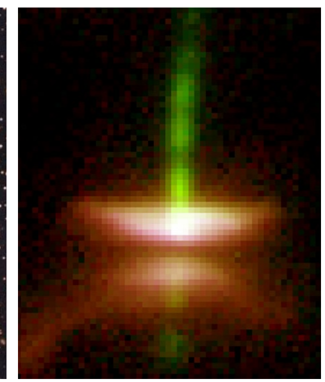
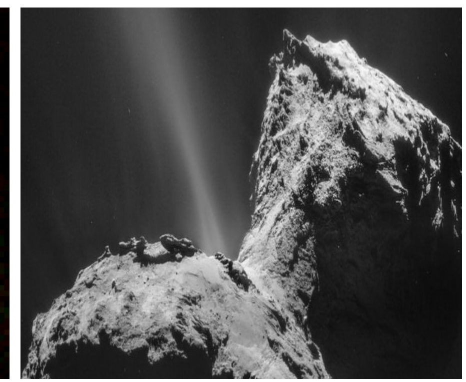
1. Introduction: Questions about Ice Formation Processes
2. H_2O-rich Ice Phase
3. CO-rich Ice Phase
4. Salts
5. Heated Ices
6. Ice Porosity
7. Back to the Gas Phase
8. Future Missions
9. Conclusions

1. A Key Question

Which processes and conditions lead from atoms to the complex molecules needed for life?

cloud → prestellar core → YSO env. → pp disk → comet

H, C, O, N, S... ⟶ glycine, ethylene glycol. ...

1. Molecule Formation

I. Gas phase chemistry (often involving ions, e.g. conversion C^+ to CO)

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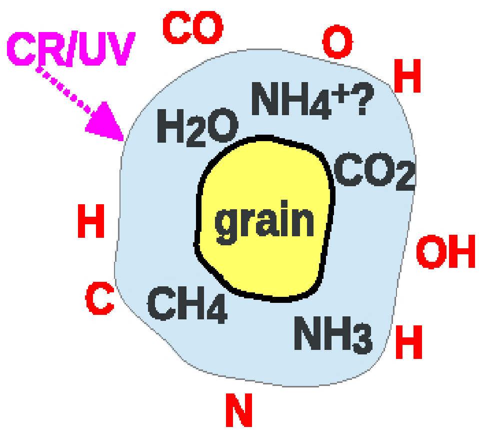
II. Grain surface chemistry (freeze out <100 K): producing simple molecules. Efficient hydrogenation due to tunneling.



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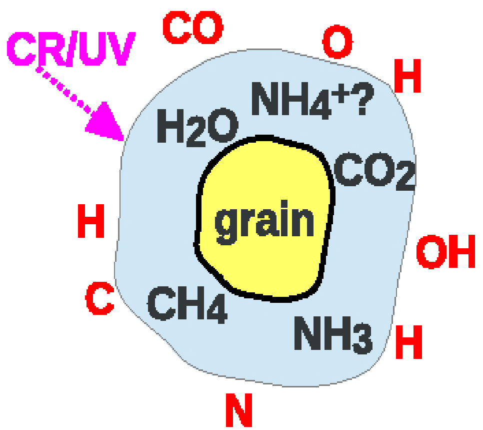
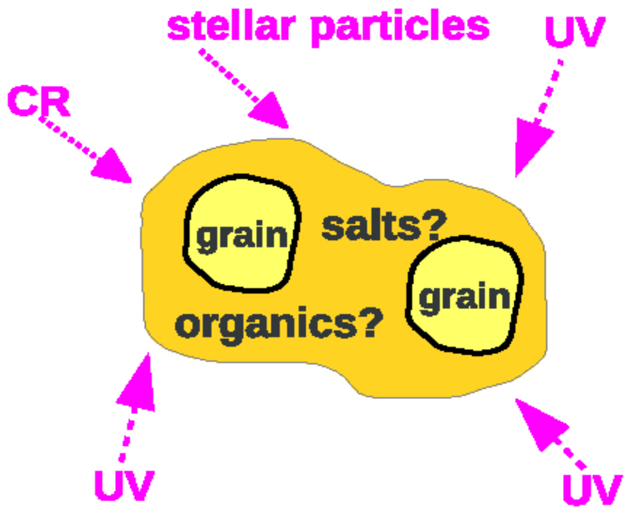
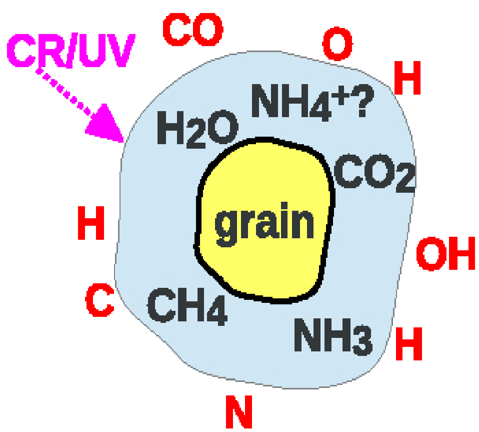




III. Energetic and thermal processing ices: converting simple to complex molecules

1. Molecule Formation

In dense clouds, grain surface chemistry rules.



This was modeled long ago:

Astron. Astrophys. 114, 245–260 (1982)

ASTRONOMY AND ASTROPHYSICS

Model Calculations of the Molecular Composition of Interstellar Grain Mantles

A. G. G. M. Tielens* and W. Hagen**

Laboratory Astrophysics Group, Rijksuniversiteit, 2300 RA Leiden, The Netherlands

Received February 1, accepted May 19, 1982

THE ASTROPHYSICAL JOURNAL, 399:L71–L74, 1992 November 1

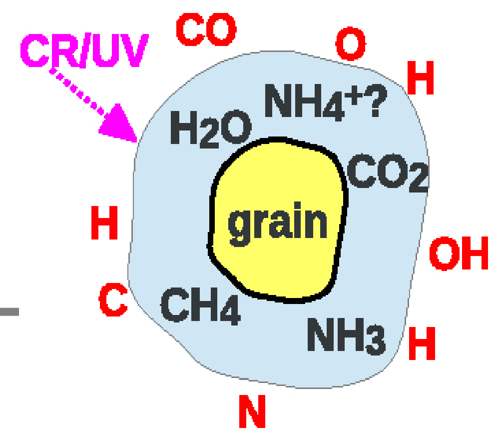
ON THE MOLECULAR COMPLEXITY OF THE HOT CORES IN ORION A: GRAIN SURFACE CHEMISTRY AS "THE LAST REFUGE OF THE SCOUNDREL"

S. B. CHARNLEY,[1,2] A. G. G. M. TIELENS,[1] AND T. J. MILLAR[3]

Received 1992 May 5; accepted 1992 August 19

1. Molecule Formation

In dense clouds, grain surface chemistry rules.



And "proven" in laboratory experiments:

The Astrophysical Journal, 571:L173–L176, 2002 June 1

EFFICIENT FORMATION OF FORMALDEHYDE AND METHANOL BY THE ADDITION OF HYDROGEN ATOMS TO CO IN H_2O-CO ICE AT 10 K

Naoki Watanabe and Akira Kouchi
Institute of Low Temperature Science, Hokkaido University, N19-W8, Kita-ku, Sapporo, Hokkaido 060-0819, Japan; watanabe@lowtem.hokudai.ac.jp
Received 2002 April 2; accepted 2002 April 25; published 2002 May 9

And "proven" in Monte Carlo simulations:

A&A 508, 275–287 (2009)
DOI: 10.1051/0004-6361/200913119

Astronomy & Astrophysics

Microscopic simulation of methanol and formaldehyde ice formation in cold dense cores

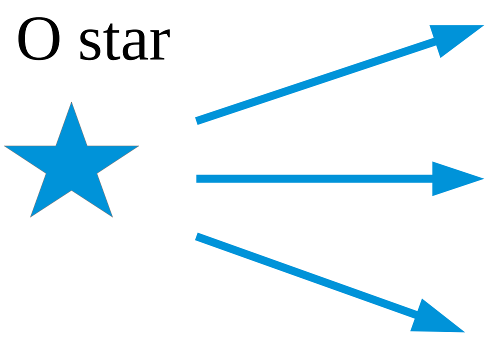
H. M. Cuppen[1], E. F. van Dishoeck[1,2], E. Herbst[3], and A. G. G. M. Tielens[1]

1. Molecule Formation

New questions:

- How complex do the molecules get via cold grain surface chemistry?
- Can we pinpoint and quantify the importance of gas phase and energetic processing?

1. Molecule Formation



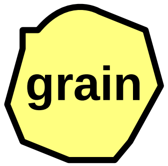
IC 1396, clustered star formation near massive star, analogous to early Earth (e.g., Adams 2010)

Reach+ 2009

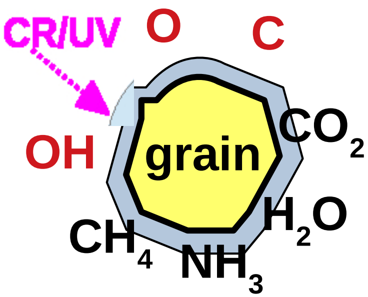
2. H_2O-rich Ices

Diffuse cloud

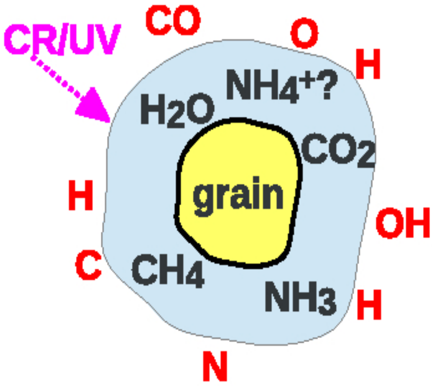
Dense cloud



A_V~0

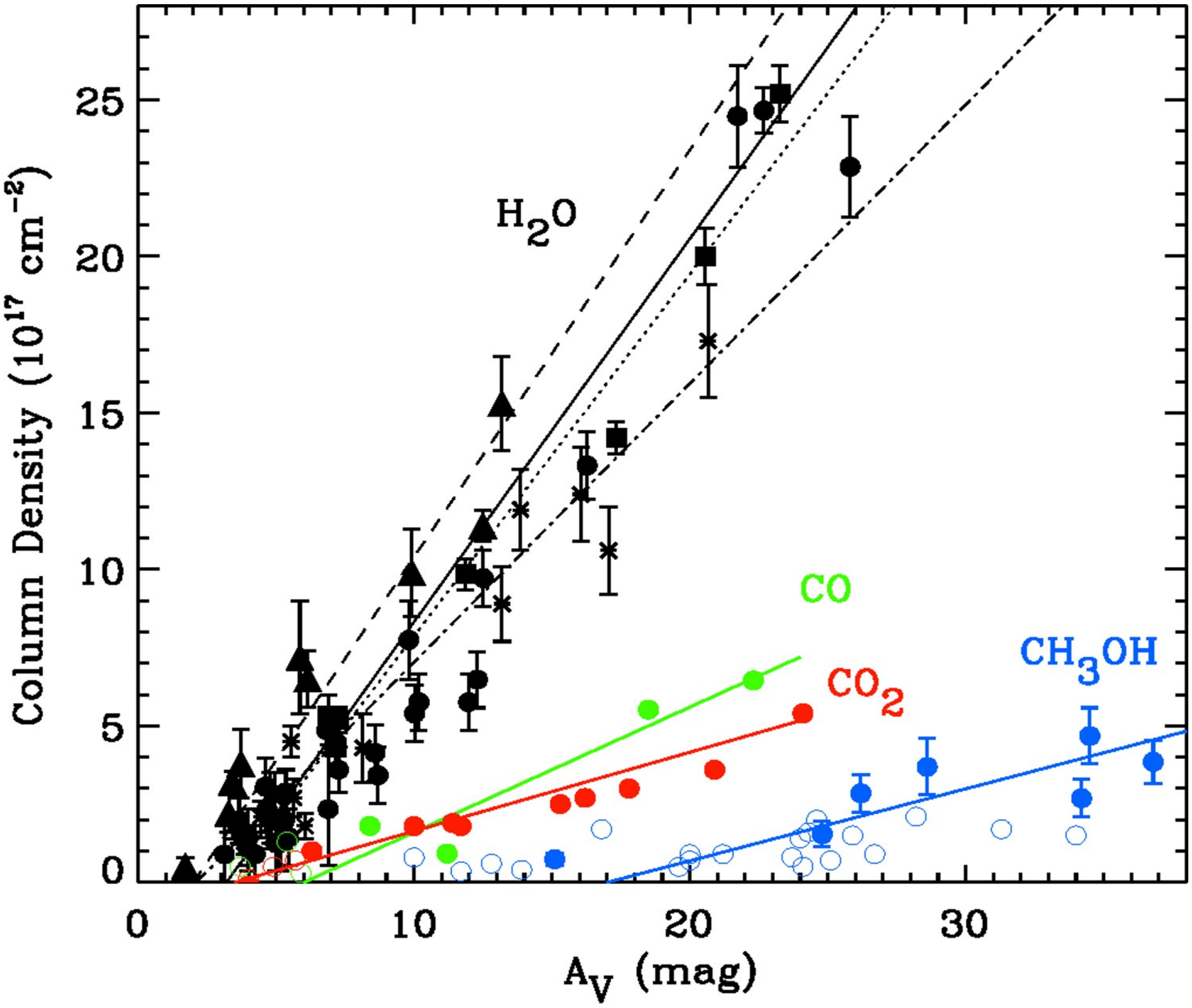


A_V<1.6
monomer, dimer



A_V>1.6
bulk H_2O
mixed

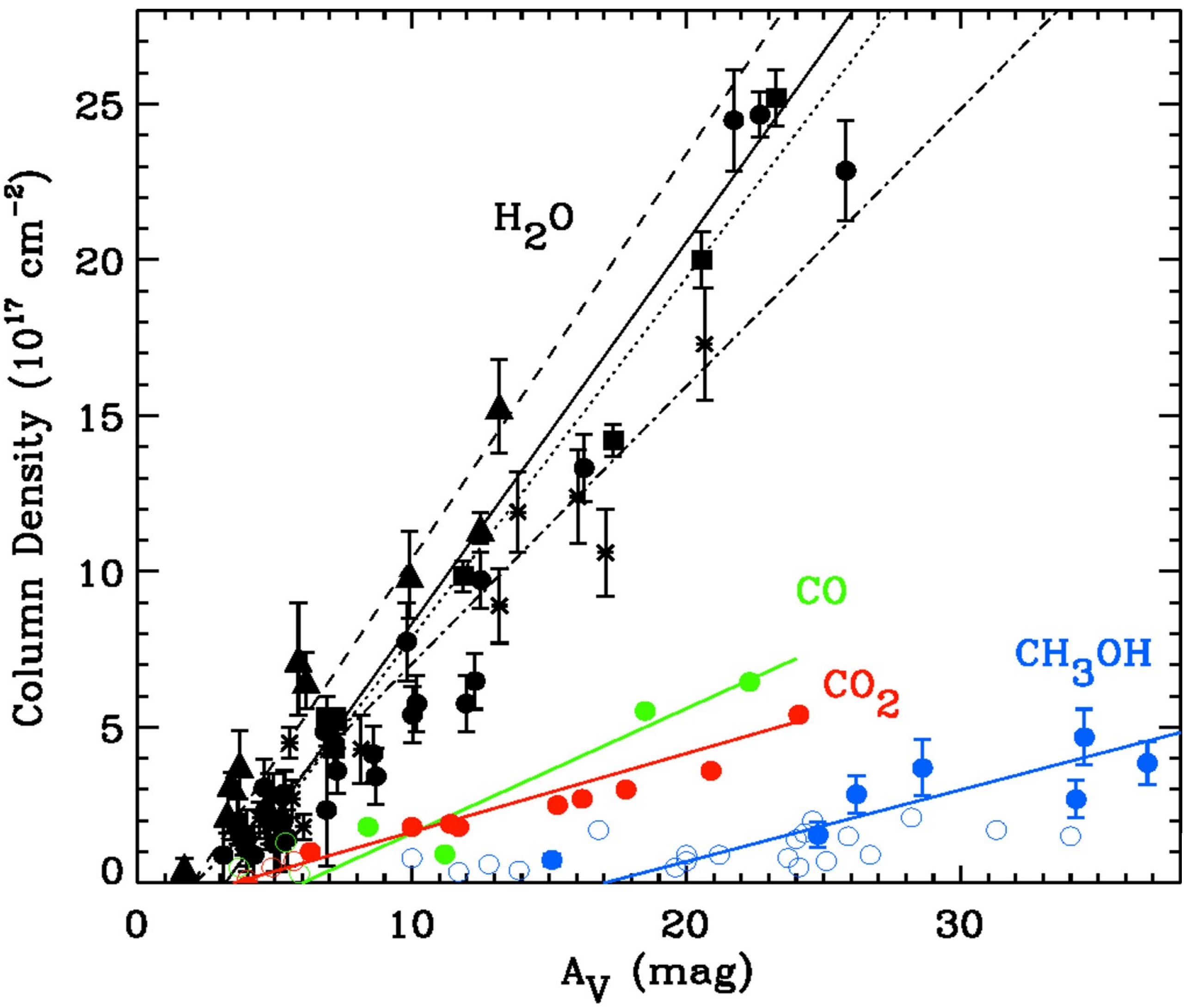
2. H_2O-rich Ices: H_2O:CO_2



Boogert, Gerakines, & Whittet, 2015

H_2O and CO_2 have same formation threshold: mixed. CO+OH → CO_2 (e.g., Ioppolo+ 2011)

