Master course: Astrochemistry I:

Lecture 7: Chemistry in star-forming regions

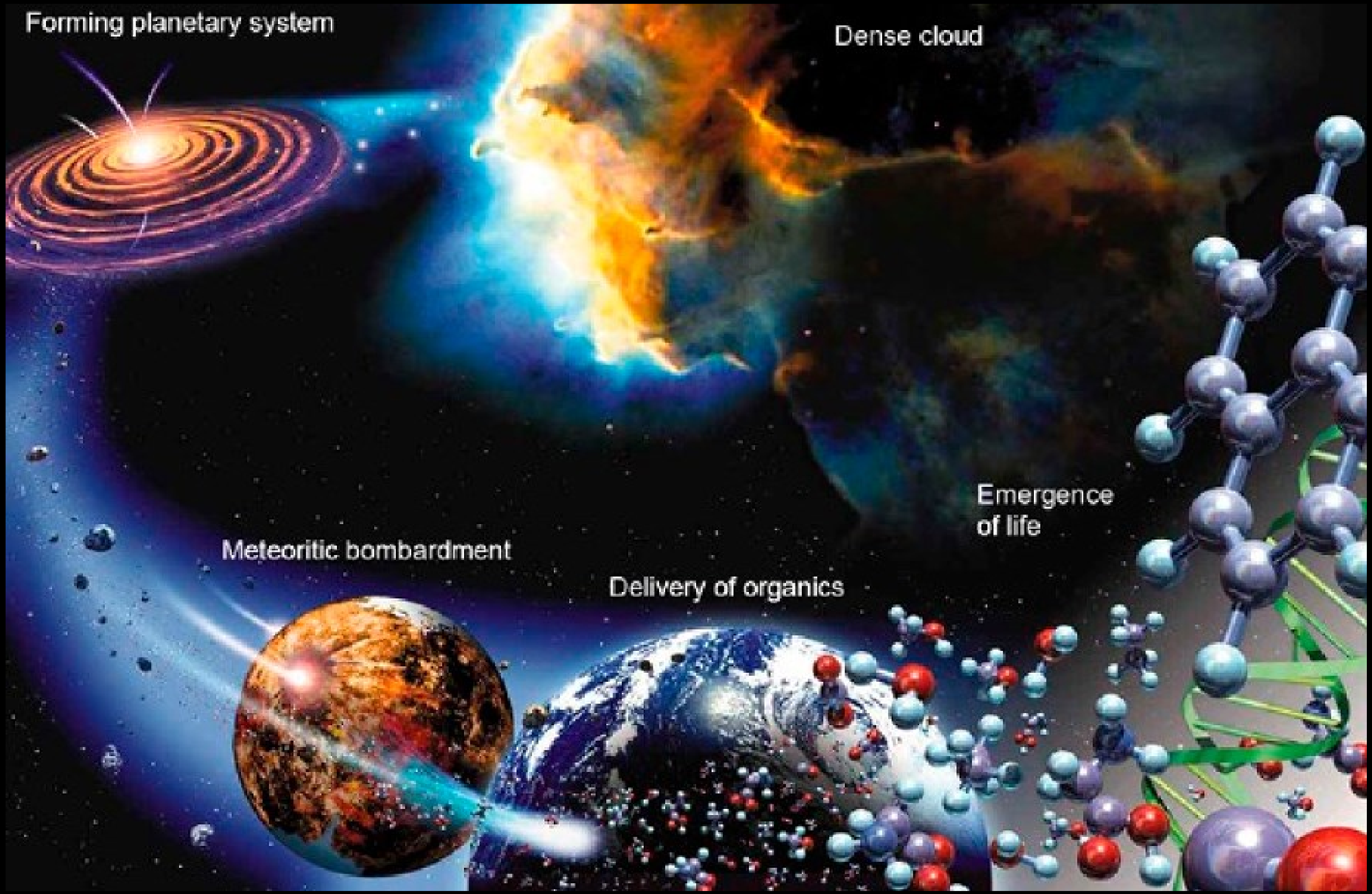
Reading list:

van Dishoeck Ch.8 “Astrochemistry of Dense Protostellar and Protoplanetary Environments” in Thronson, Stiavelli, Tielens (2009)

van Dishoeck (2014) Faraday discussions

Caselli & Ceccarelli (2012)

Herbst & van Dishoeck (2009) ARAA



Dr. Helgi Rafn Hrodmarsson – UPEC – 2026-2027

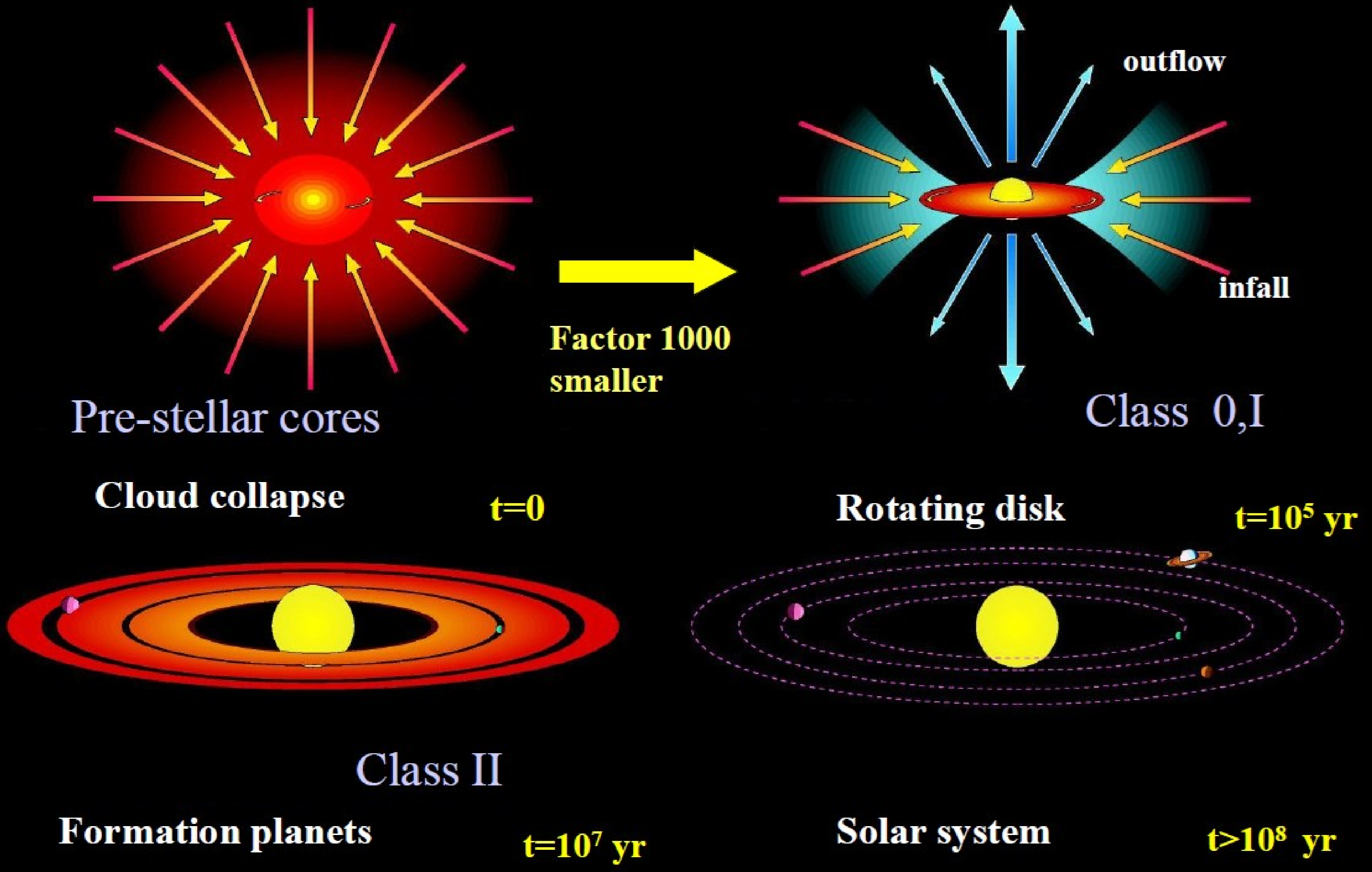
Outline

- Introduction
- Observational techniques
- Chemical scenario
- Cold outer envelopes around YSOs
- Warm inner envelopes around YSOs
- Hot cores
- Protoplanetary disks
- Comets

7.1 Introduction

- Star formation accompanied by enormous changes in physical parameters *n*, *T* => response of chemistry?
- Which molecules are good diagnostics of various stages: collapse, outflow, hot cores?
- Molecular lines are used to probe physical conditions and dynamics => need to choose the right molecule!
- In which form are molecules incorporated into circumstellar disks and new planetary systems?

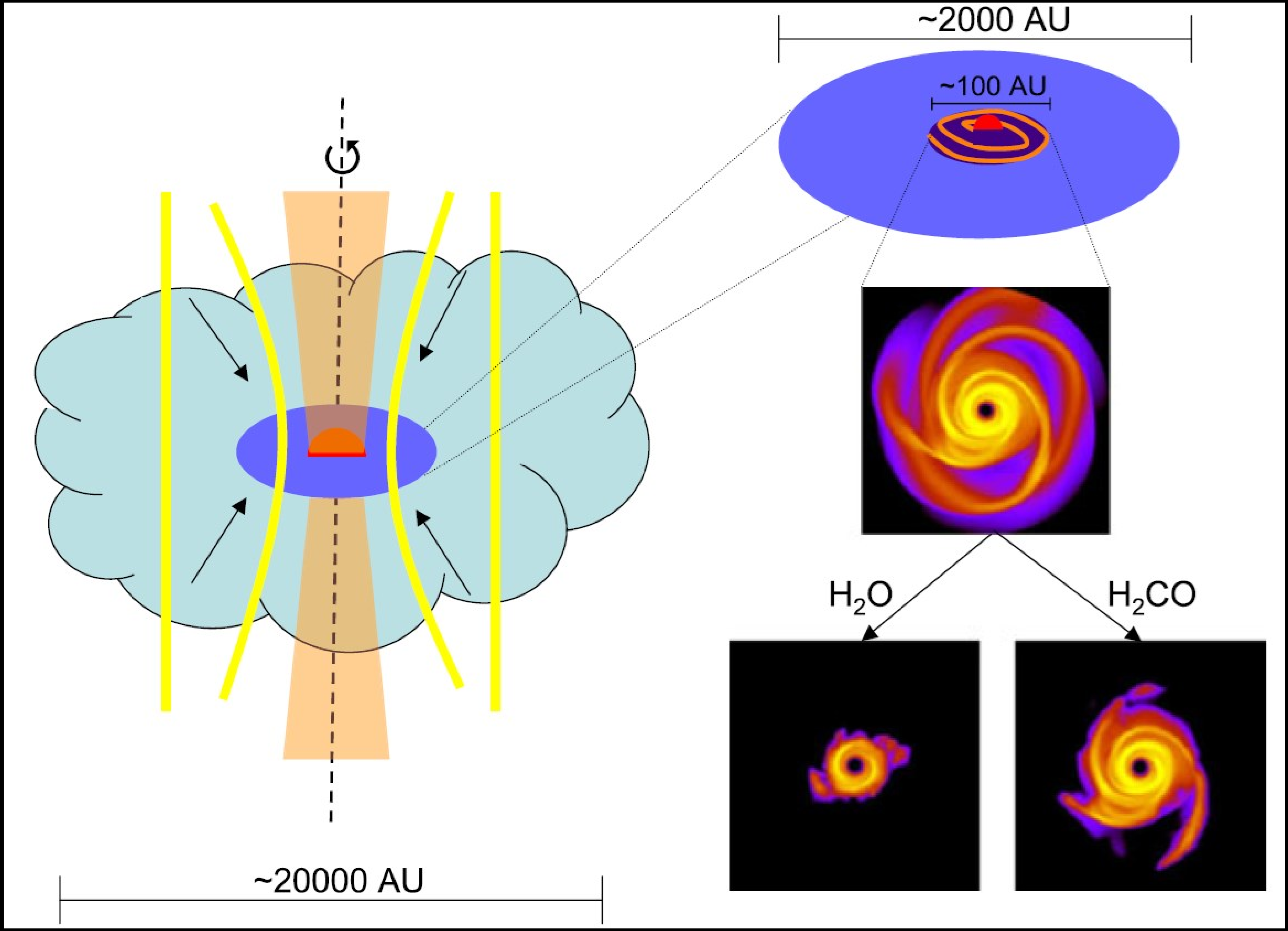
Scenario for star- and planet formation



7.2 Observations

- **Submillimeter:**
  - Very high spectral resolution ($R > 10^6$, < 0.1 km/s)
  - Many gas-phase molecules with abundances down to 10^{-11} wrt H_2
  - Emission => map of region
- **Infrared:**
  - Moderate spectral resolution ($R \sim 10^3$–10^5)
  - Gases and solids with abundances down to 10^{-7}–10^{-8} wrt H_2
    - Probe major reservoirs of C, N, and O
  - Molecules without permanent dipole moments (H_2, C_2H_2, CH_4, CO_2, CH_3, …)
  - Absorption => pencil beam line-of-sight; emission only from hot gas

Typical sizes



Caselli & Ceccarelli (2012)

Typical sizes

Linear size	**Angular size**	
	Taurus 140 pc	Orion 450 pc
5 AU Inner disk	0.04”	0.01”
100 AU Outer disk	0.7”	0.2”
1000 AU YSO envelope	7”	2”
10000 AU = 0.05 pc Cloud core	74”	23”