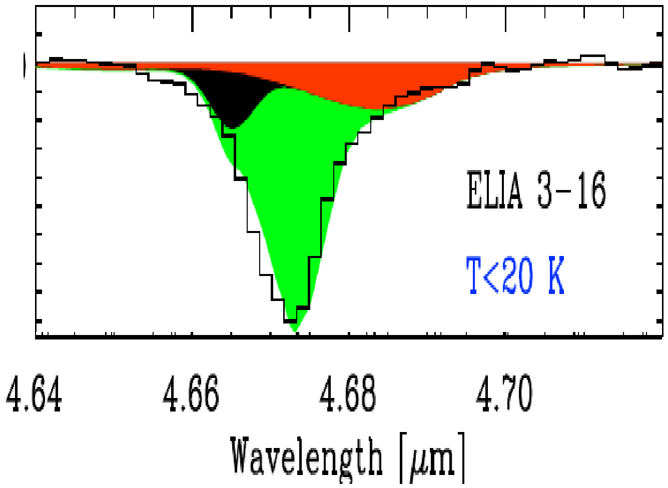
2. H_2O-rich Ices: ~~H_2O:CO~~



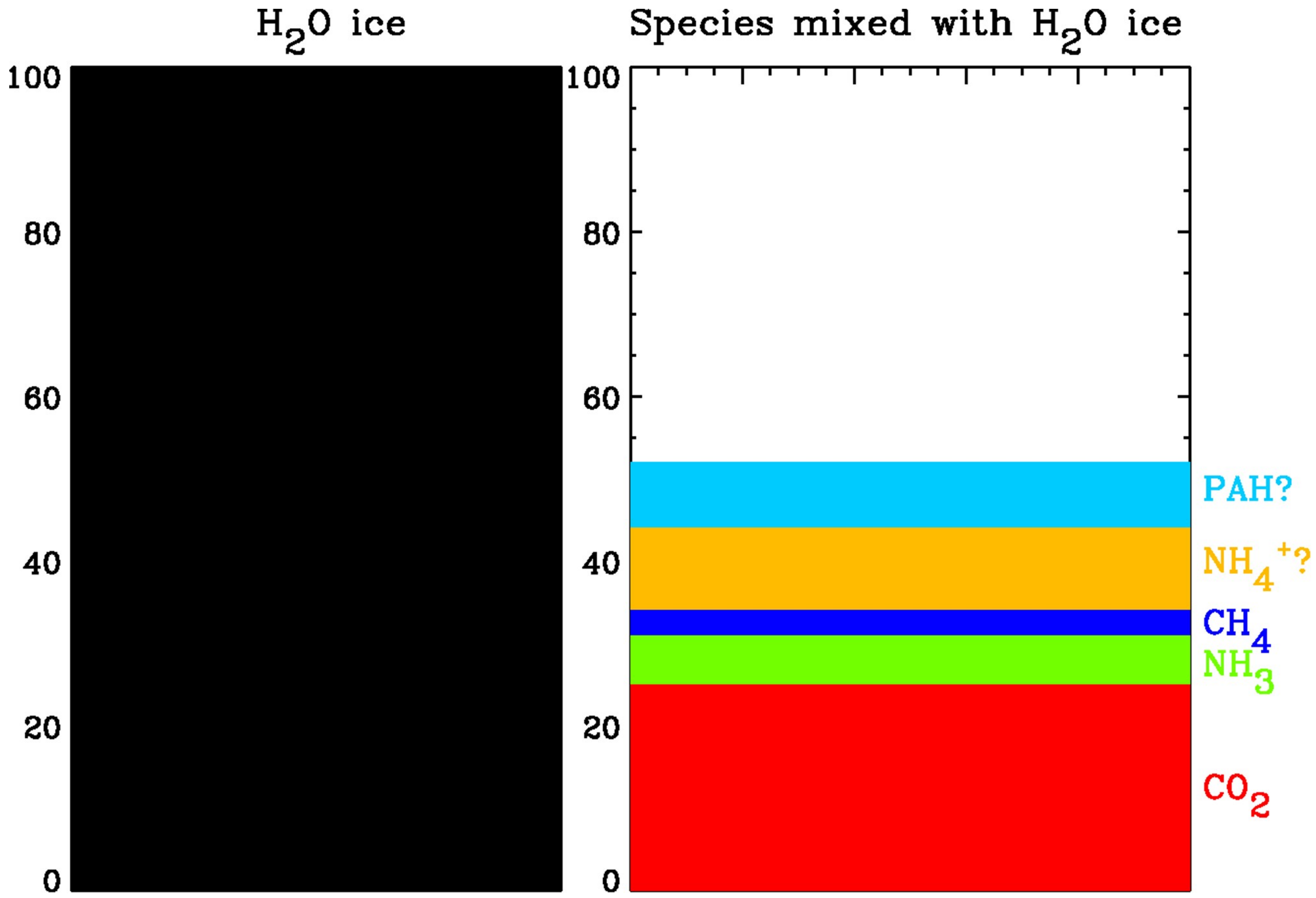
Boogert, Gerakines, & Whittet, 2015

H_2O and CO_2 have same formation threshold: mixed CO+OH → CO_2

H_2O not mixed with CO and CH_3OH (<1%)



2. H_2O-rich Ices: "Dirty Ice"



H_2O ice "dirty": mixed with >35% other species

2. H_2O-rich Ices: Homogeneity

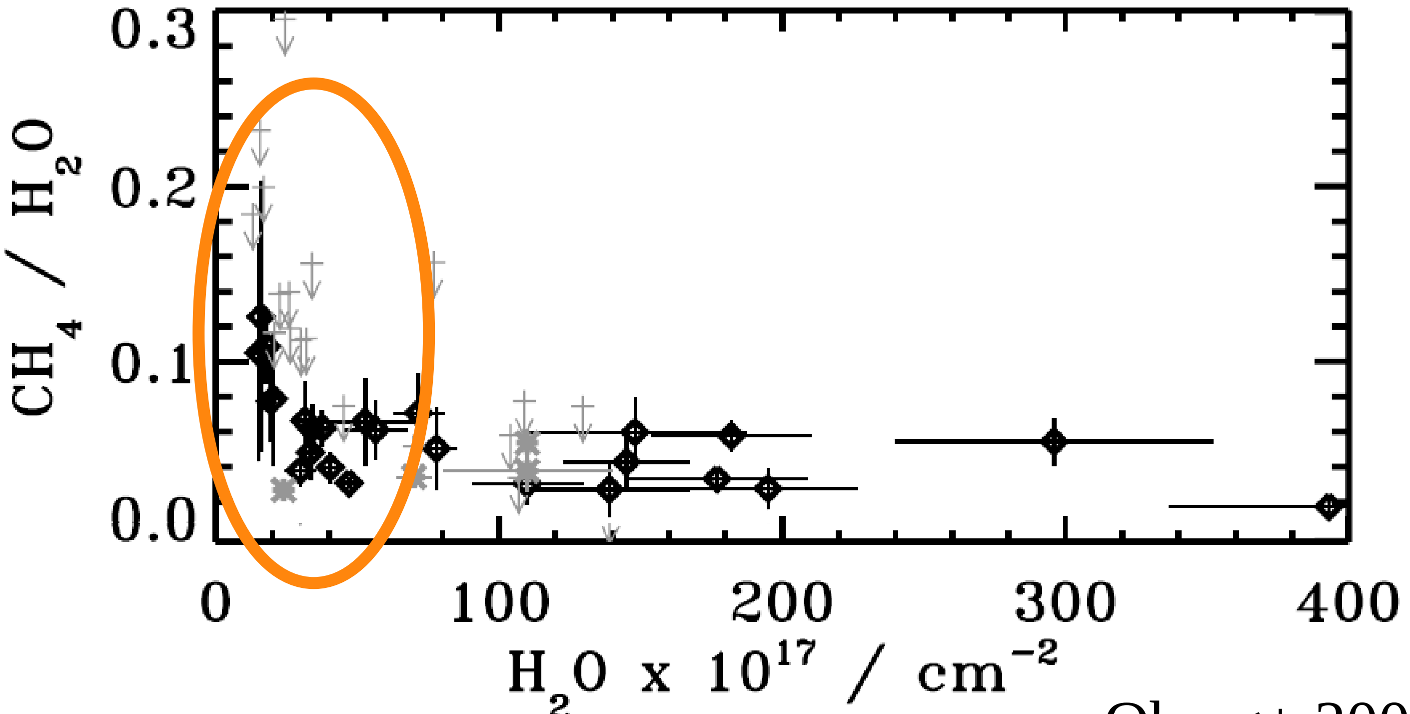
The H_2O-rich ice is probably not homogeneously mixed due to:

- gradient C/CO ratio at cloud edge
- mixing between layers
- ...

2. H_2O-rich Ices: $H_2O:CH_4$

CH_4 forms together with H_2O:

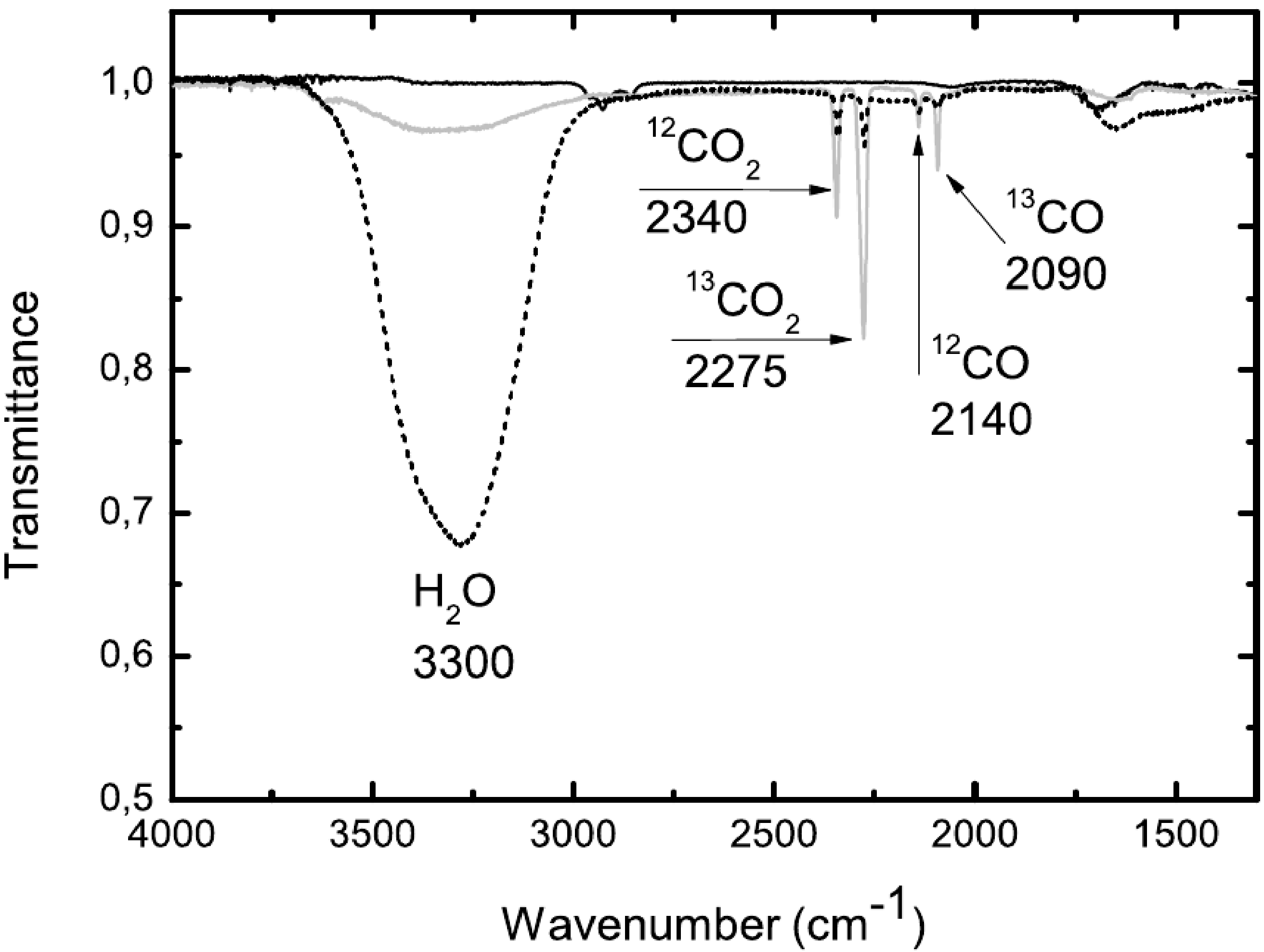
- CH_4 absorption profile
- CH_4/H_2O enhanced at cloud edge due to incomplete CO formation?
  - Could be source of C-chain COMs



Oberg+ 2008

2. H_2O-rich Ices: Carbon Dust

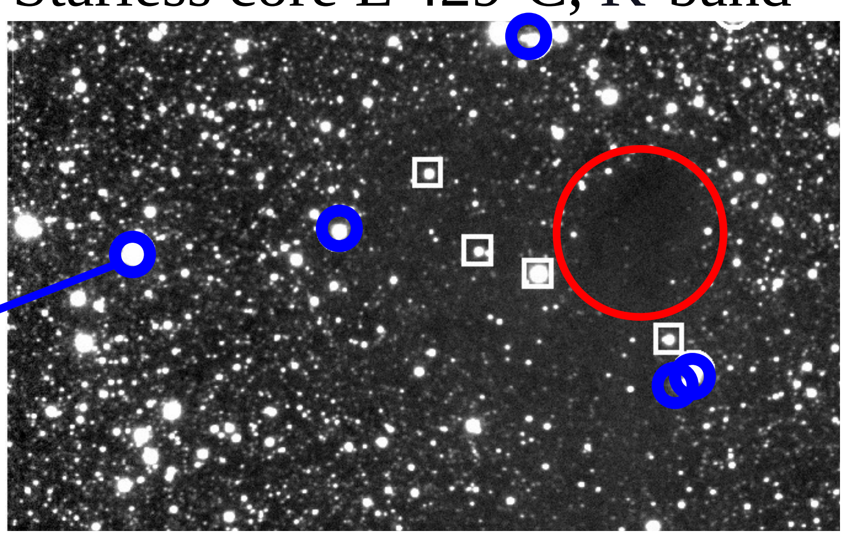
H_2O ice on top of or mixed with carbonaceous dust leads to CO_2 by energetic particle radiation.



- Proposed as explanation carbon deficiency solar system objects (Sabri+ 2015)
- Observed CO_2 reproduced on time scale of 10^7 yr (Ioppolo+ 2013), much slower than grain surface route.
- By-products?