ALMA needed to resolve relevant scales; most data spatially unresolved pre-ALMA

Information from lines

- Line strength => abundances
- Line ratios => temperatures, densities
- Line profiles => kinematics

7.3 Chemical scenario

- **Starless cores:** $T \approx 10\text{–}20$ K, $n \approx 10^4$ cm^{-3}
  - Quiescent ion-molecule chemistry
  - Radicals and carbon chains
  - Ices start forming
- **Pre-stellar cores and collapse:** $T \approx 10$ K, $n \approx 10^5\text{–}10^8$ cm^{-3}
  - Heavy freeze-out of molecules onto grains
  - Grain surface reactions produce new species:

$$\mathrm{O, C, N, CO} \xrightarrow{\mathrm{H}} \mathrm{H_2O, CH_4, NH_3, H_2CO, CH_3OH}$$

$$\mathrm{CO} \xrightarrow{\mathrm{O}} \mathrm{CO_2}$$

Chemical scenario (continued)

- **Embedded YSO phase:** $T \approx 10$–300 K, $n \approx 10^5$–10^9 cm^{-3}
  - Gas and dust heated by accretion luminosity, UV + X rays from young star; production of more complex molecules
  - Sublimation of molecules from grains: H_2O, CH_3OH, CH_4, complex organics…
    - Sequence according to sublimation temperatures
  - Hot core chemistry: complex organics, HCN, …
- **Bipolar outflows:** $T \approx 200$–2000 K, $n \approx 10^5$–10^7 cm^{-3}
  - Interaction between outflow and envelope => shocks
  - High-T chemistry: H_2O, …
  - Return of icy mantles to gas: H_2O, CH_3OH, CH_4, …
  - Destroy grain cores: SiO, …

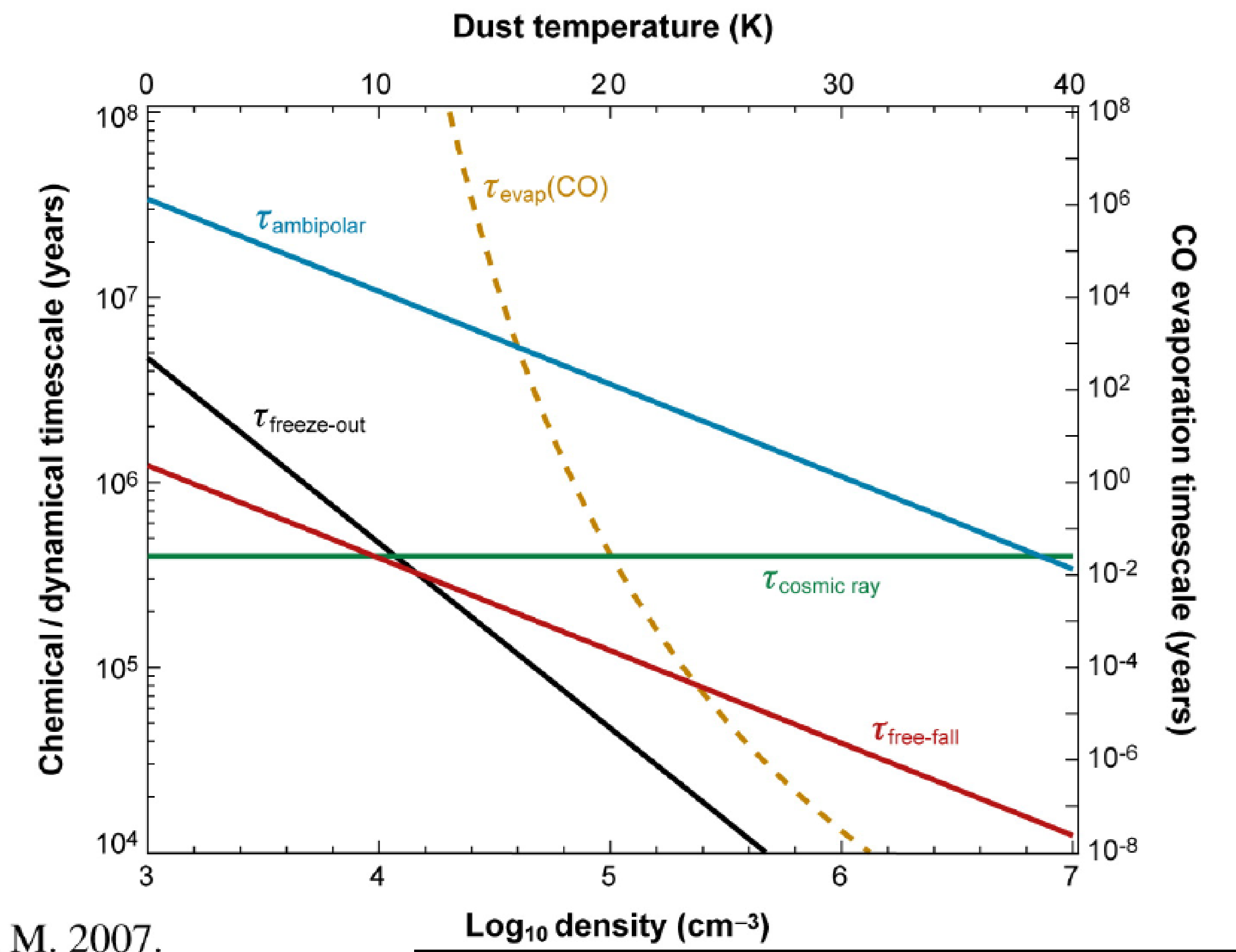
Lecture 5

7.4 Cold outer envelopes: freeze-out

- When protostar starts to heat its surroundings, temperature gradient set up through envelope
  - Outer envelope cold => significant freeze-out expected, as in pre-stellar cores

    Lecture 6
  - Inner envelope warm => sublimation of ices
- Surveys of low- and high-mass YSOs
  - Constrain T, n from dust continuum data
  - Use line data to fit abundance
    - Simplest model: constant abundance with radius
    - More sophisticated models: drop, jump abundance profiles

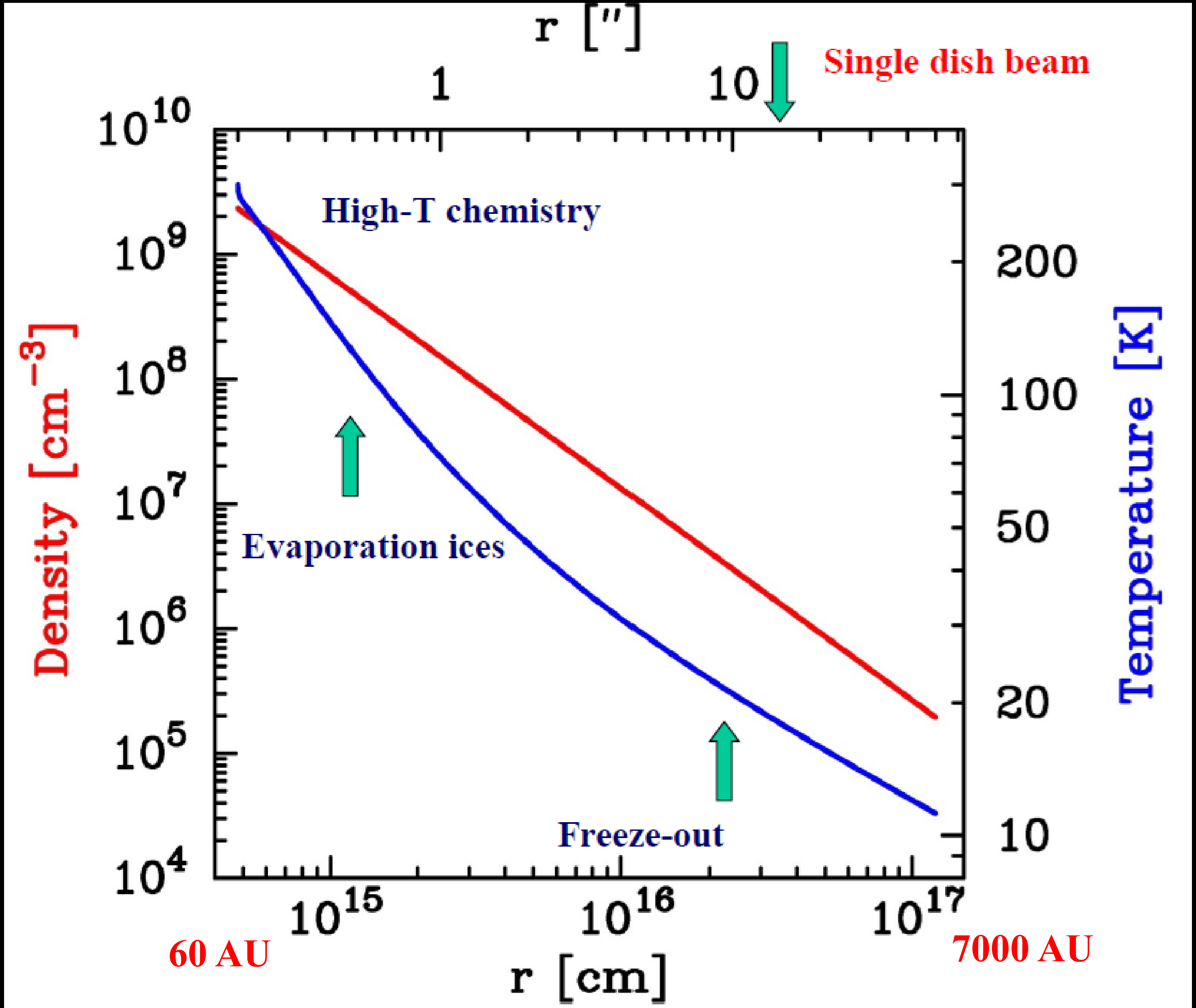
Time scales



Bergin EA, Tafalla M. 2007.
Annu. Rev. Astron. Astrophys. 45:339–96

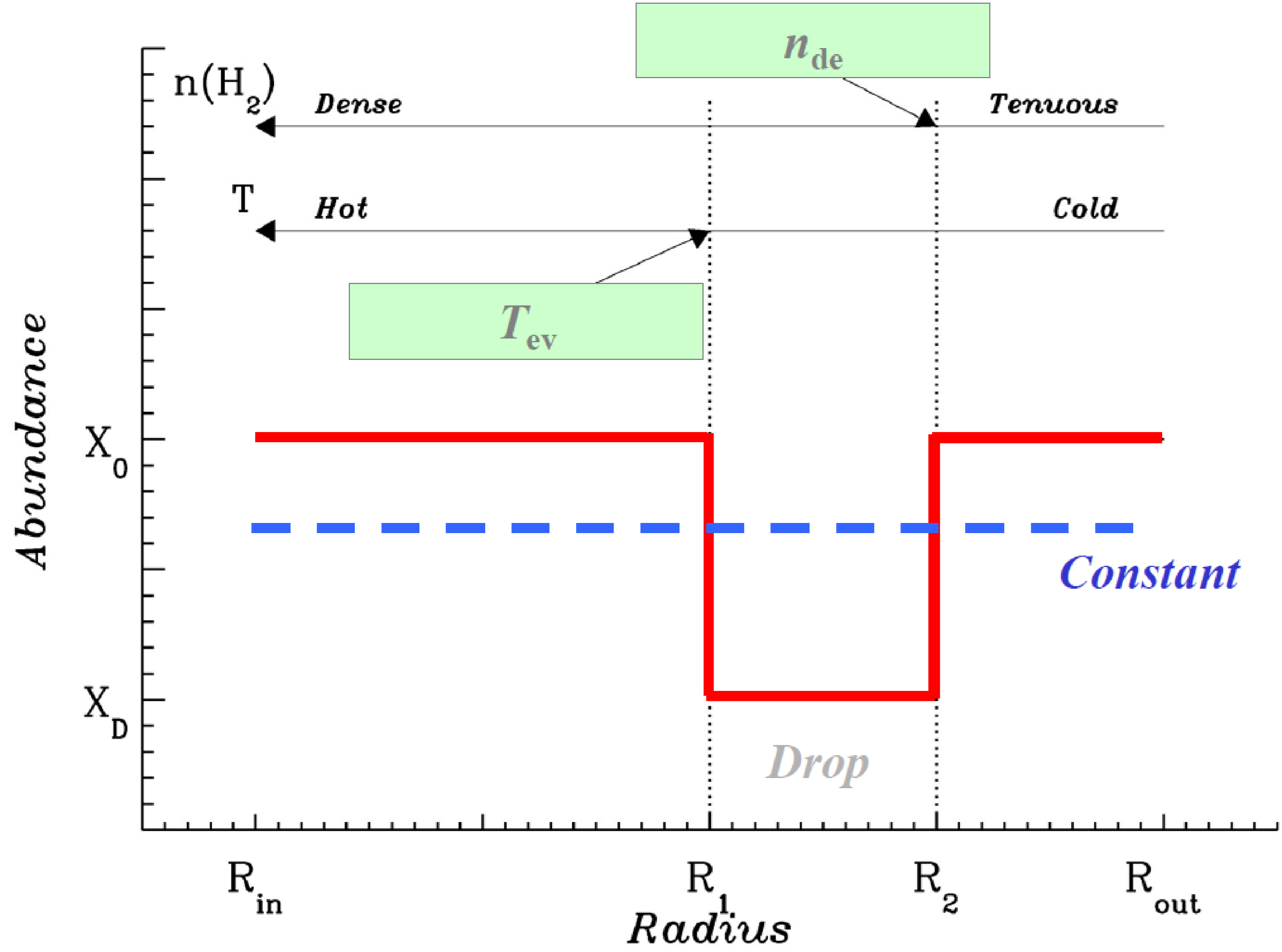
Note: $t_{freeze\text{-}out} < t_{freefall}$
At high densities