3. CO-rich Ices

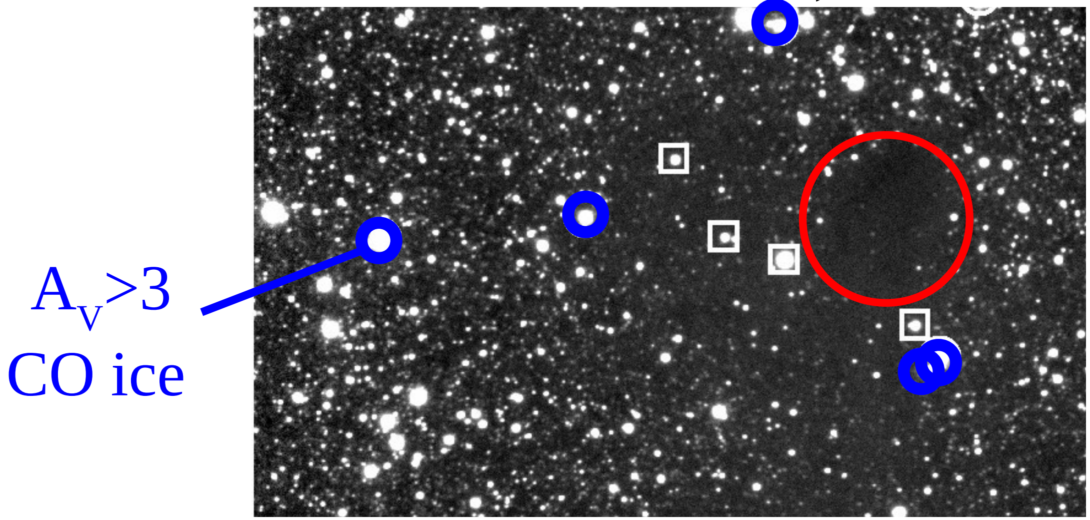
Starless core L 429-C, K-band

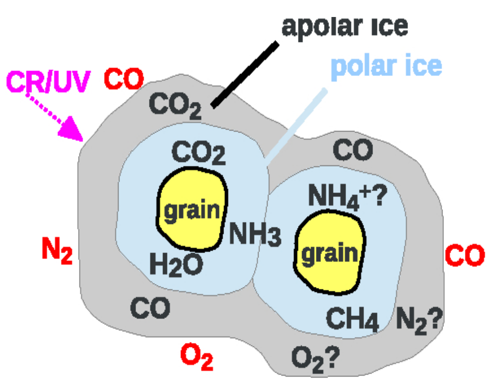


A_V>3
CO ice

3. CO-rich Ices

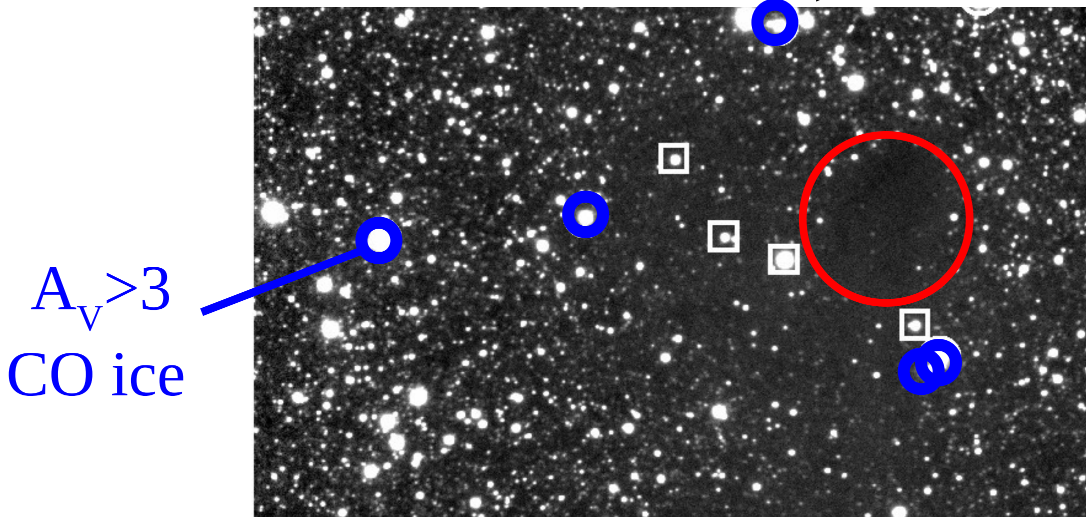
Starless core L 429-C, K-band

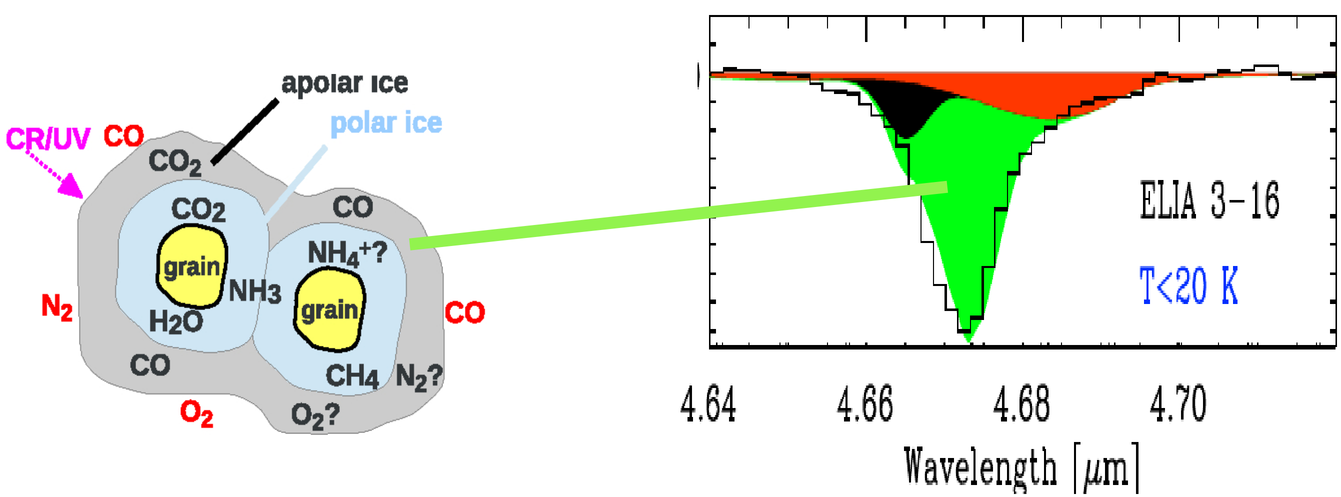




3. CO-rich Ices: Pure CO

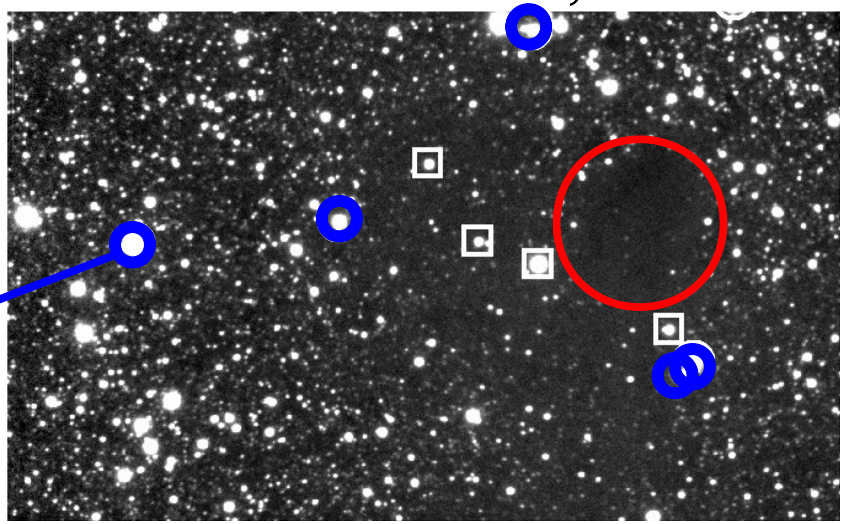
Starless core L 429-C, K-band



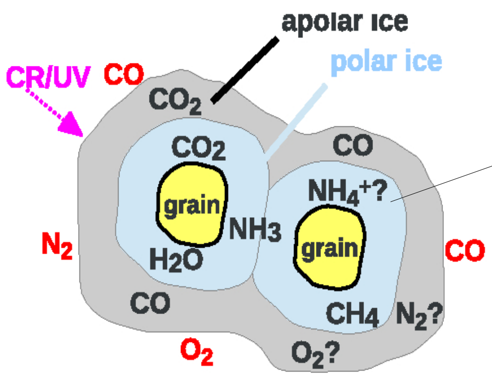


3. CO-rich Ices: “Polar” Wing

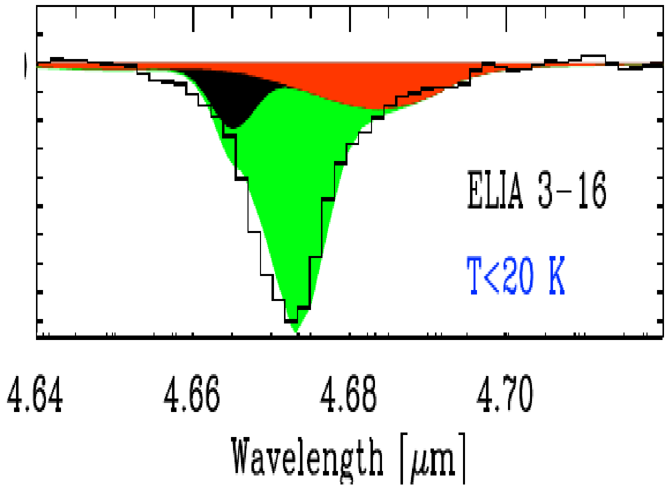
Starless core L 429-C, K-band



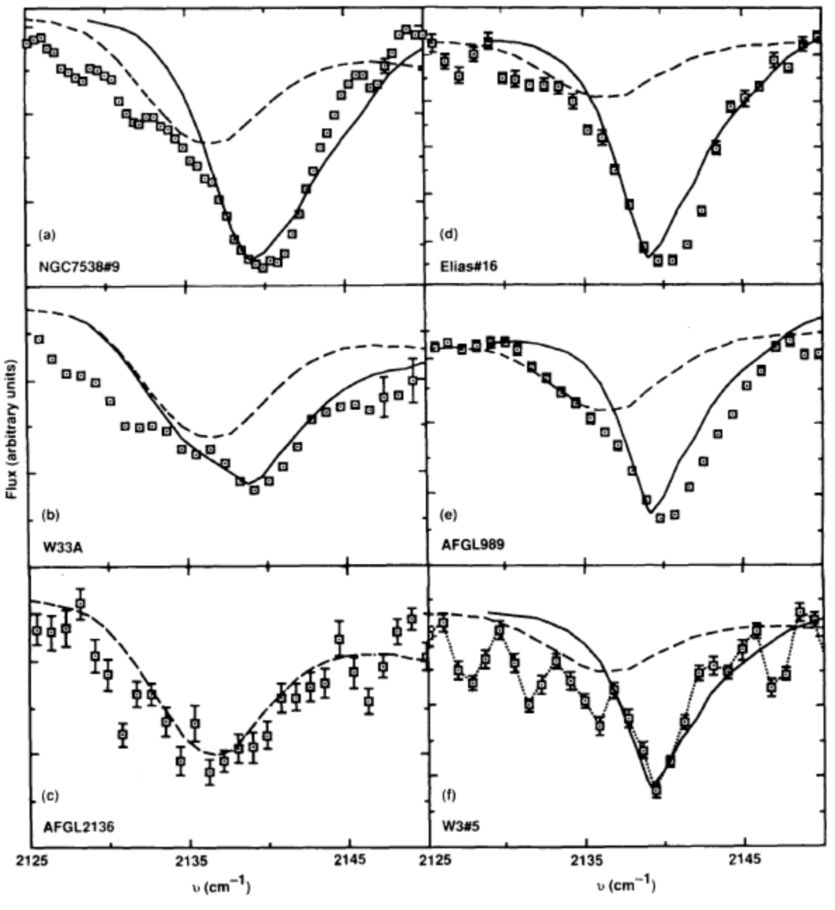
A_V>3
CO ice



Migration of CO into H_2O-rich ice is feasible (Collings+ 2003, Lauck+ 2015)



Intermezzo: Ice Band Profiles

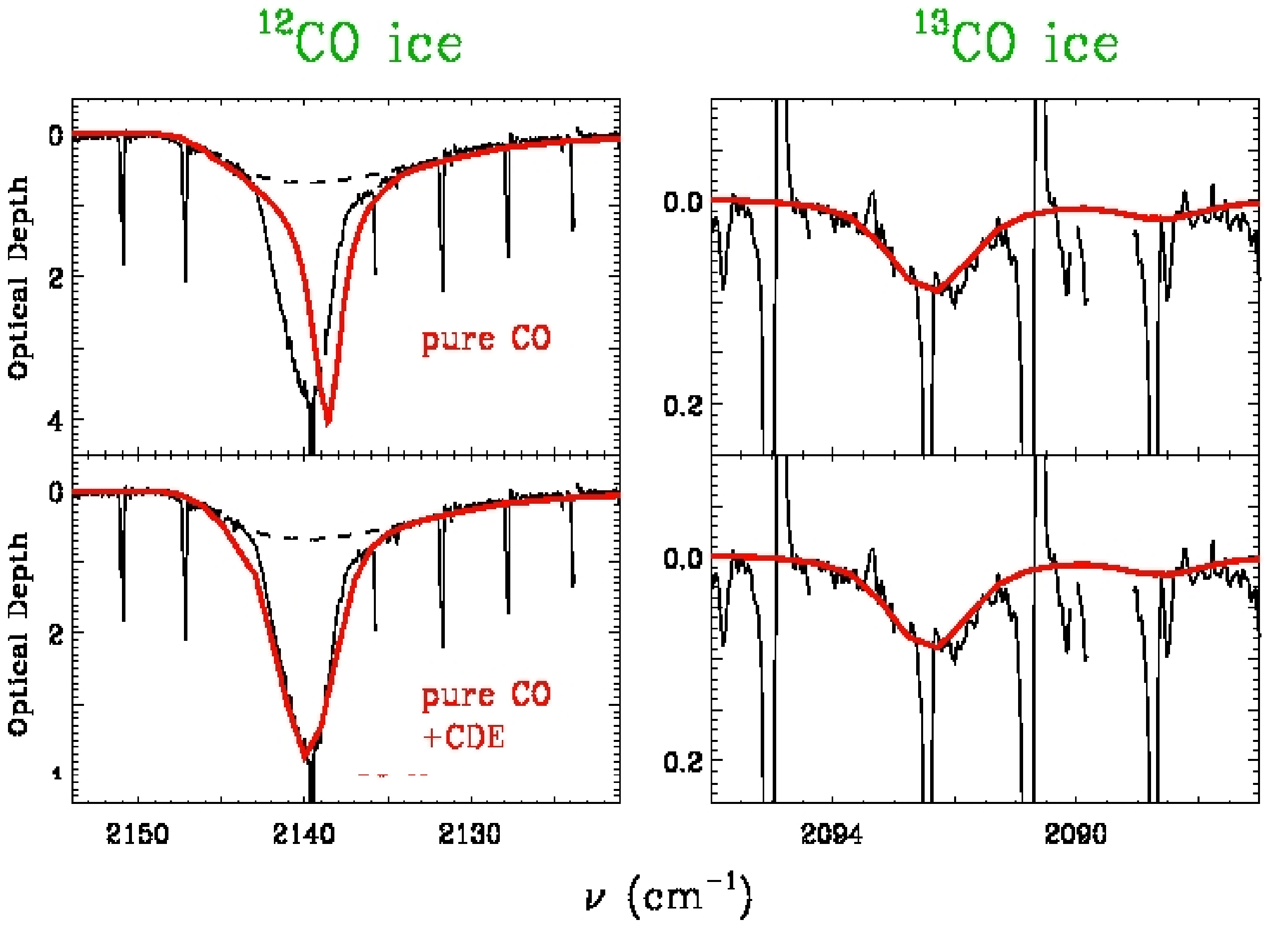


Tielens+ 1991

CO present in apolar and polar ices:

- Apolar: nearly pure CO.
- Polar: CO mixed with H_2O and/or CH_3OH
- Requires grain shape corrections for analysis.

Intermezzo: Ice Band Profiles

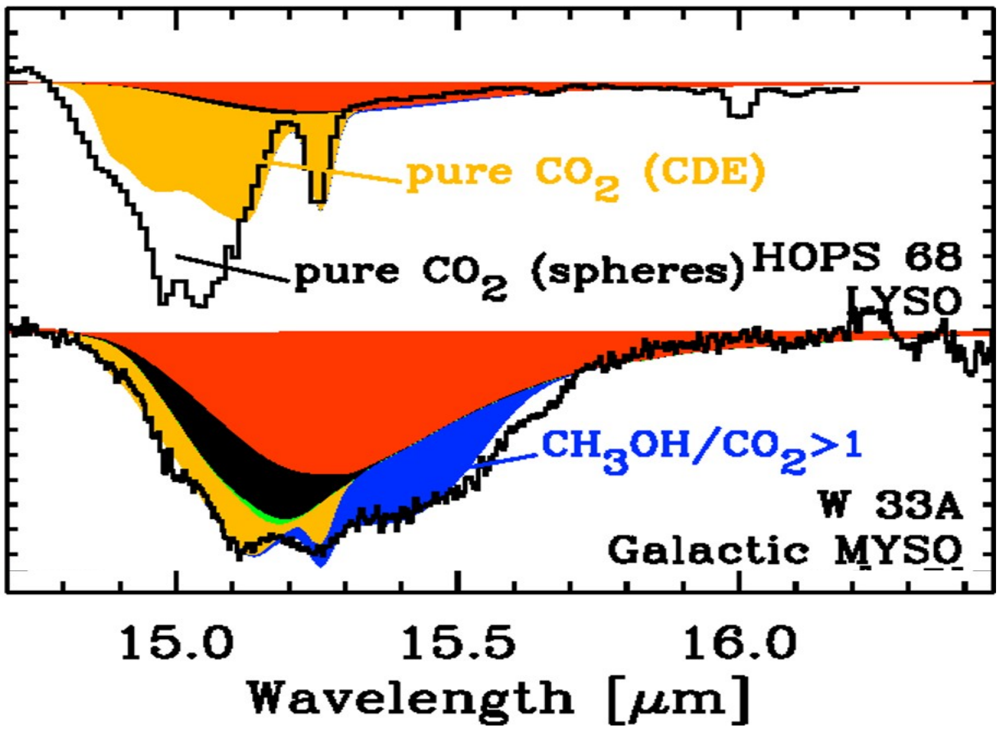


Better data:

- grain shape corrections crucial
- apolar CO is ~90% pure.

Boogert, Blake, & Tielens (2004)

Intermezzo: Ice Band Profiles

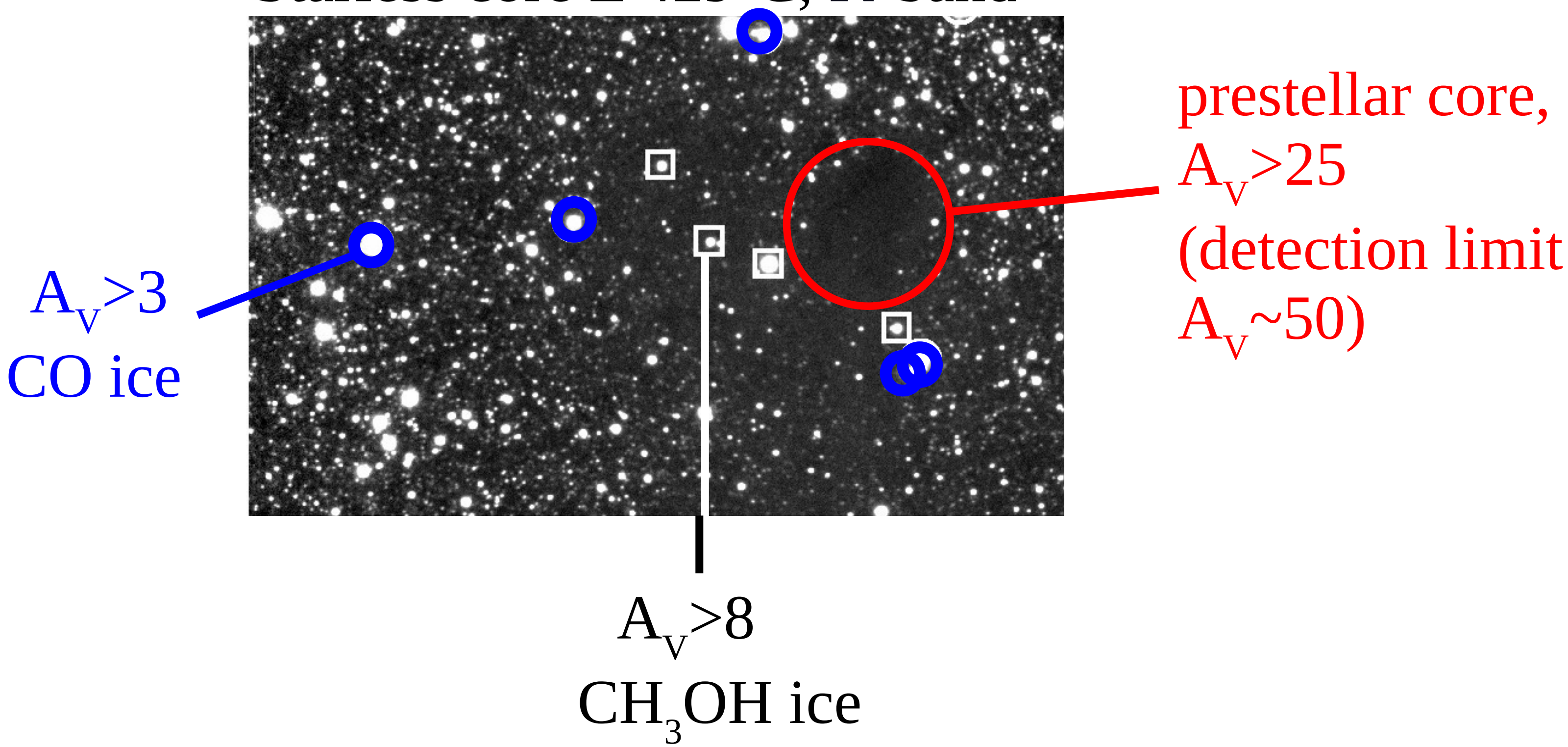


Application of grain shape corrections:

- Most ice bands fitted by "CDE" (irregular) grain shapes.
- One low mass YSO has spheres component (Poteet+ 2013):
  - likely due to eruption, sublimating ices and rapid recondensation at high temperature, in crystalline phase.

3. CO-rich Ices: CH_3OH

Starless core L 429-C, K-band



3. CO-rich Ices: CH_3OH

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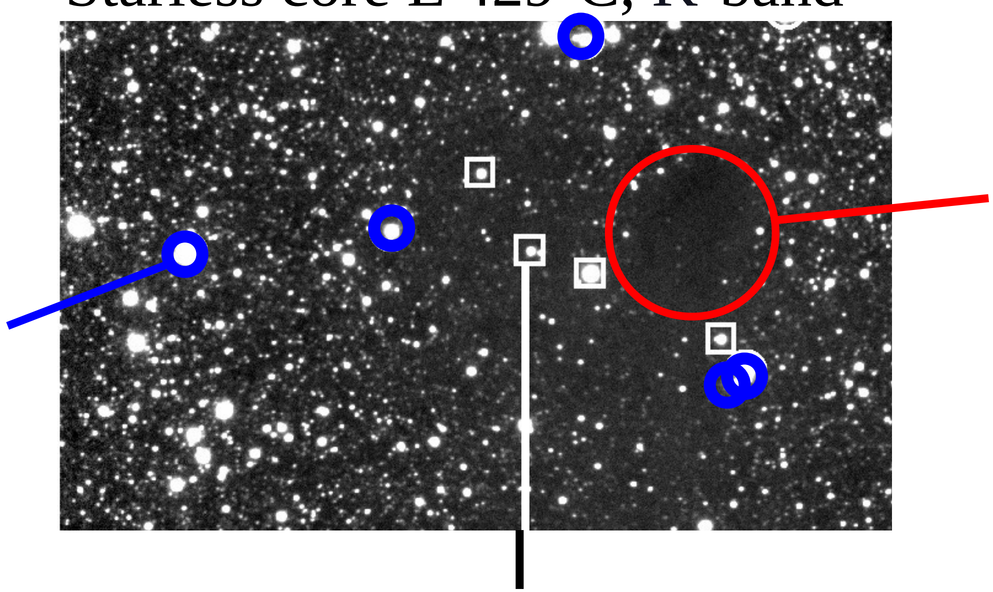
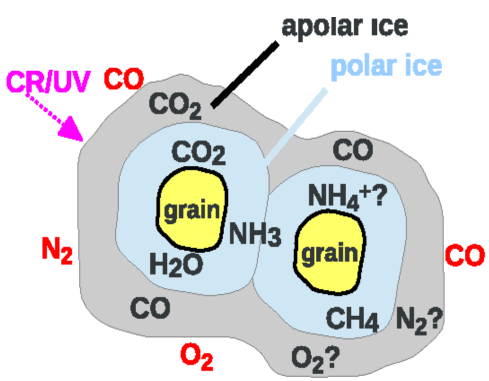
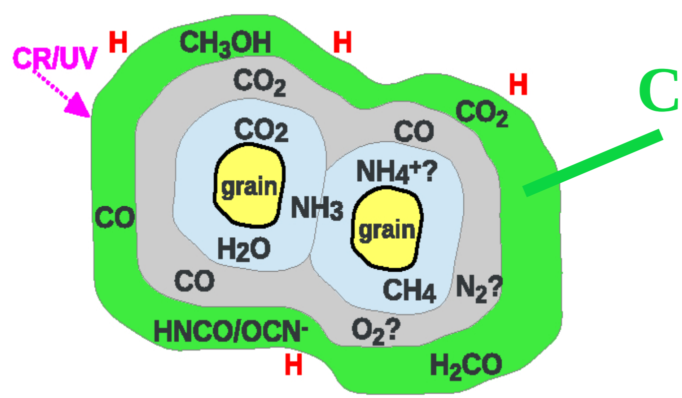


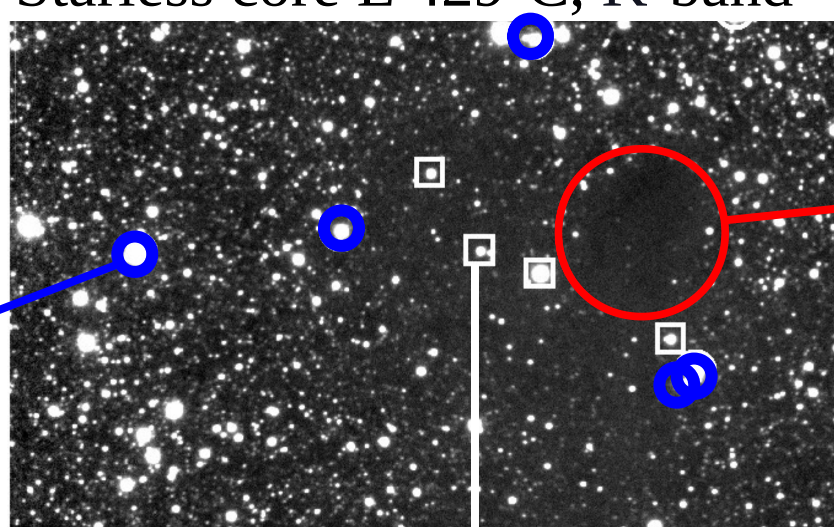




COM formation!