Physical structure of protostellar envelope



Schöier et al. 2002
Jørgensen et al. 2002

“Drop” abundance model



Sublimation temperatures

Species	$T_{evap\text{-}lab}$ (K)
H_2O	150
CH_3OH	99
HCN	95
SO_2	83
NH_3	78
CO_2	72
H_2CO	64
H_2S	57
CH_4	31
CO	25
N_2	22

Mumma et al. 1993, PPIII

Collings et al. 2004

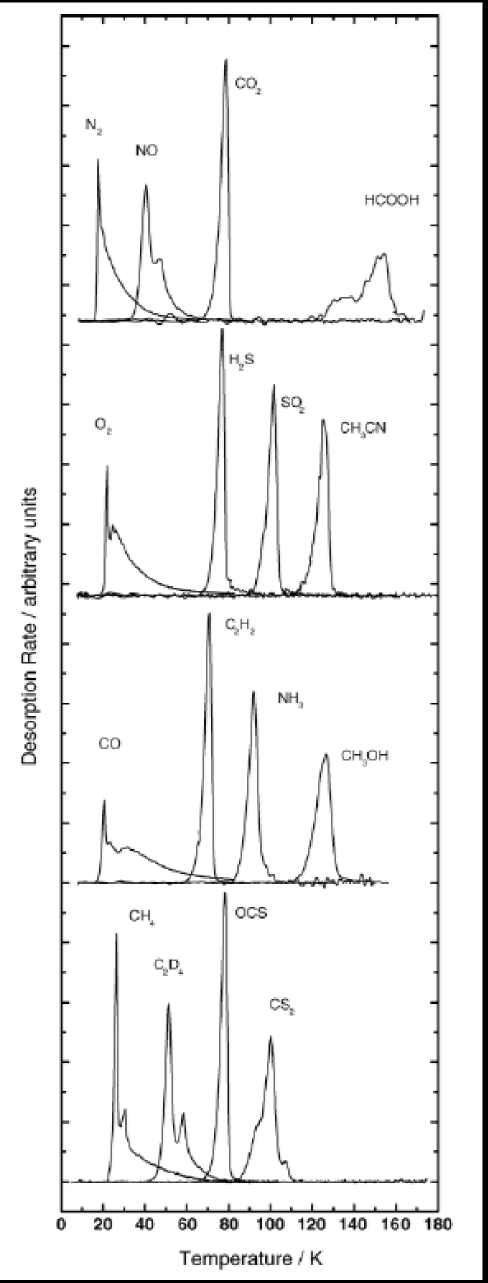
Sublimation temperatures for ***pure*** ices as measured in ***lab***; values in space are lower because of lower densities

TPD experiments

- TPD = Temperature programmed desorption

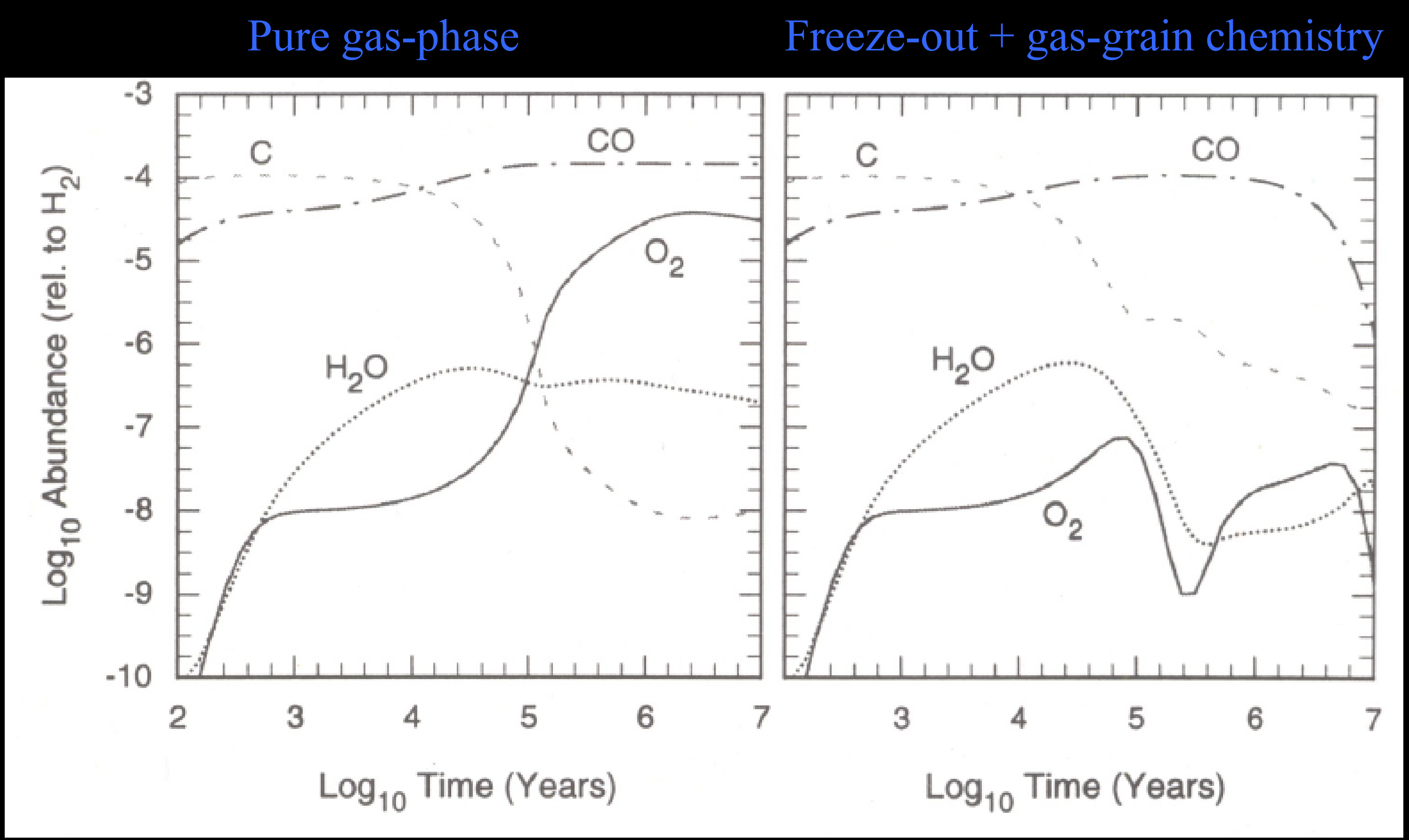
- Experiments for pure ices
- Results for mixed ices depend on mixing ratio and environment

- Example: fraction (~5%) of CO mixed in H_2O ice evaporates at ~100 K in space rather than ~20 K.



Collings et al. 2004
Viti et al. 2004

Oxygen chemistry: freeze-out

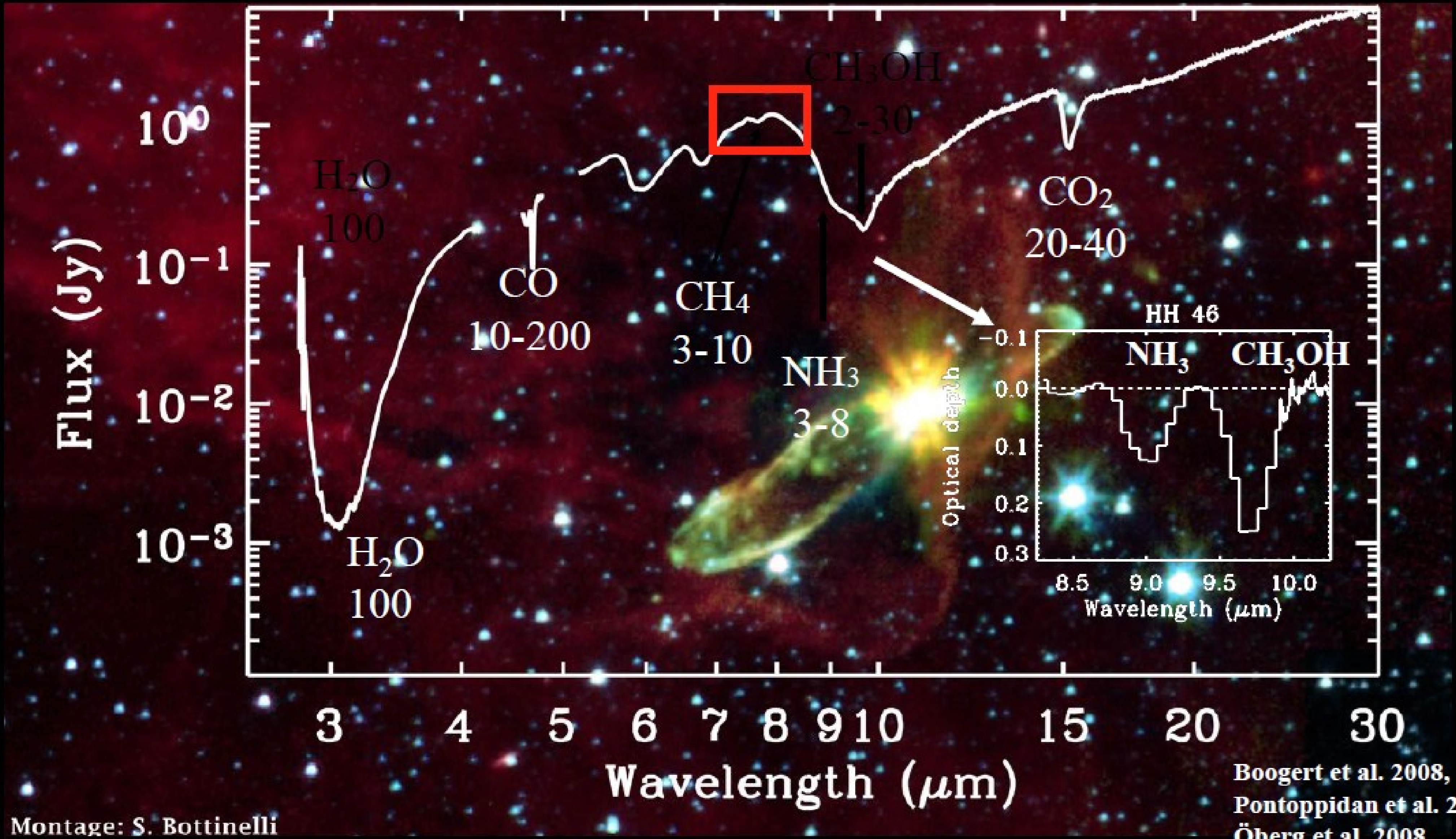


$O \rightarrow H_2O^{gr} \rightarrow$ sticks
$C \rightarrow CH_4^{gr} \rightarrow$ evaporates

Bergin et al. 2000

- Gas-grain chemistry and differential evaporation can explain low H_2O and O_2 in dark clouds, as found by SWAS, ODIN, and Herschel

Ices around low-mass protostars



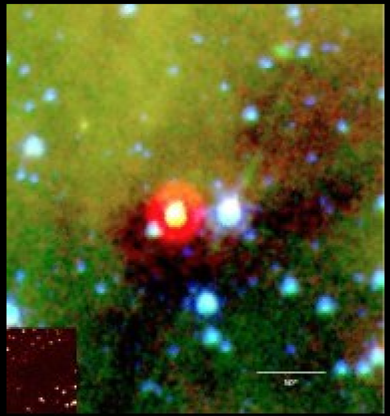
- Variations seen in NH_3, CH_3OH and OCN^-

Boogert et al. 2008,
Pontoppidan et al. 2008,
Öberg et al. 2008
Bottinelli et al. 2010