3. Maps Needed!

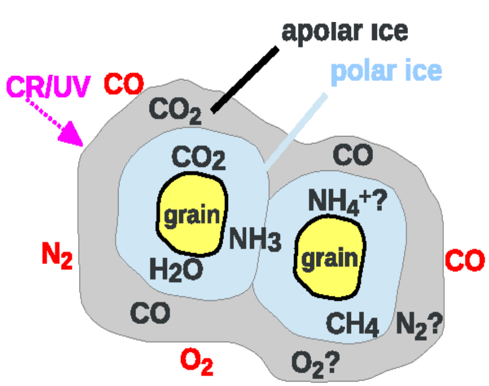
Starless core L 429-C, K-band

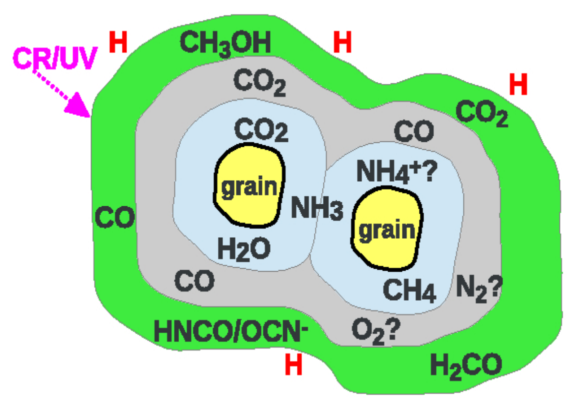


A_V>3
CO ice

prestellar core,
A_V>25
(detection limit
A_V~50)

A_V>8
CH_3OH ice



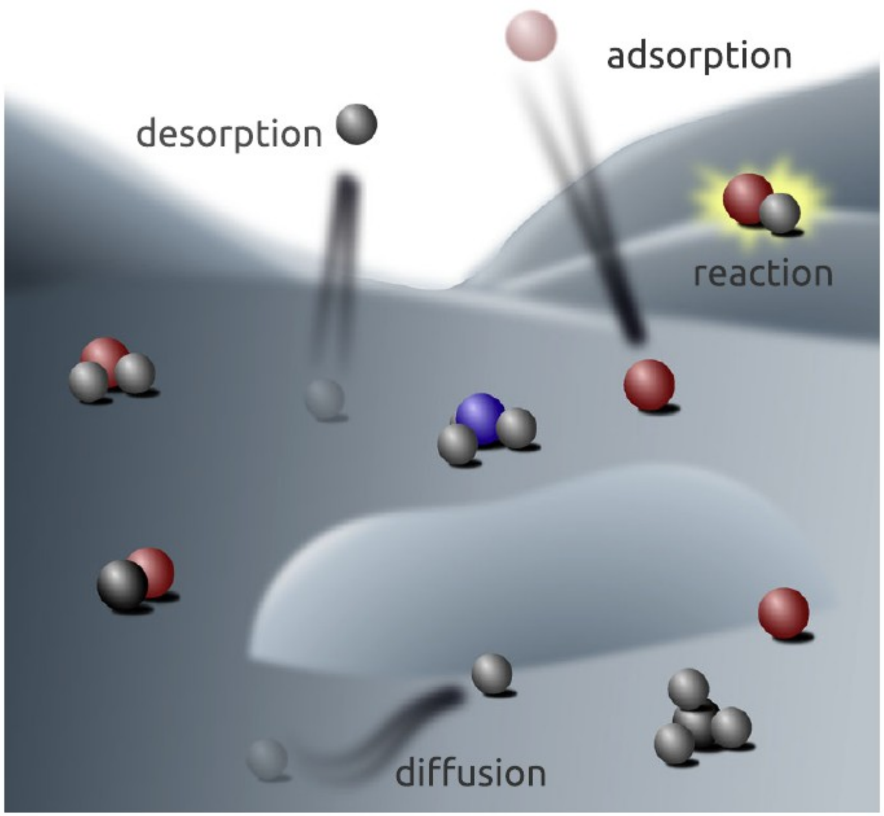


Ice mapping is important!

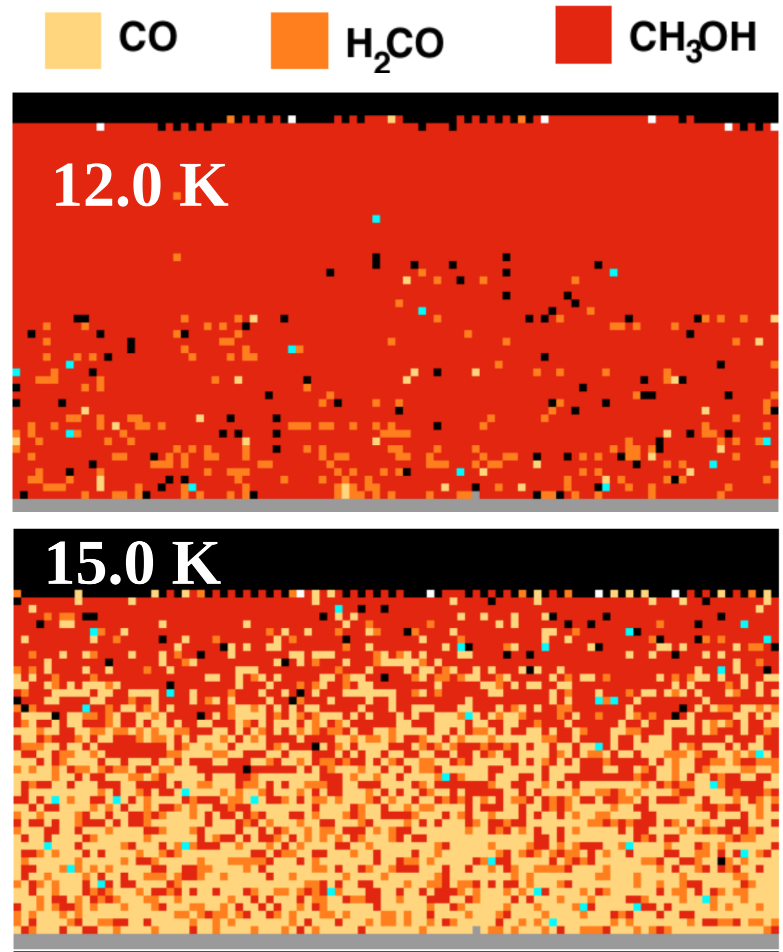
For recent results on CO and CH_3OH ice observations and JWST preparations see talk by Laurie Chu and poster by Klaus Hodapp

3. CO-rich Ices: CH_3OH

Molecular level (Monte Carlo) simulations of H reacting with frozen CO depend on ice structure, energy barriers, rates, binding energies, etc.

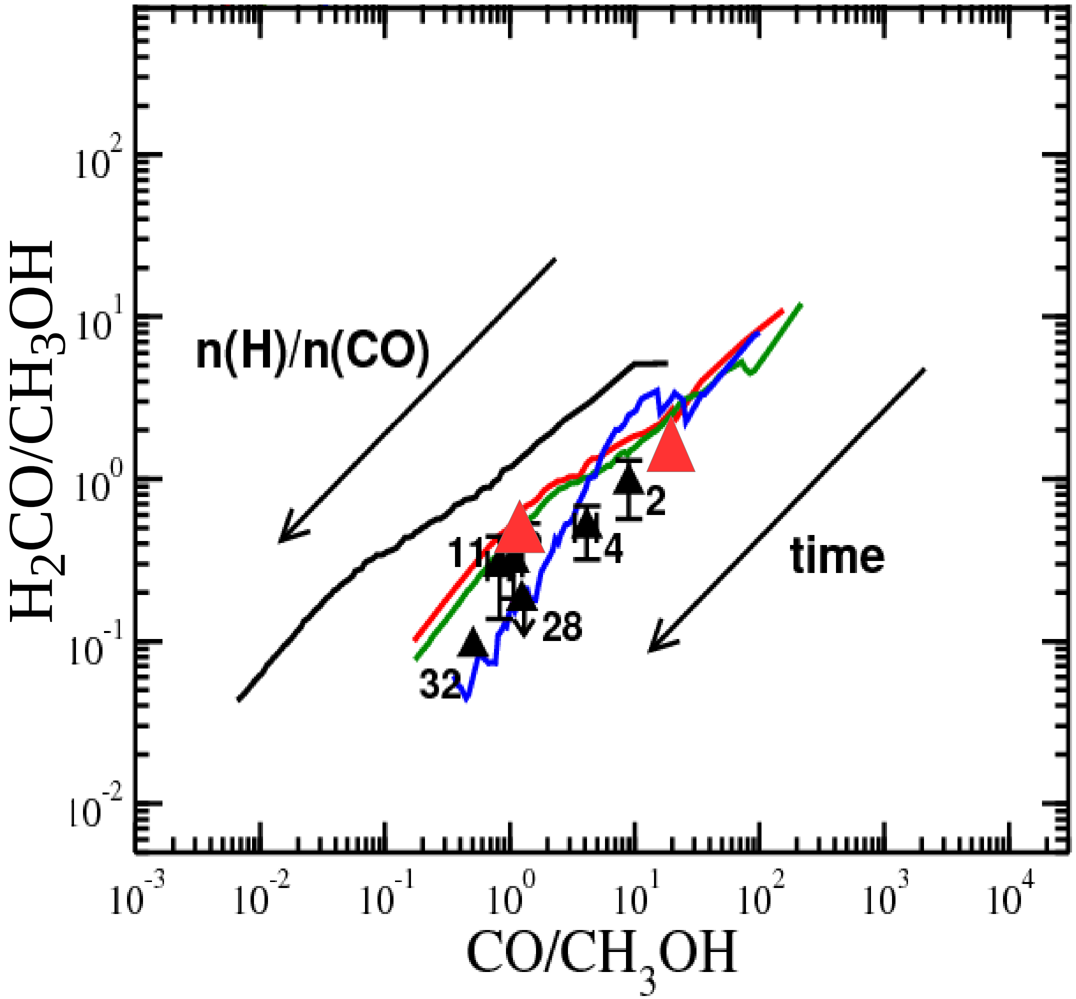


Cuppen+ 2017



Cuppen+ 2009

3. CO-rich Ices: CH_3OH



Cuppen+ 2009

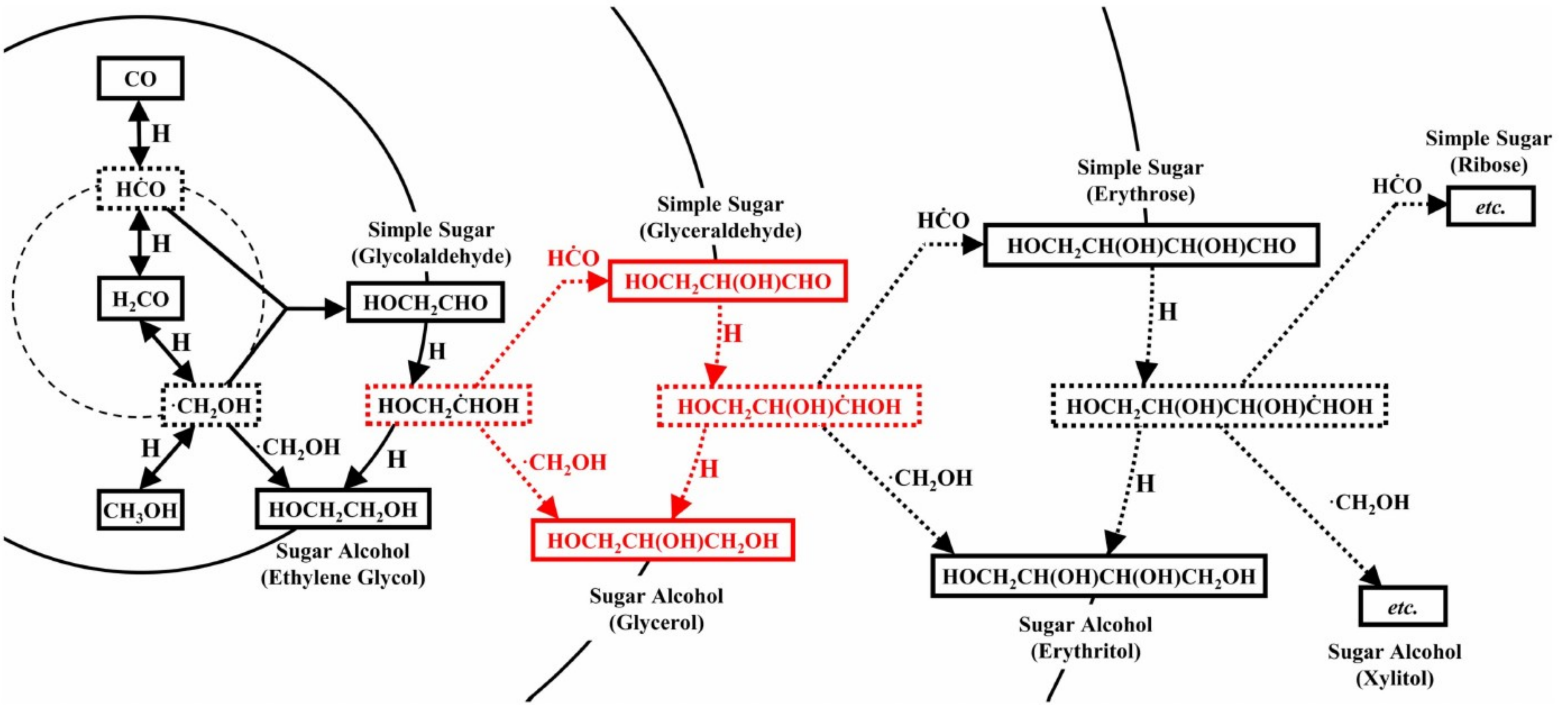
- YSOs: increasing CH_3OH ice abundances could be time effect. But also:
  - dust temperature (freeze out, H residence time)
  - density (freeze out, gas H/H_2)

▲Background stars: abundance varies by 1-12%:

- temperature, density or time effect?

3. CO-rich Ices: COMs

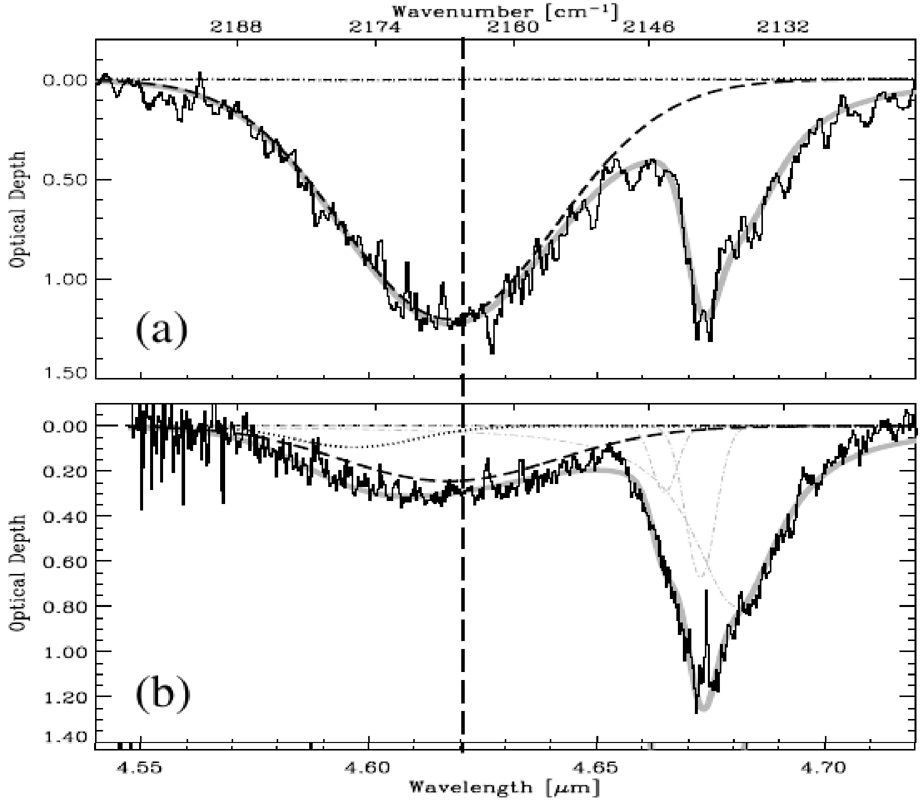
Laboratory experiments of cold, grain surface formation of COMs ongoing (Linnartz+ 2015, Fedoseev+ 2017). Microscopic Monte Carlo modeling too (Cuppen et al.).



4. Identification Challenges

Several ice absorption bands hard to identify and some still uncertain

4.62 μm "XCN" band



Van Broekhuizen+ 2005

4. Salts

“The OCN^- Wars of the 1990s” (Reggie Hudson)

Identification of the 4.62 μm band with OCN^- more or less settled.
Easily produced by low-T acid-base chemistry (Raunier+ 2004):

$$\mathbf{NH_3 + HNCO \rightarrow NH_4^+ + OCN^-}$$

4. Salts

And how about NH_4^+?