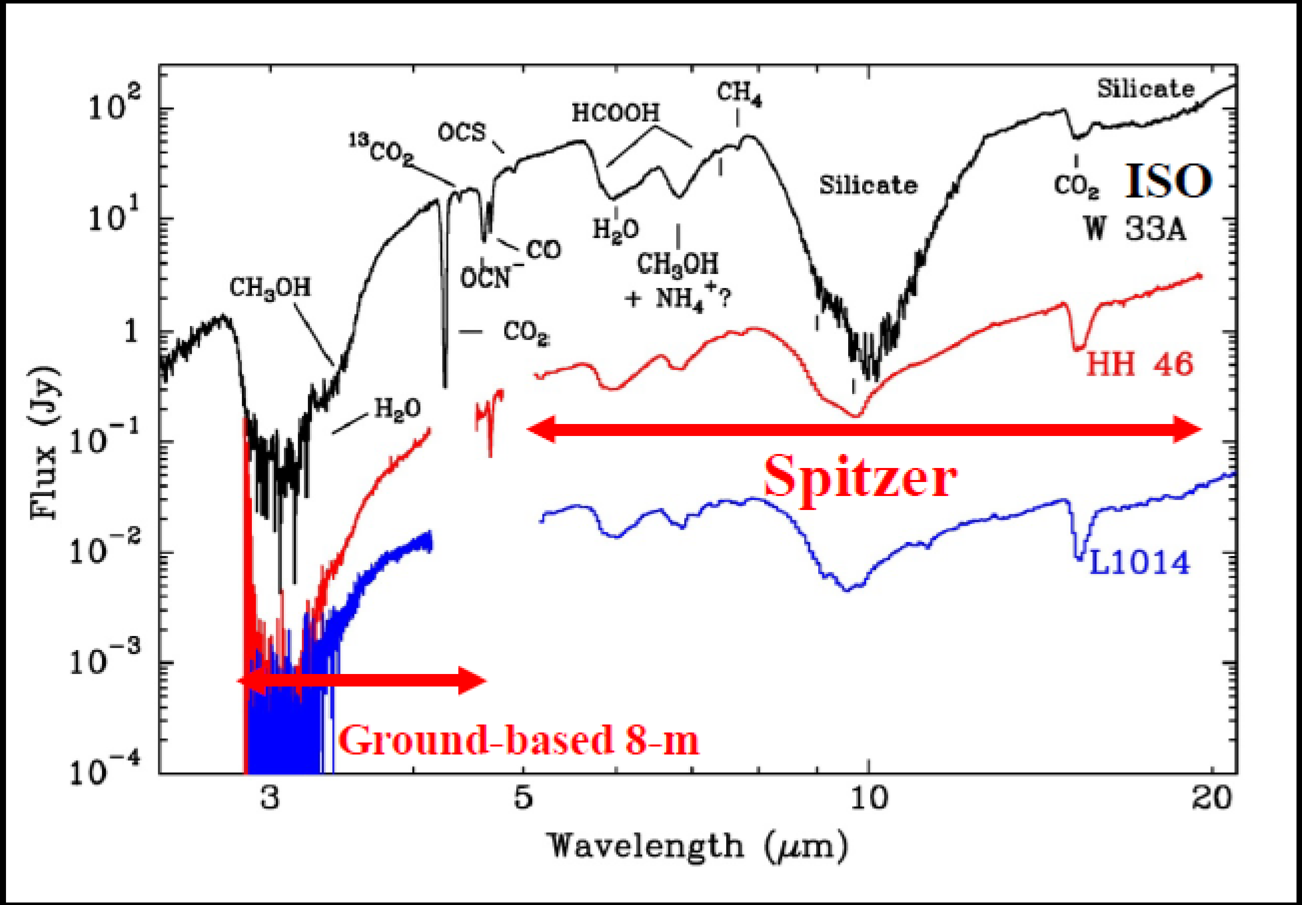
Infrared observations of ices

HH 46: solar-mass YSO

L1014: substellar YSO



From 10^5 to < 0.1 $L_\odot$ objects



- Note similarity of ices over large range of luminosities
- Ices contain significant fraction of heavy elements

Boogert et al. 2004, 2008
Pontoppidan et al. 2008
Öberg et al. 2008, 2011
Bottinelli et al. 2010, 2015

Median ice abundances

Ice feature	Low mass	High mass	Background
H_2O	100	100	100
CO	29	13	31
CO_2	29	13	38
CH_3OH	3	4	4
NH_3	5	5	-
CH_4	5	2	-
OCN^-	0.3	0.6	-