√ 6.85 µm band seen in ISM

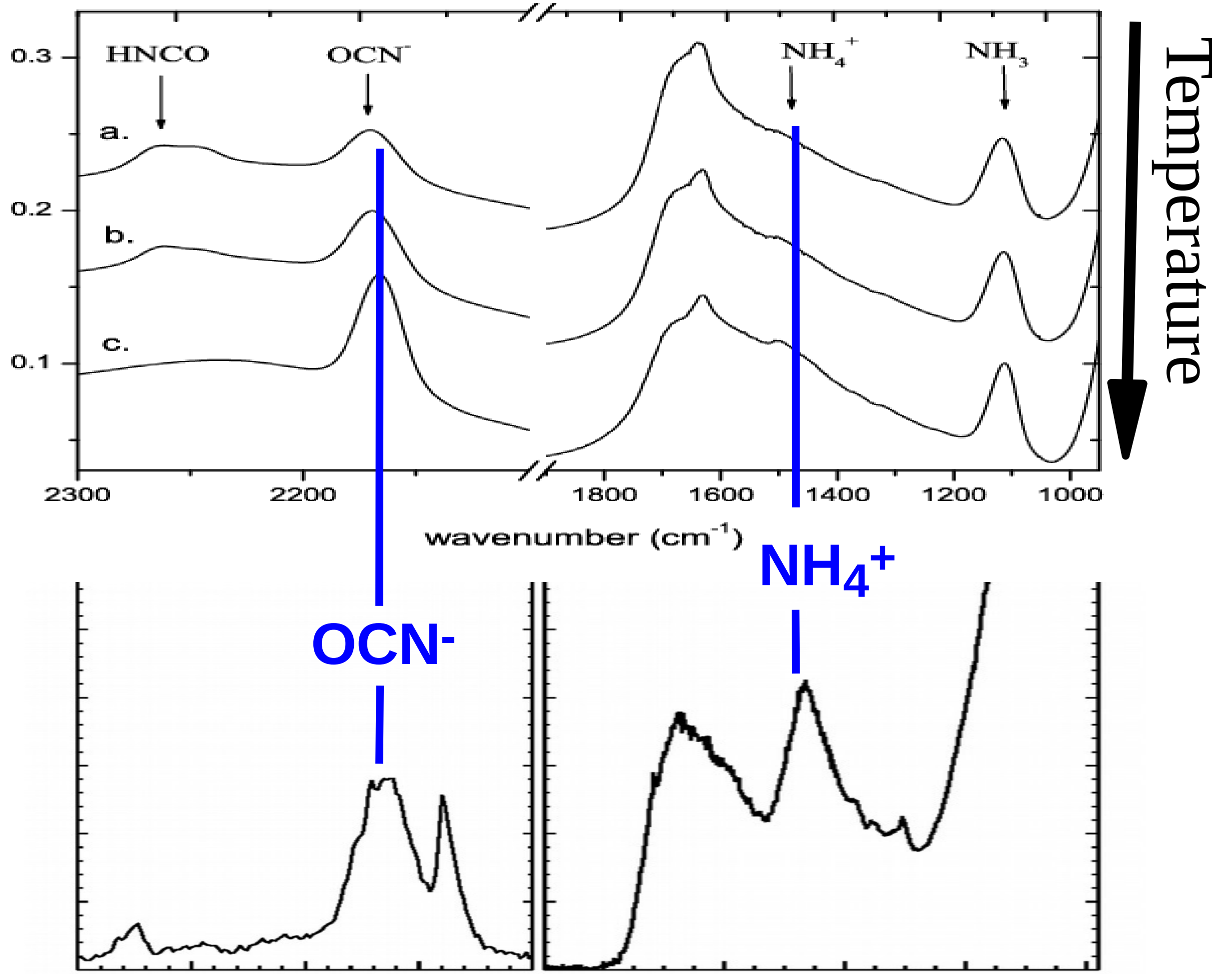
√ Band shifts at higher T.

χ Band too broad and shallow in H_2O mixtures (Galvez+ 2010).

χ "observed" OCN^-/NH_4^+~0.1 Need more counter-ions.

NH_3+HNCO → NH_4^++OCN^-

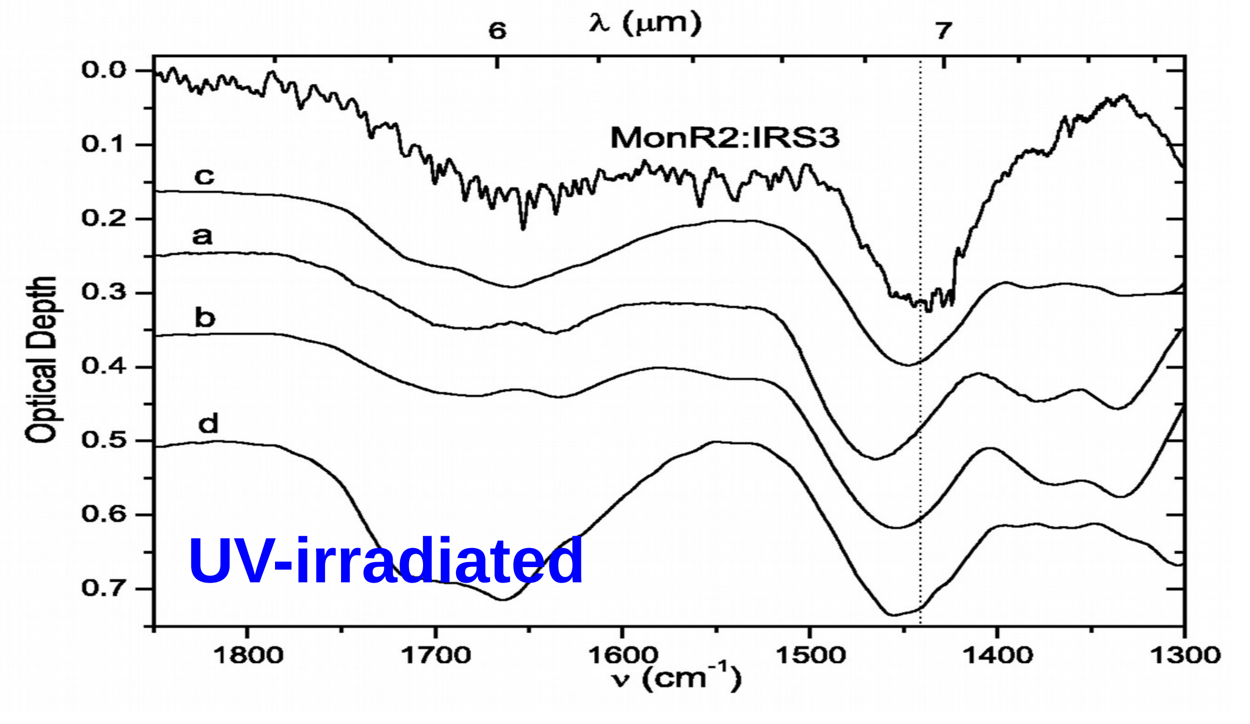
Mixed with H_2O ice



4. More Salts?

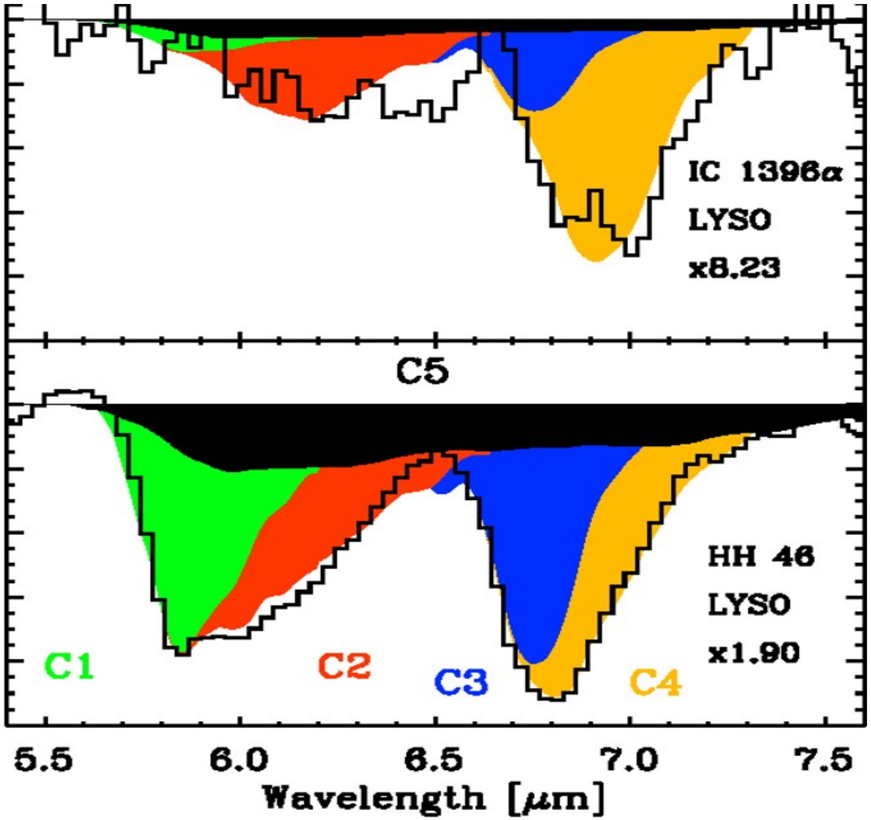
Where are the counter ions?

UV irradiation
H_2O:CO_2:NH_3:O_2 produces NH_4^+ and many more ions, e.g., NO_2^- NO_3^- and HCO_3^- (Schutte & Khanna 2003).



4. Salts: Observ. Constraints

IC 1396; Reach+ 2009



- 6.85 μm band has distinct temperature dependence
- Carrier sticks around longer than H_2O ice, but not as long as silicates: a salt (Boogert+ 2008)?

4. Salts: Comet 67P

Altwegg et al., ARAA 57 (2019), on in situ measurements with Rosetta/Rosina in comet 67P/Churyumov-Gerasimenko

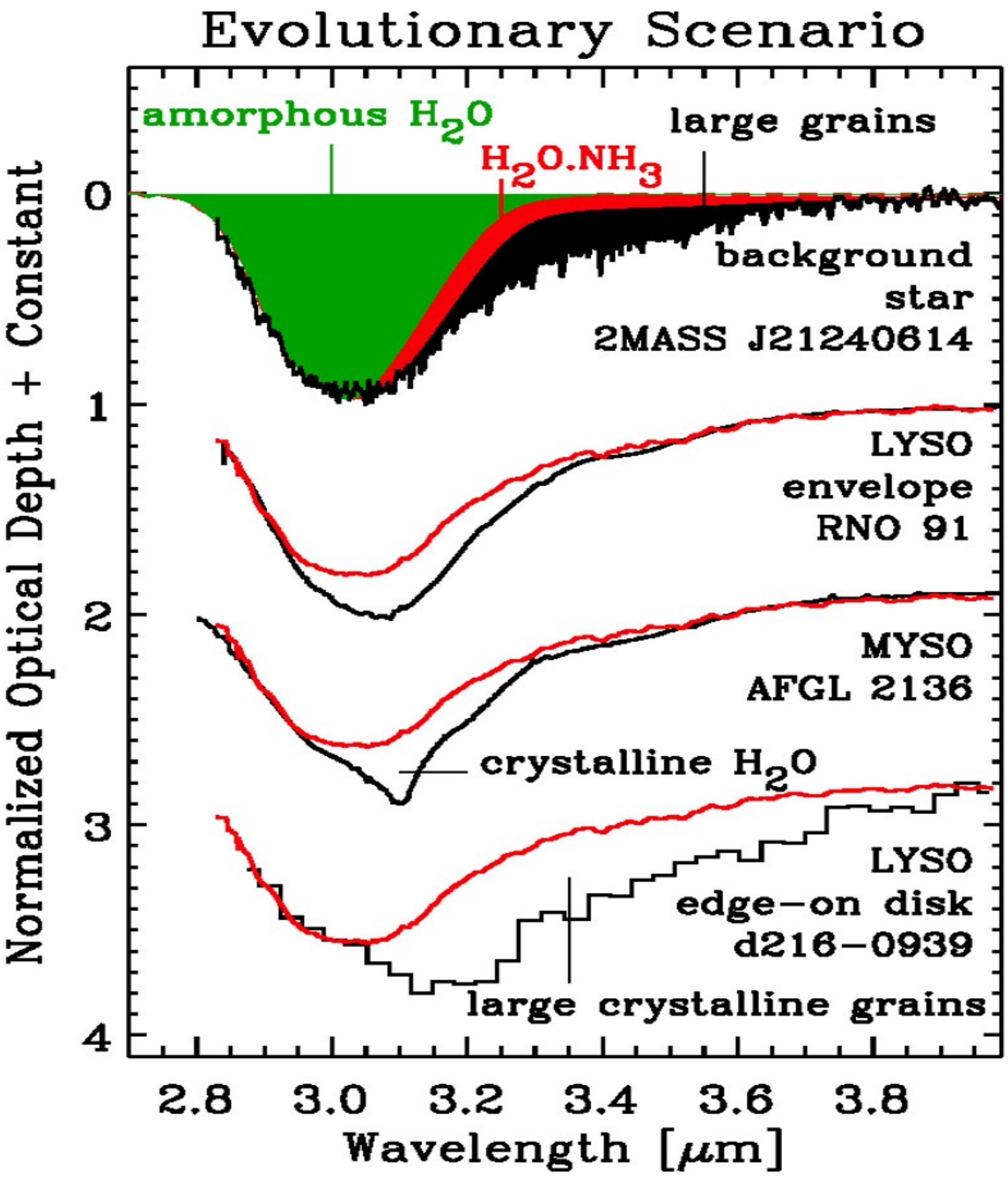
"...NH_3 seems to be, at least partly, in a more refractory phase, probably as ammonium salt (Altwegg et al., 2019) than as pure NH_3 in H_2O..."

https://ui.adsabs.harvard.edu/abs/2019arXiv190804046A/abstract

K. Altwegg at IAUS 350, Cambridge, UK (April 2019):

Rosina detector was hit, but not permanently damaged, by a particle, likely containing NH_4^+ salt.

5. Heated Ices



H_2O ice crystallization "commonly" observed (T~70-90 K).

CO sublimation (T~20 K) and CO_2 ice segregation (T~45 K) often observed.

5. Heated Ices: Chemistry

- Diffusion radicals creates new, more complex species (Herbst & Van Dishoeck 2009)

- Purely thermal reactions among species formed by grain surface chemistry (Theule+ 2013). Comprehensive laboratory experiments:

Acid-base reactions

$H_2O + HNCO \rightarrow H_3O^+OCN^-$

$NH_3 + HCOOH \rightarrow NH_4^+HCOO^-$

$NH_3 + HNCO \rightarrow NH_4^+OCN^-$

$NH_3 + HCN \rightarrow NH_4^+CN^-$

Nucleophilic additions

$CO_2 + NH_3 \rightarrow NH_2COOH$

$CO_2 + CH_3NH_2 \rightarrow CH_3NHCOOH$

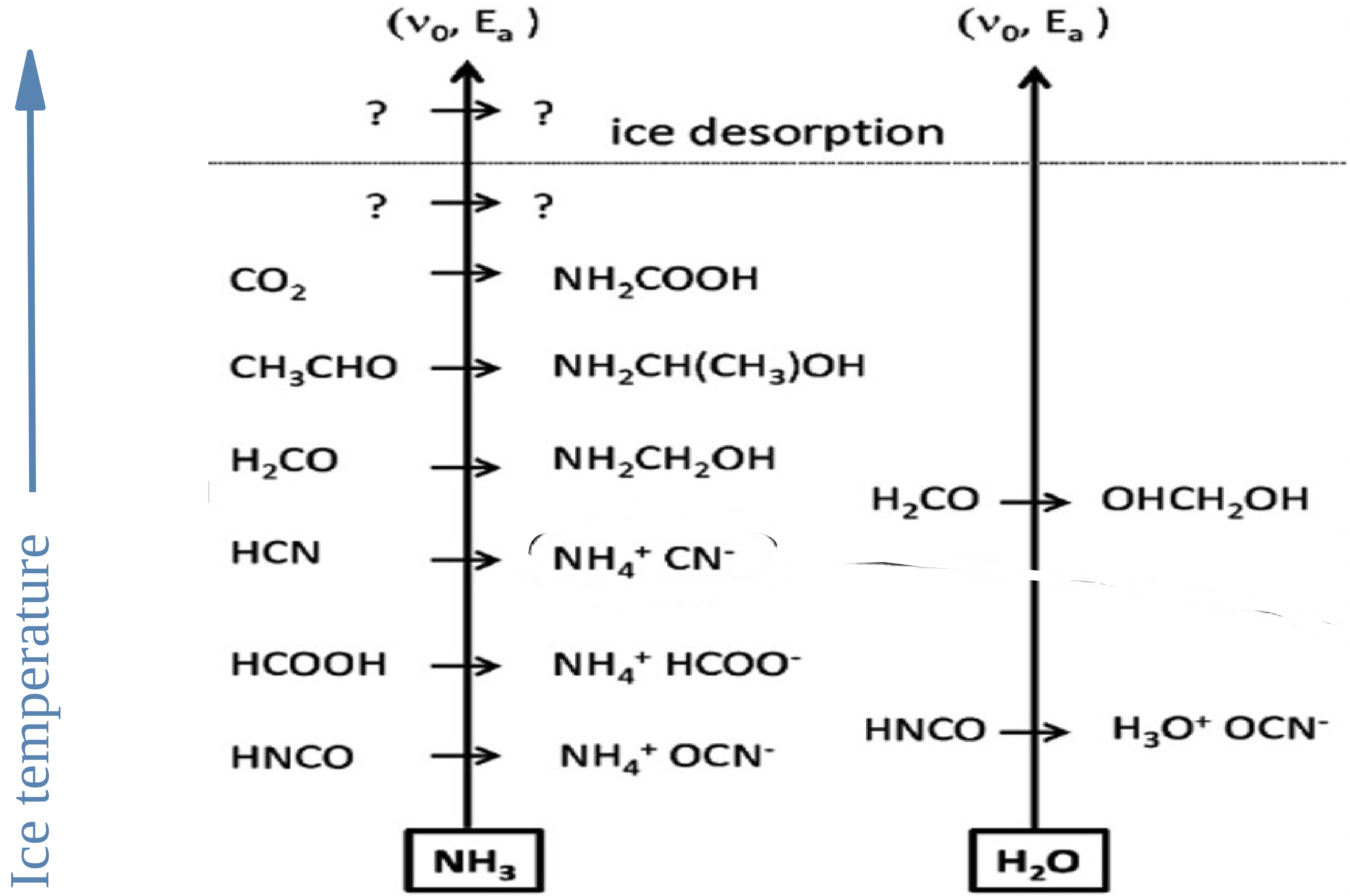
$H_2CO + H_2O \rightarrow HOCH_2OH$

$H_2CO + NH_3 \rightarrow NH_2CH_2OH$

$H_2CO + CH_3NH_2 \rightarrow CH_3NHCH_2OH$

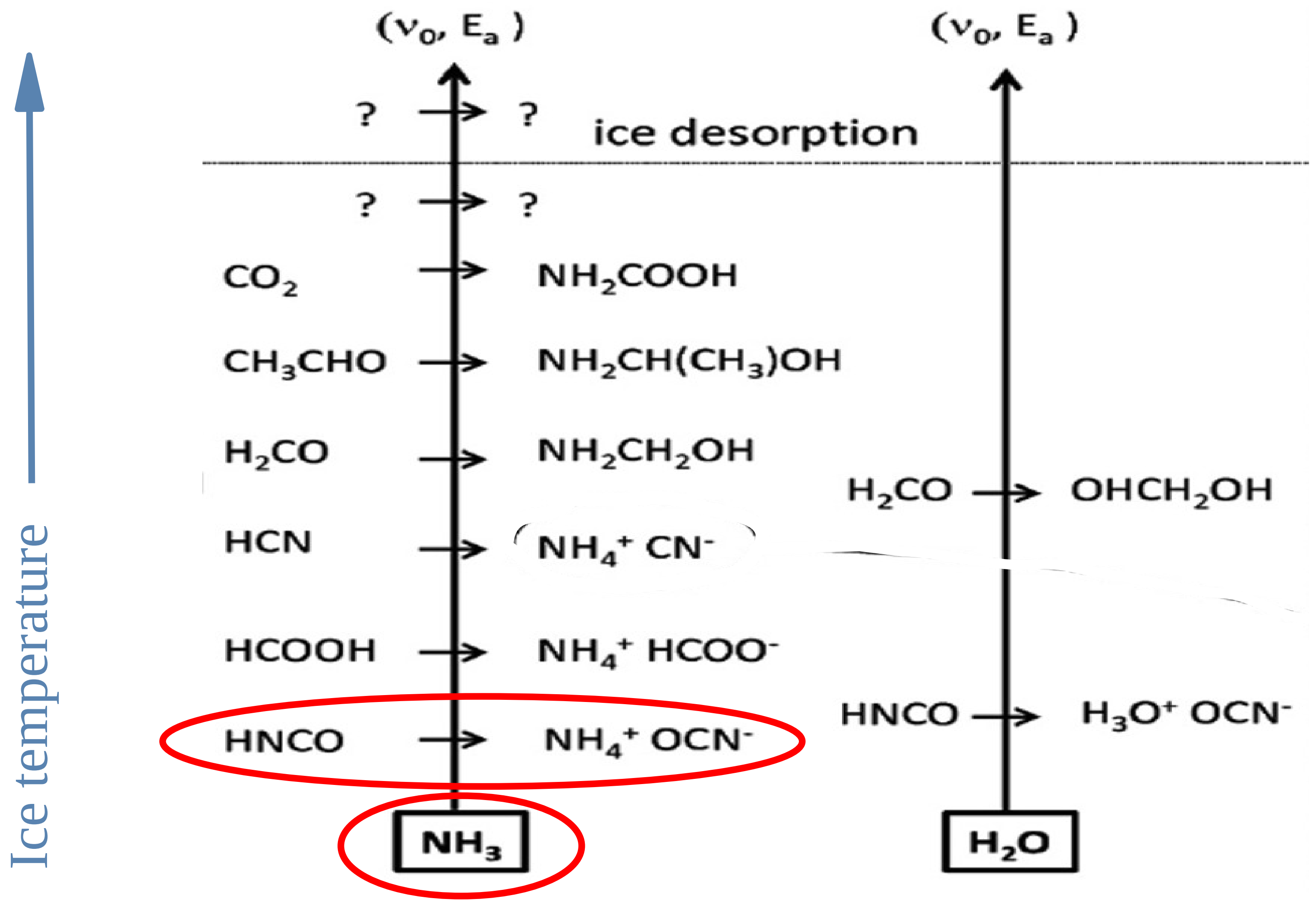
$CH_3CHO + NH_3 \rightarrow NH_2CH(CH_3)OH$

5. Heated Ices: Chemistry



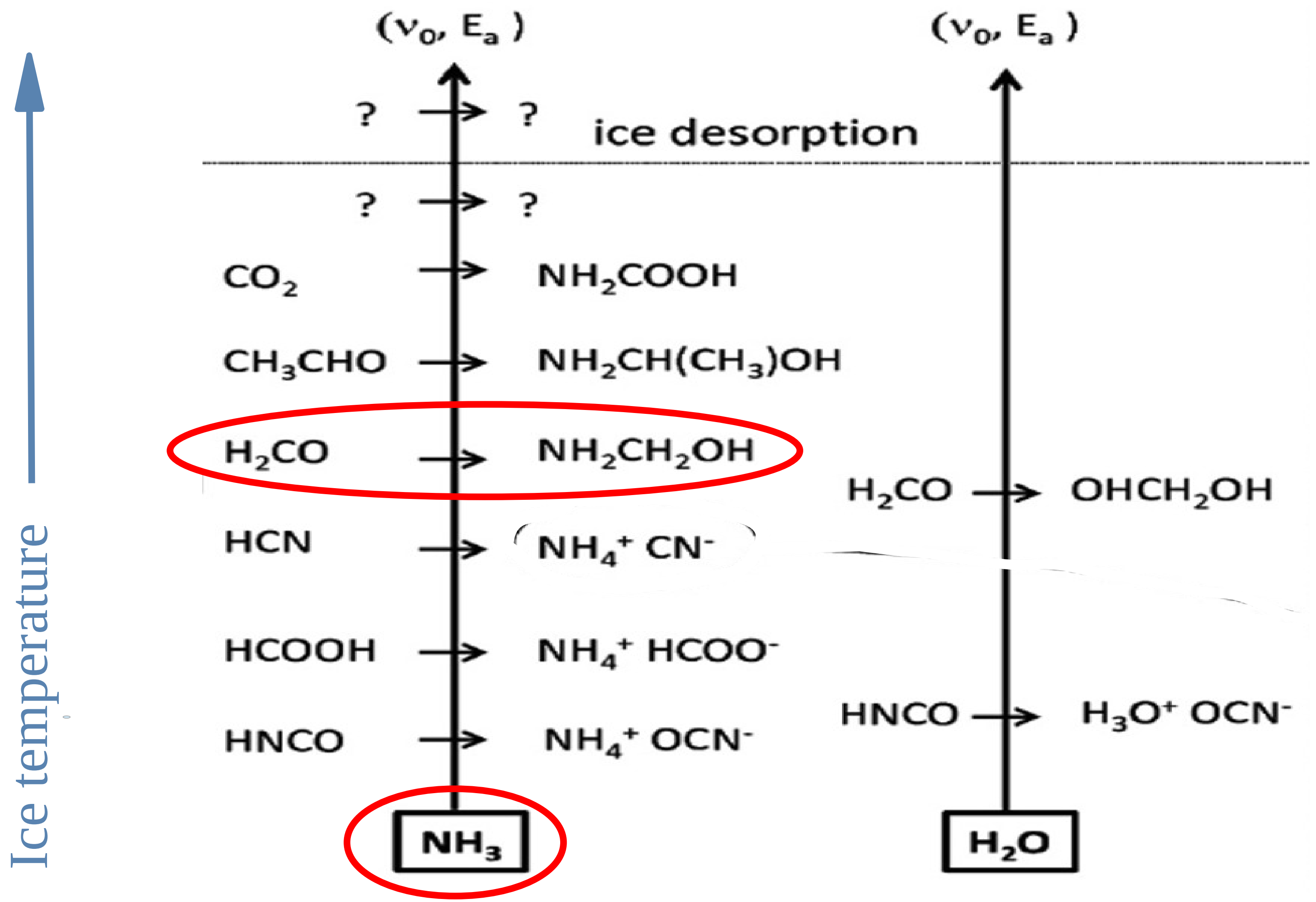
Theule+ 2013

5. Heated Ices: Chemistry



Theule+ 2013

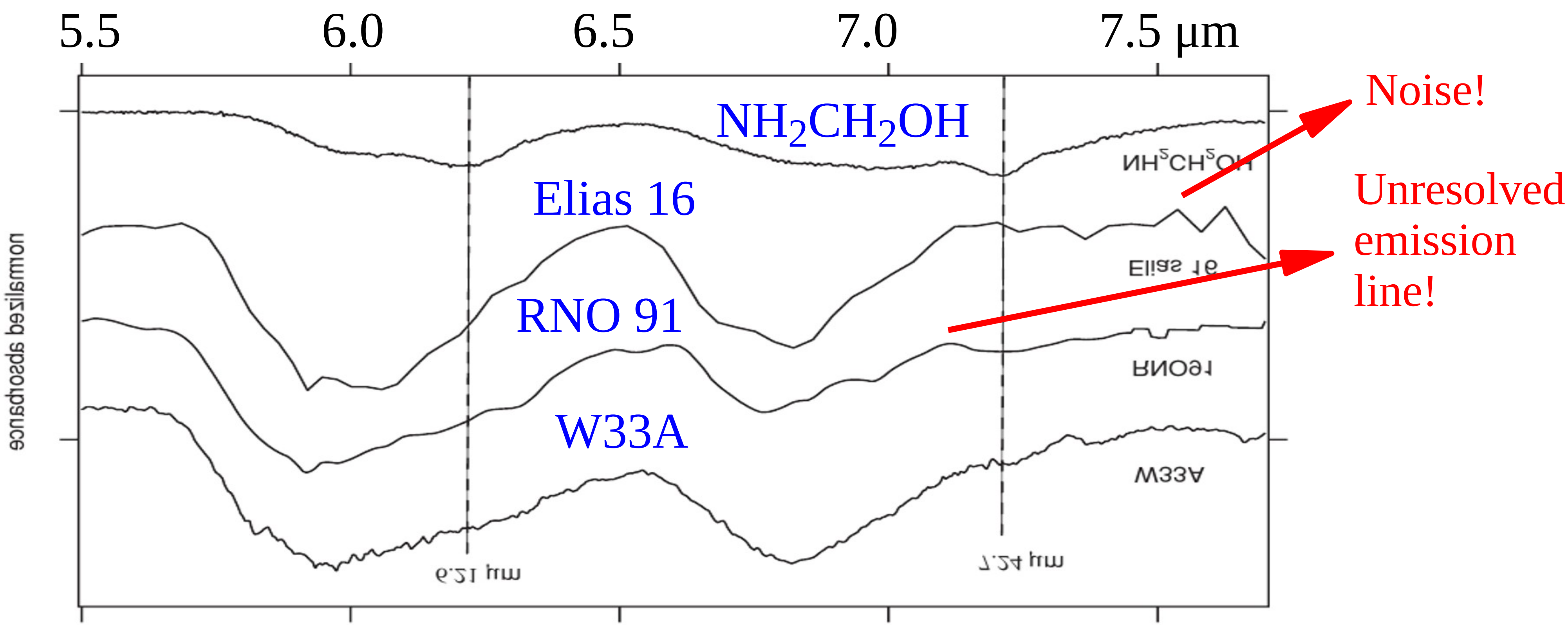
5. Heated Ices: Chemistry



Theule+ 2013

5. Heated Ices: Chemistry

Aminomethanol (NH_2CH_2OH) compared to observations (Bossa+ 2009):



For frozen COMs, running into infrared confusion limit.
But better observations will help (see also Terwisscha van Scheltinga+ 2018)

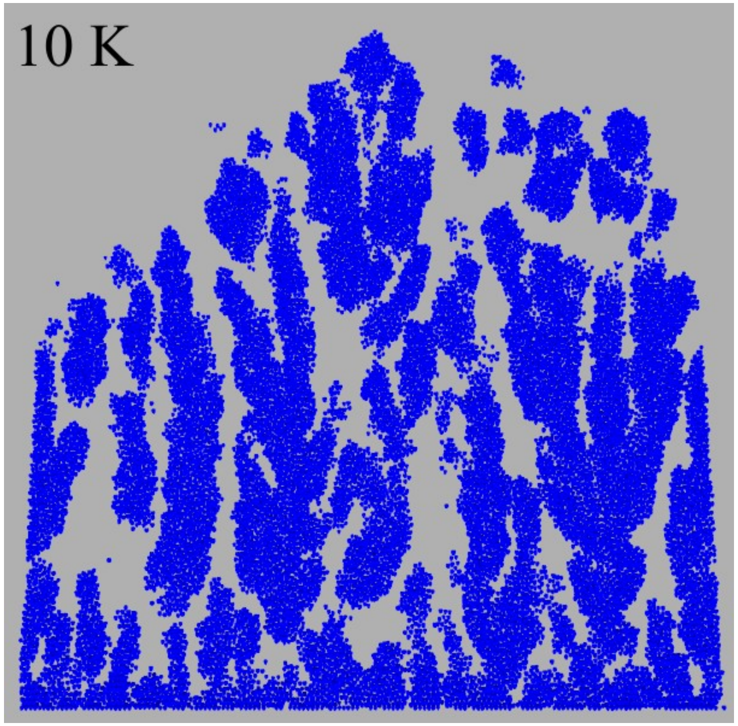
5: Heated Ices

Complication wit these reactions is location of reaction partners:

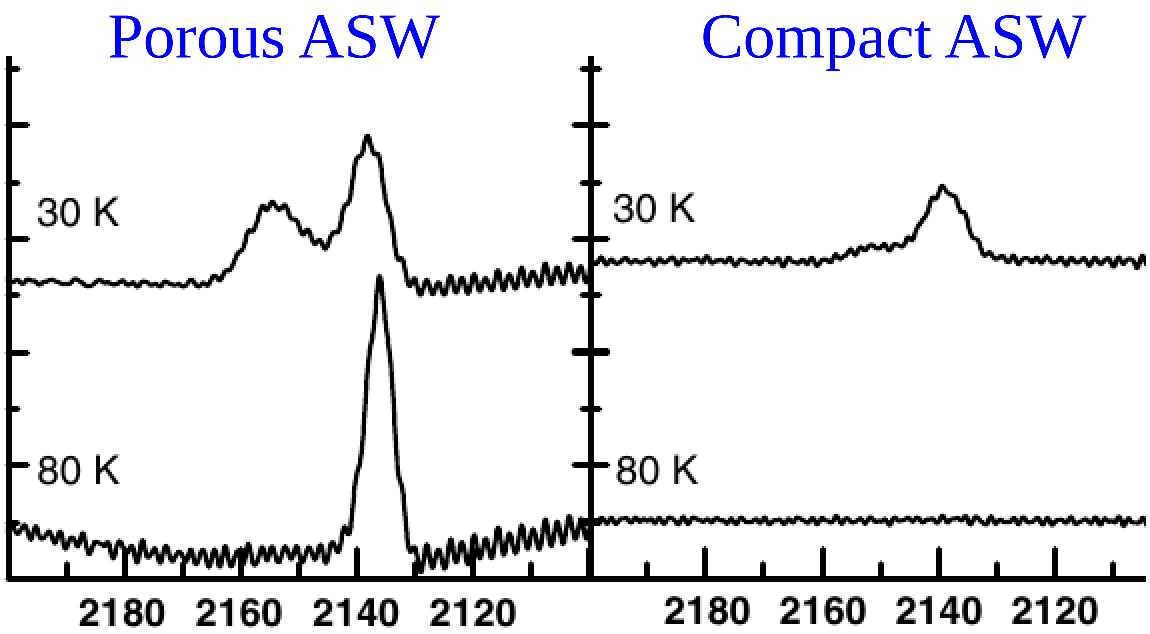
- Are reaction partners in same ice phase (CO versus H_2O-rich)?
- Diffusion in bulk ice much slower than on surface. Pores and cracks will improve diffusion and thus COM formation.

6. Porosity

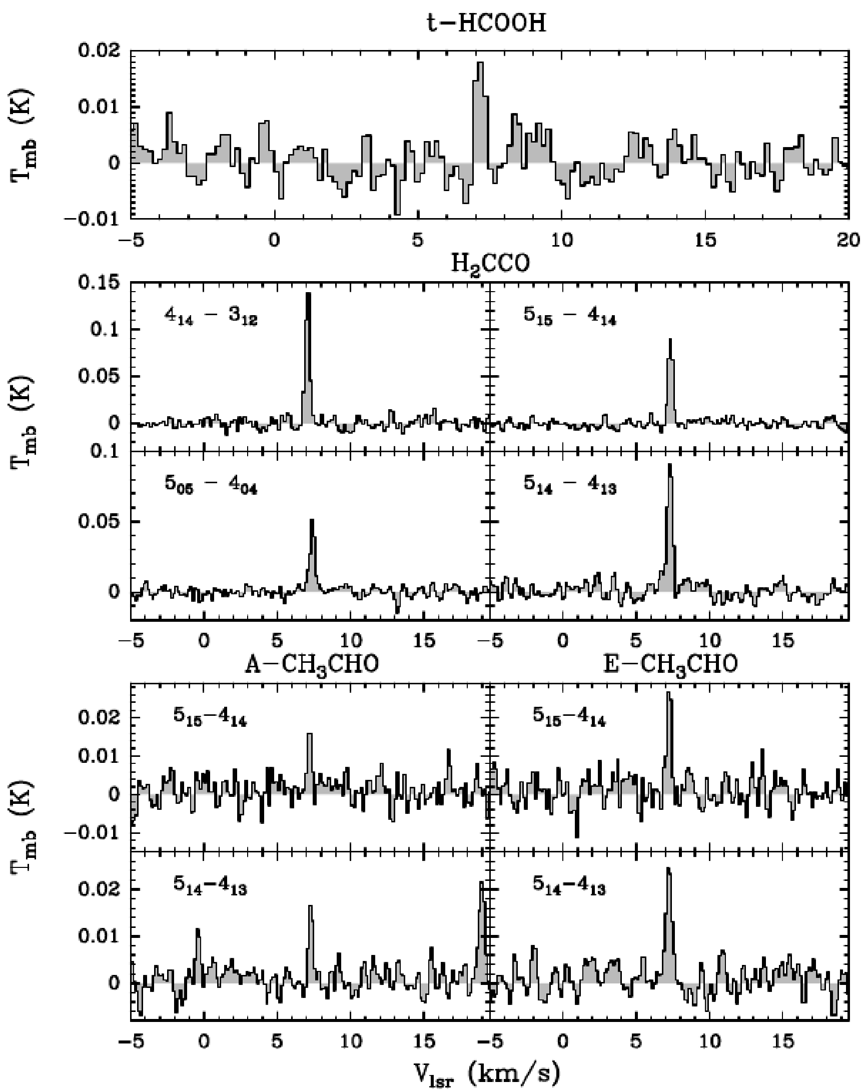
- Simulation by He+ 2019:



- Porosity hard to determine in ISM ice.
- Absence CO-OH band 2152 cm^{-1} at CO-H_2O interface likely due to mixed H_2O (NH_3, CH_4)
- Fraser+ 2004:



7. Back to Gas: Prestellar Core



Vastel+ 2014

Detection of COMs at ~8000 AU from center prestellar core (Vastel+ 2014):

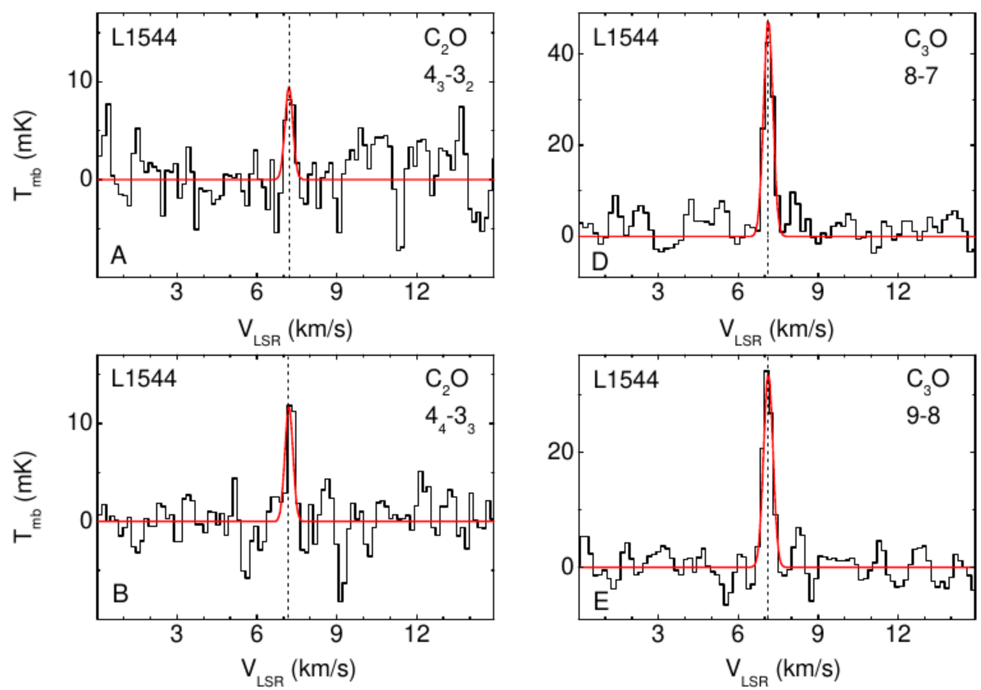
- non-thermal desorption mechanism, liberating H_2O and other simple species
- followed by a gas phase route to COMs.

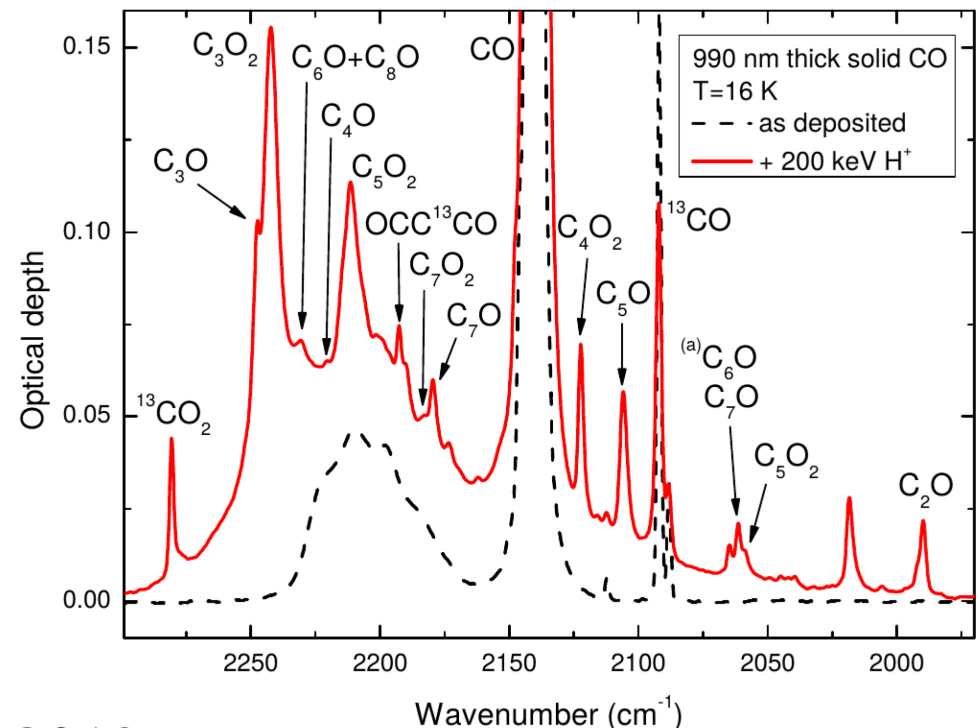
Prime desorption mechanism is not ice mantle explosions (Holdship+ 2019).

7. Back to Gas: Cosmic Rays

Gas phase C_2O and C_3O suggested to originate from CO ices after 1000 yr irradiation. Should be short-lived in the gas, confirmed by the observations.

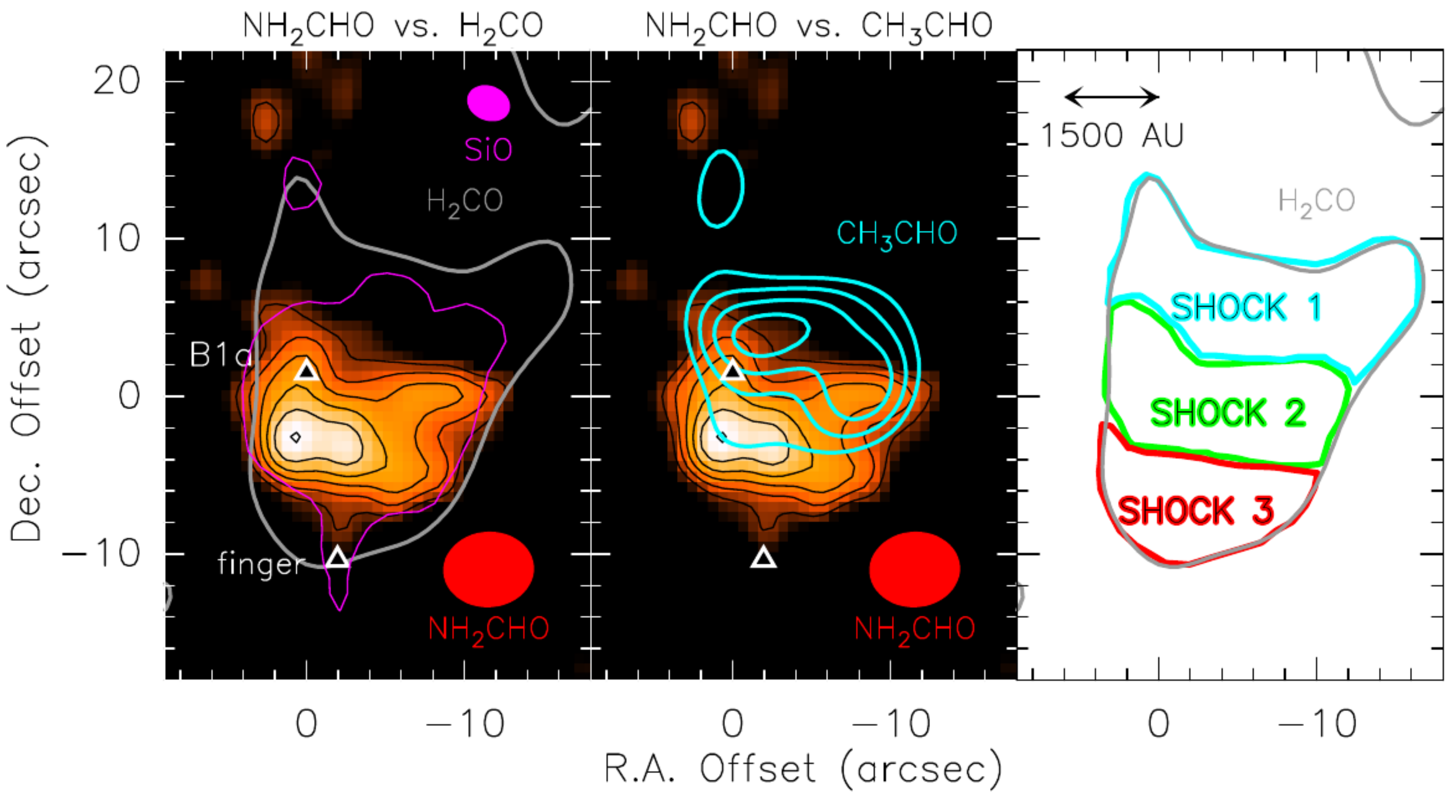
- How about other species produced by irradiation?
- Desorption process?





Urso+ 2019

7. Back to Gas: Shocks



Codella+ 2017

Formamide (NH_2CHO) detected in L1157-B1 shock:

- different distribution than other organics, so formamide does not come from ice. Plus, formamide released from ice destroyed in 2000 years.
- gas phase chemistry simple ice sublimation species can reproduce it.

8. Future: Ice Maps

Limited new work on H_2O ices in past ~10 years.

Missing: maps of ice abundance and processing gradients on large scale (dense cores) and small scale (envelope, disk)

Upcoming missions will shake up this field:

JWST—map individual cores and YSOs, in all abundant ices

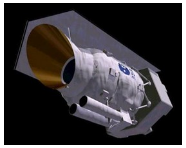
study weaker species in individual sight-lines

SPHEREx – map entire sky in H_2O, CO_2, CO ice

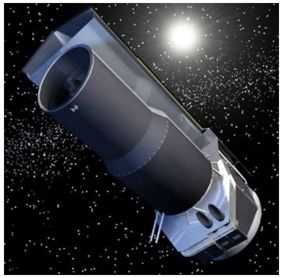
8. Future: Ice Maps with JWST

Interstellar ice knowledge jumps with each space mission:

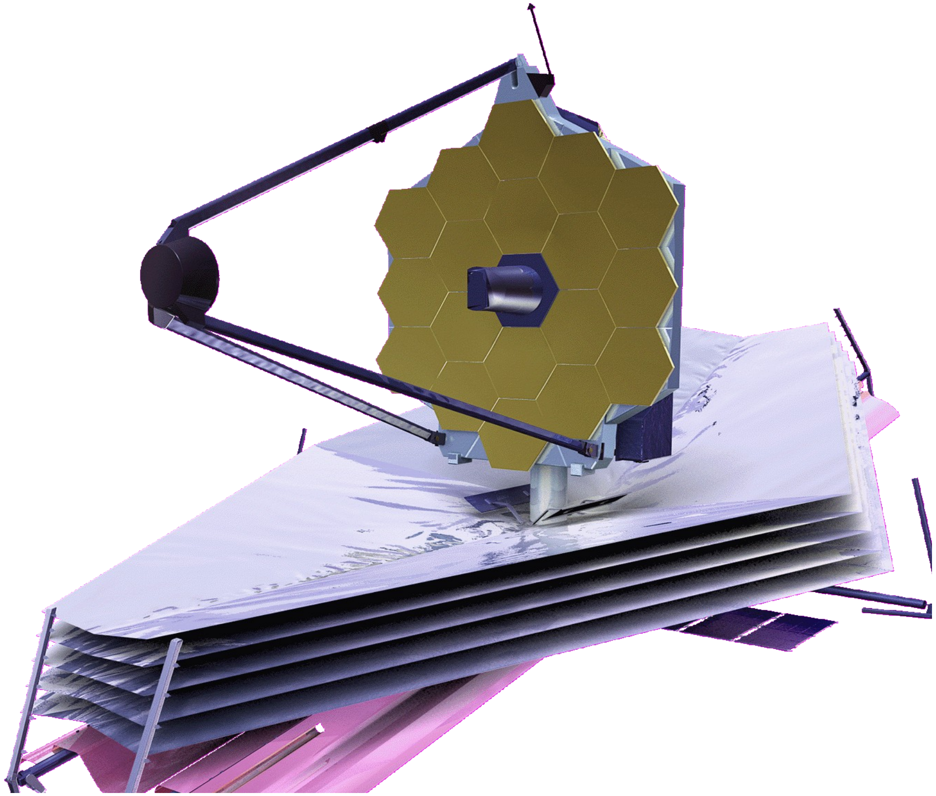
- Sensitivity
- Spectral resolution
- Spectral coverage
- Mapping speed
- Large samples
- Availability



Infrared Space Observatory
1995-1998

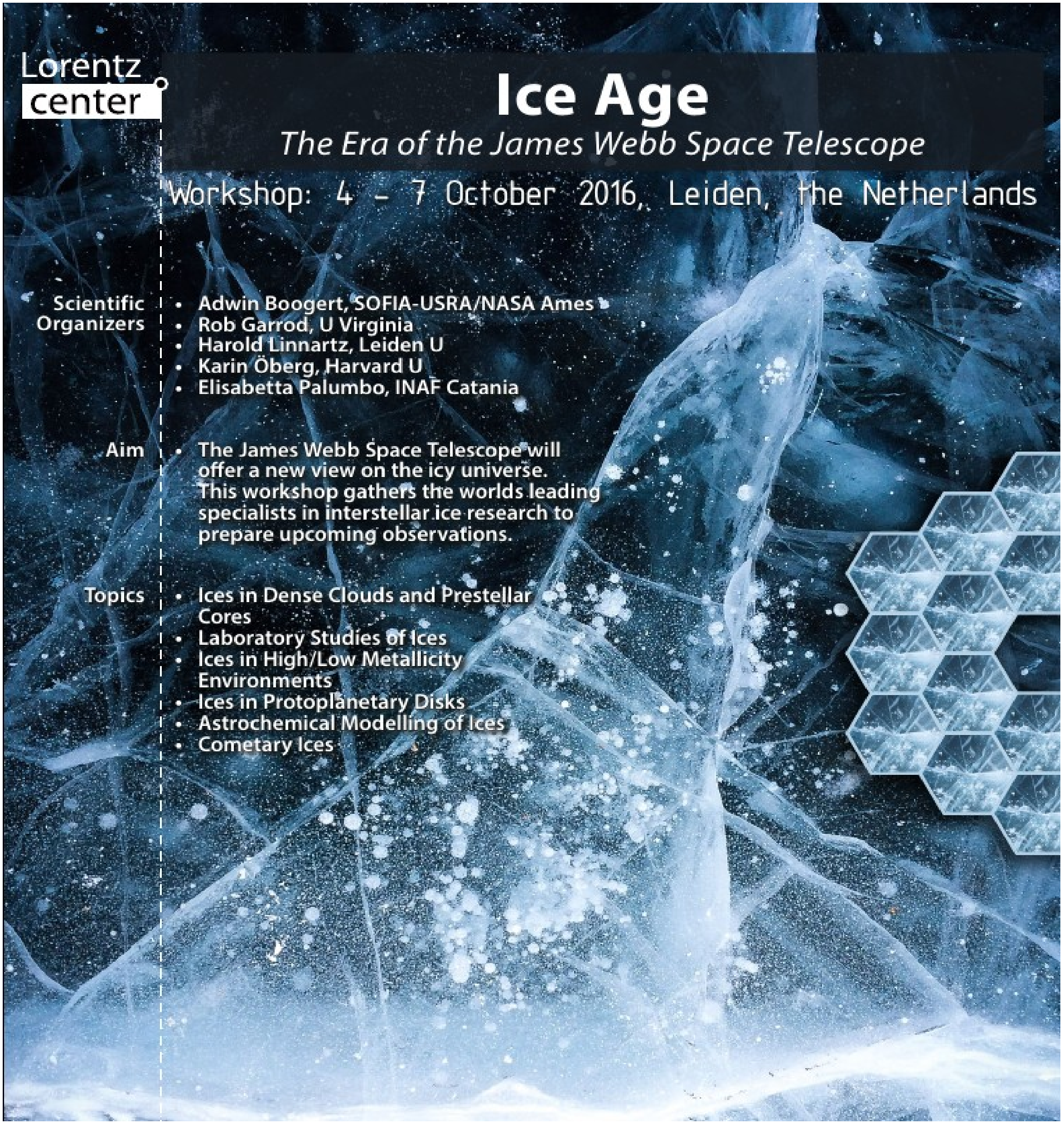


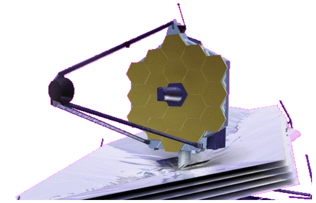
Spitzer Space Telescope
2003-2009



James Webb Space Telescope (JWST)
2021-20??

8. Future: Ice Maps with JWST





Selections Made for the JWST Director's Discretionary Early Release Science Program

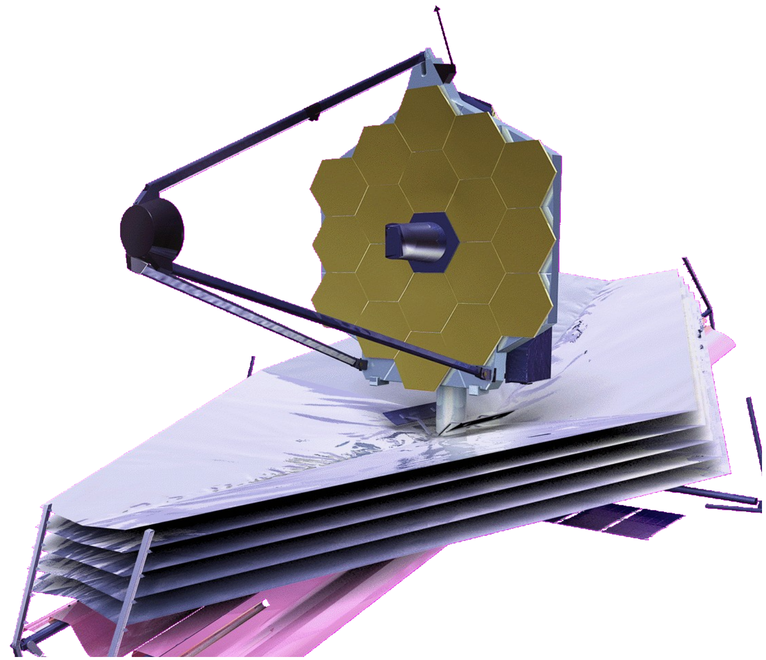
News Feature • November 13, 2017

ID	ERS Program	PI & Co-PIs
1288	Radiative Feedback from Massive Stars as Traced by Multiband Imaging and Spectroscopic Mosaics	**PI:** Olivier Berne (Universite Toulouse) **CoPIs:** Emilie Habart (Institut d'Astrophysique Spatiale) and Els Peeters (University of Western Ontario)
1309	IceAge: Chemical Evolution of Ices during Star Formation	**PI:** Melissa McClure (Universiteit van Amsterdam) **CoPIs:** Adwin Boogert (University of Hawaii) and Harold Linnartz (Universiteit Leiden)
1324	Through the Looking GLASS: A JWST Exploration of Galaxy Formation and Evolution from Cosmic Dawn to Present Day	**PI:** Tommaso Treu (University of California - Los Angeles)
1328	A JWST Study of the Starburst-AGN Connection in Merging LIRGs	**PI:** Lee Armus (California Institute of Technology)
1334	The Resolved Stellar Populations [illegible]	**PI:** Daniel Weisz (University of [illegible]

8. Future: Ice Maps SPHEREx

Interstellar ice knowledge jumps with each space mission:

- Sensitivity
- Spectral resolution
- Spectral coverage
- Mapping speed
- Large samples
- Availability



Infrared Space Observatory
1995-1998

Spitzer Space Telescope
2003-2009

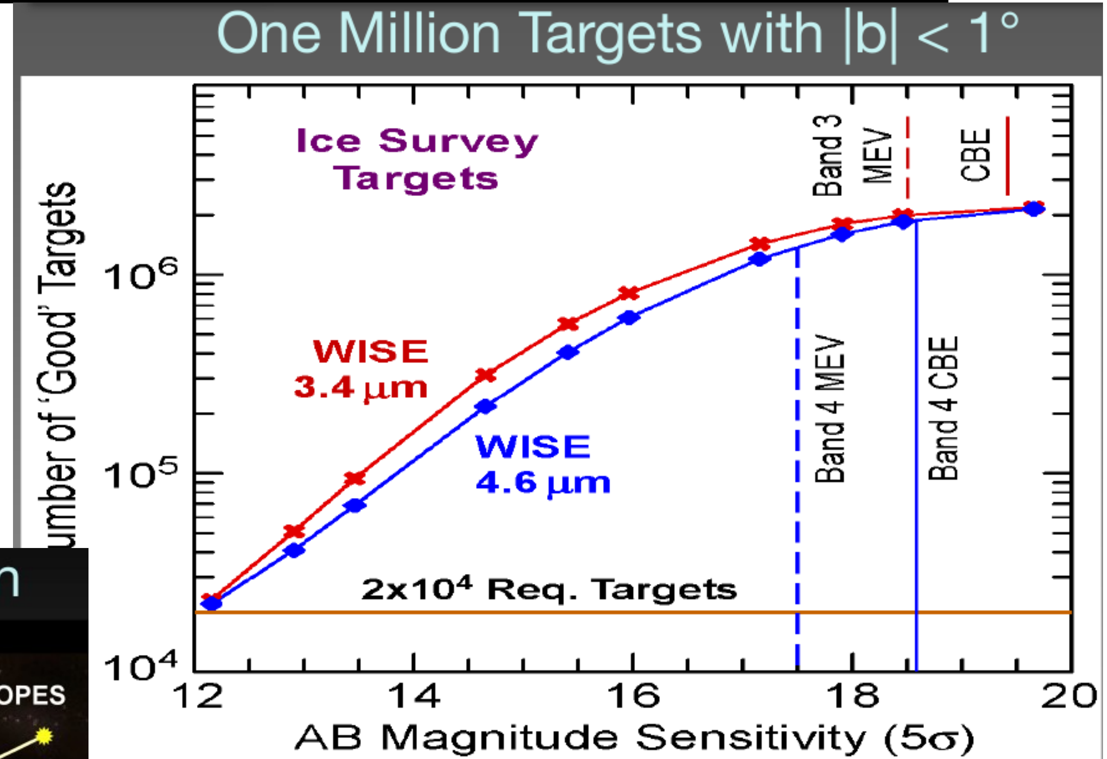
James Webb Space Telescope (JWST)
2021-20??

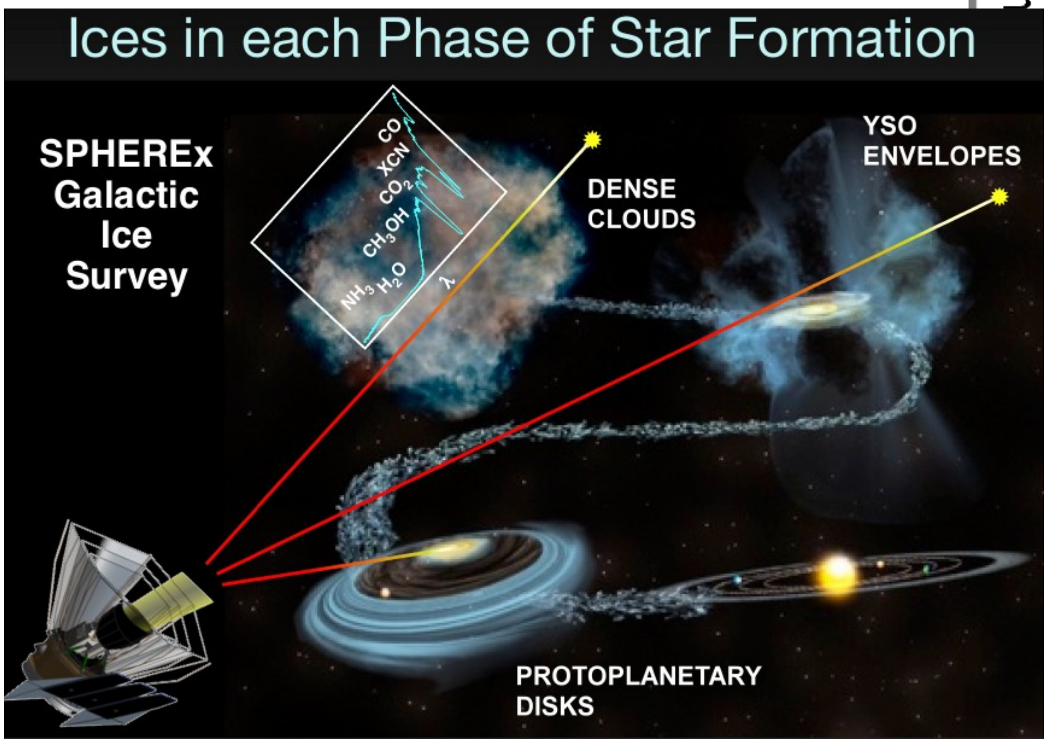
SPHEREx
2023-2026

8. Future: Ice Maps SPHEREx

All sky spectra 0.7-5 μm at low spectral (40-150) and spatial (6 arcsec) resolution

SPHEREx ice catalog will increase number of ice targets from ~200 to >20,000

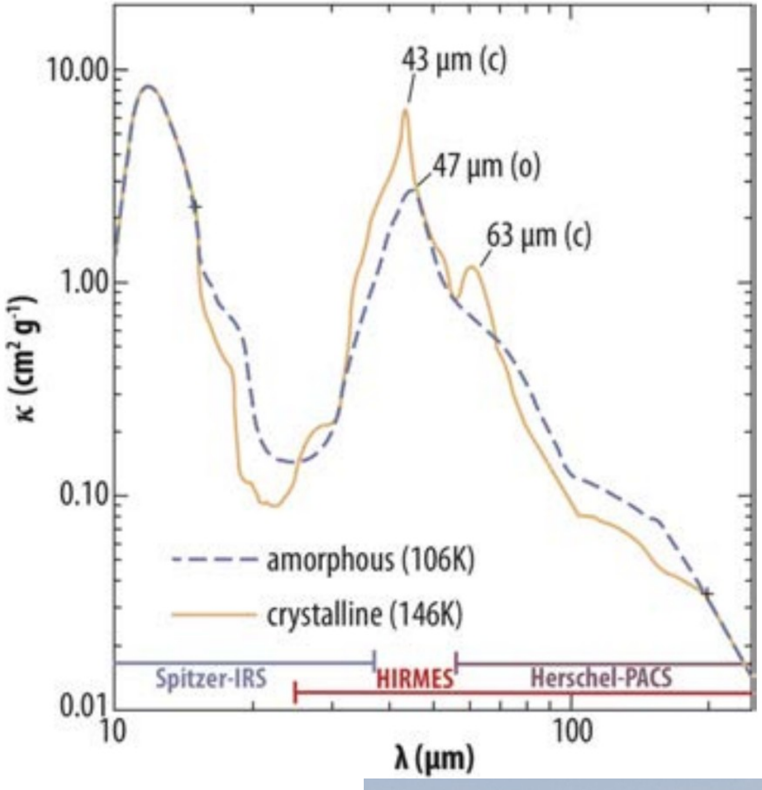




Well timed for follow up with JWST at higher spatial, spectral resolution and sensitivity.

See http://spherex.caltech.edu/
See talk by Gary Melnick tomorrow.

8. Future: Ice Maps with SOFIA



H_2O ice lattice modes observable in emission, enabling ice mapping.

Very limited instrumentation.

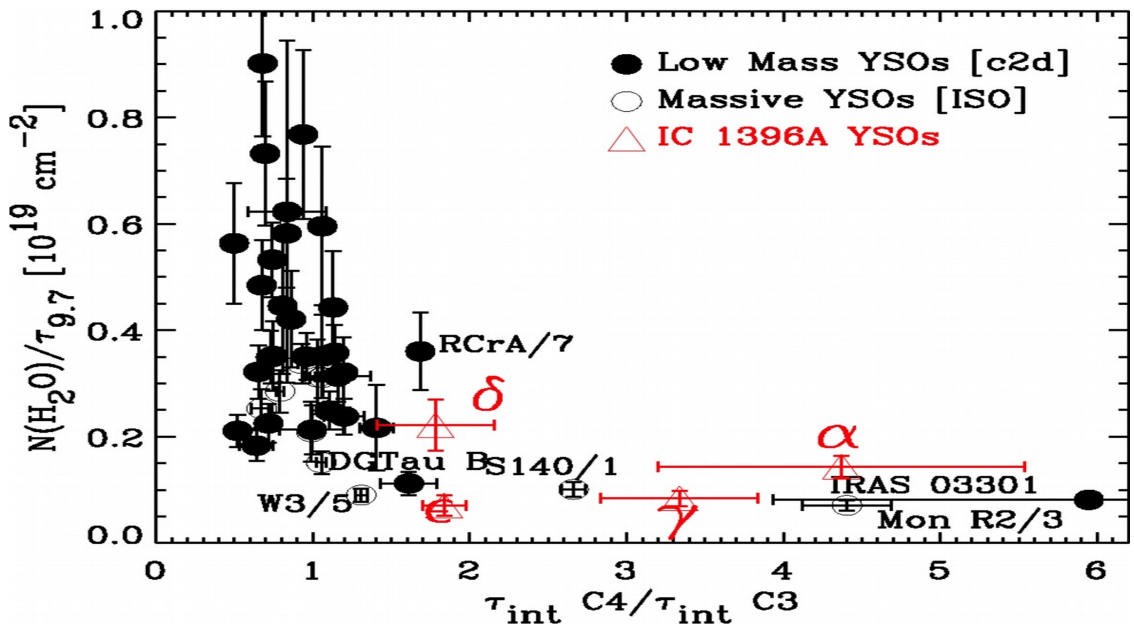
SOFIA/HIRMES to be commissioned in next year or two.

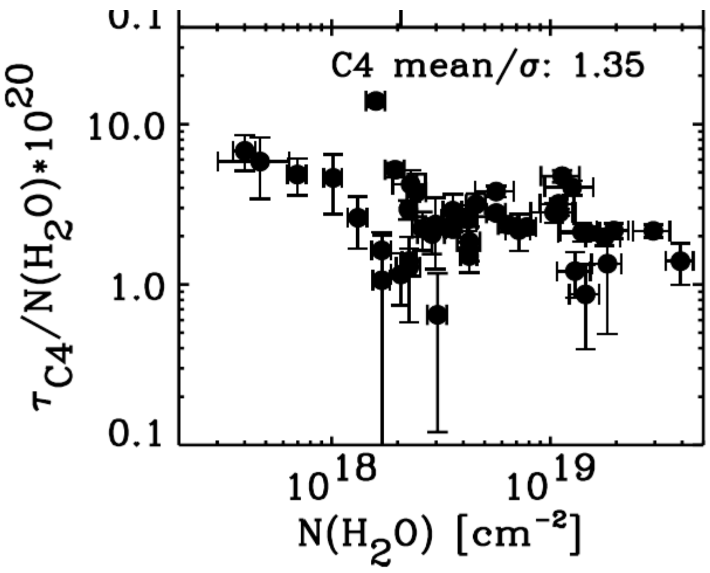
9. Conclusions

- Grain surface chemistry rules.
- COMs likely formed under cold, non-energetic conditions in CO-rich ices. CH_3OH best studied and observed.
- Energetic formation processes plausible but at low level in dense clouds.
- Ice heating often observed, and likely leading to COMs.
- Salts important component of grain mantles and comets.
- Degree of porosity amorphous H_2O observationally not constrained.
- Desorption of COMs and in dense cores not well understood.
- Much-needed ice maps for study ice evolution available within a few years with JWST and SPHEREx.

Extra Slides

Salts: Observ. Constraints



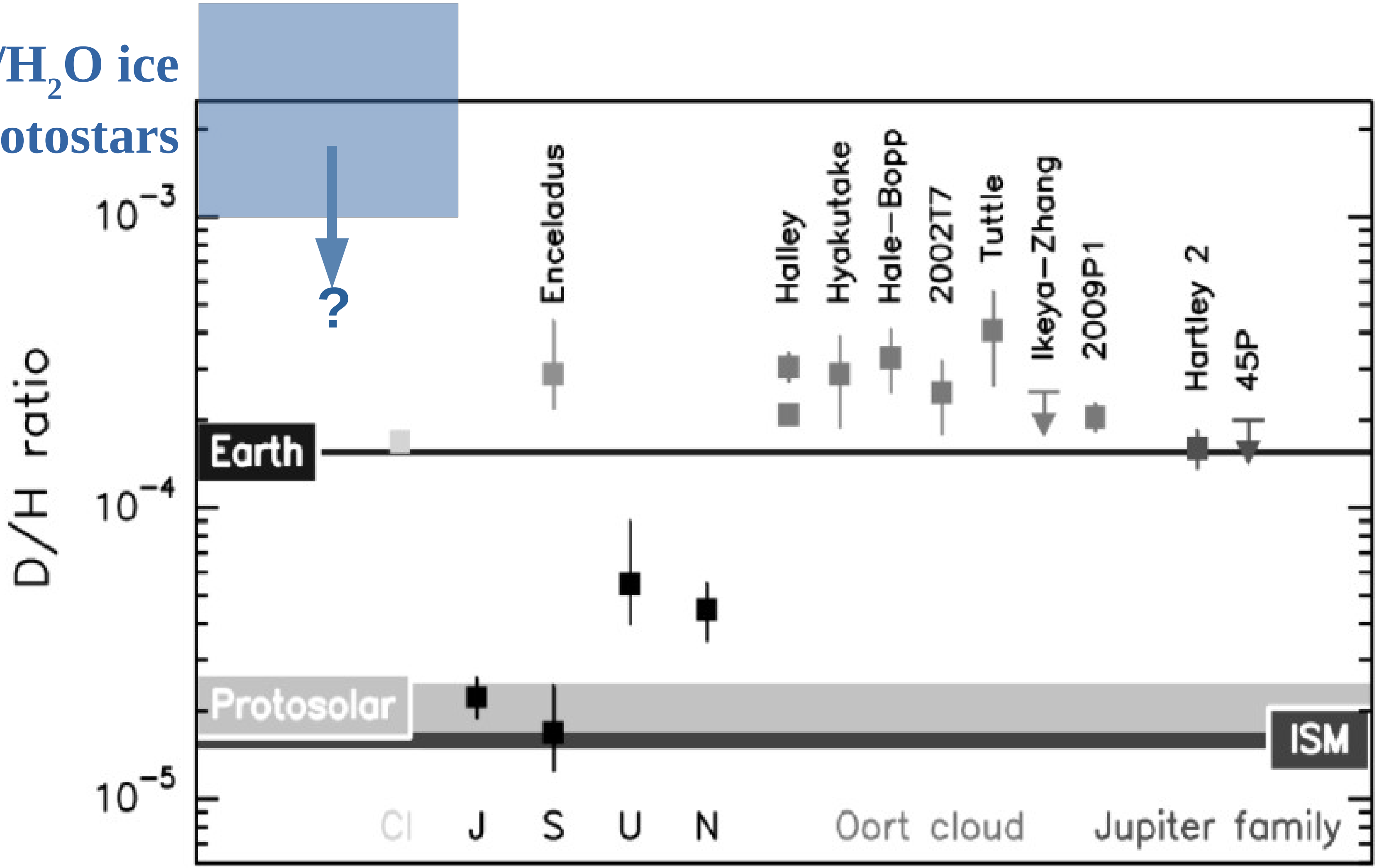


Carrier of 6.85 um band seems sticks around longer than H2O ice, but not as long as silicates: a salt?

HDO Ice: Link with Comets

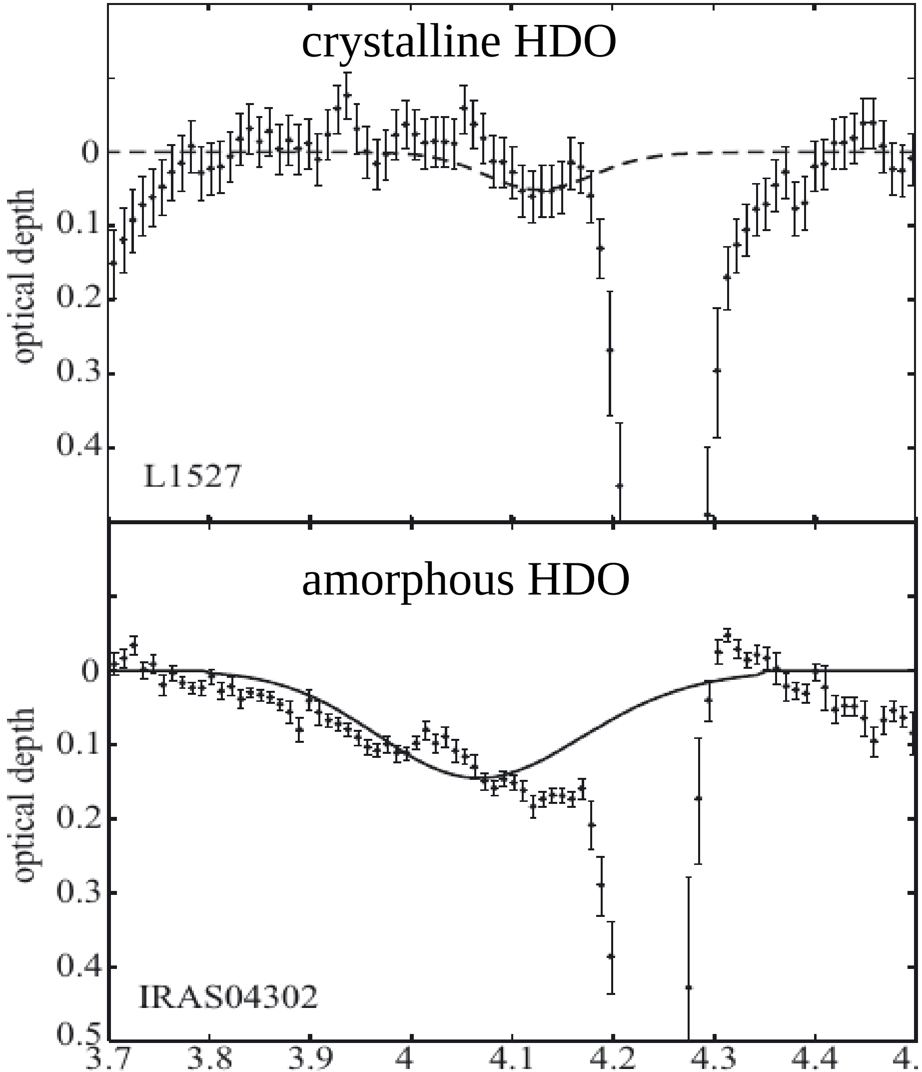
HDO/H_2O ice ratio measurements important:

HDO/H_2O ice protostars



Lis et al. 2013, Ceccarelli et al. 2014

HDO Ice: Link with Comets



Aikawa et al. 2012

HDO/H_2O ice ratio measurements

- Difficult!
- <1% in YSO envelopes (Paris et al. 2003)
- 2-22% in disks (tentative; Aikawa et al. 2012)
- Deuteration H_2O lower than CH_3OH: formed at warmer, earlier conditions (Ceccarelli et al. 2014).

Envelopes+Disks: Heated Ices