Öberg et al. 2011

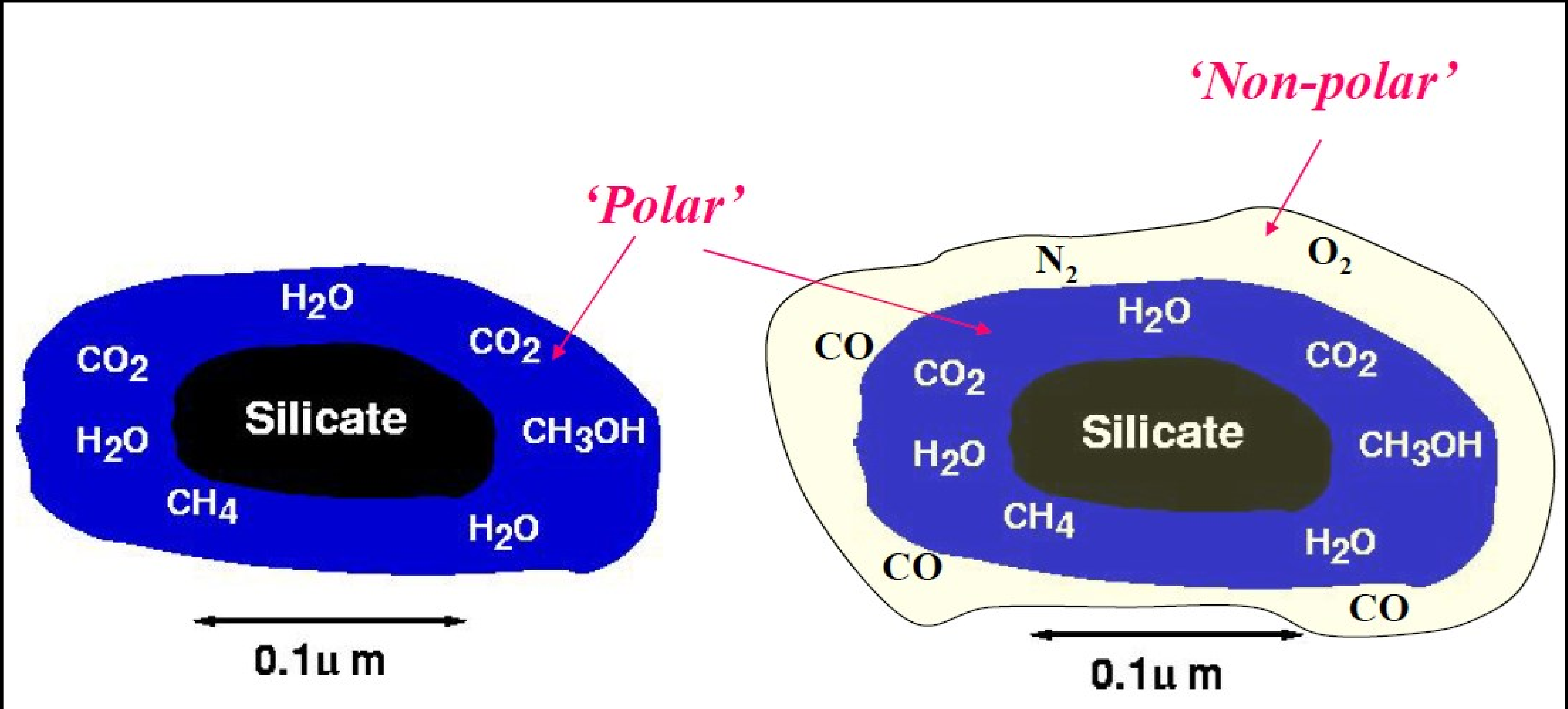
Boogert et al. 2015

H_2O ice / H_2 ~ (0.5–1) x 10^{-4}

Different ice phases

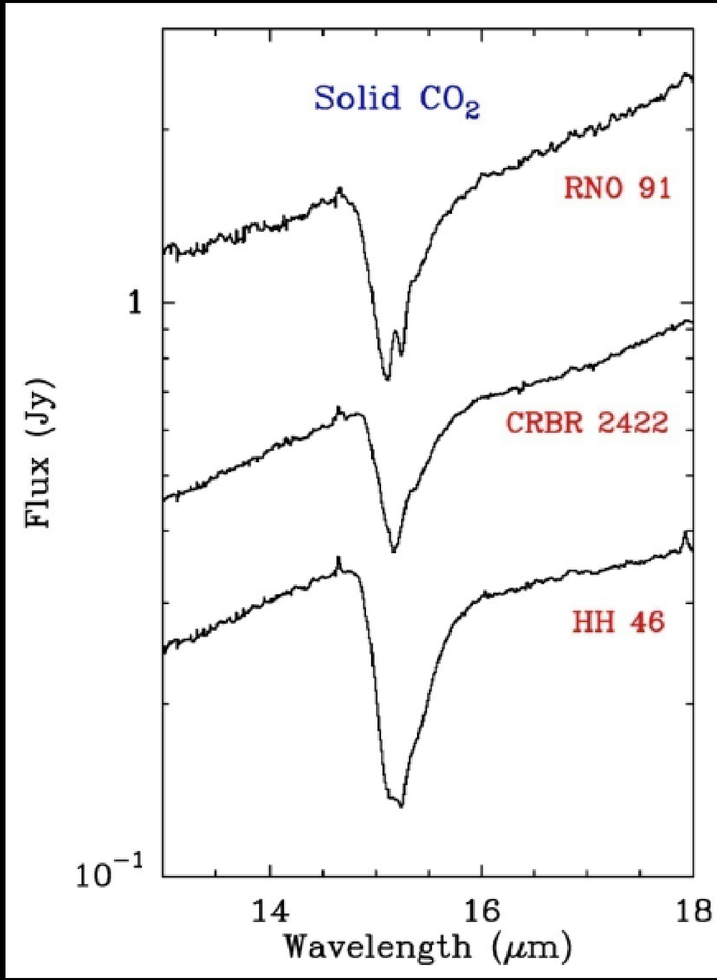
- Comparison of observed CO, CO_2 line profiles with lab spectra => multiple phases
  - **’Polar’:** H_2O-rich, hydrogen bonding
  - **’Apolar’ or ’Non-polar’:** CO-rich, van der Waals bonding
  - **Segregated:** CO_2-rich, CH_3OH-rich
- Possible explanations
  - *Diverse condensation:* H-rich vs CO-rich gas
    - See Fig. Tielens Lecture 6
  - *Diverse sublimation:* temperature gradient results in differential outgassing and restructuring of ices

Different ice phases



- Different ice phases can be seen in IR spectra!

Observations CO_2 15 μm



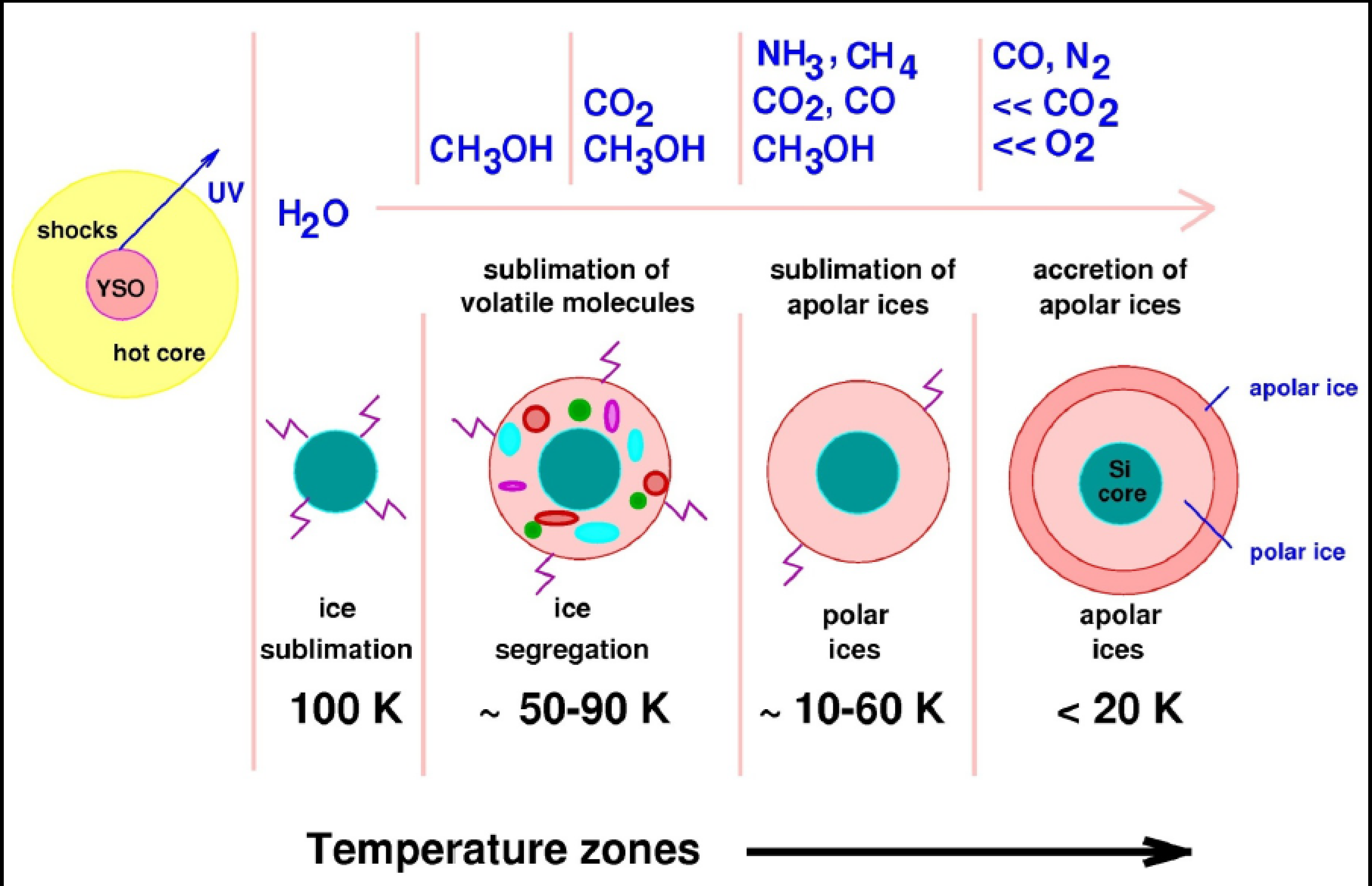
T

Low-mass YSOs

Obs: Pontoppidan et al. 2008
Lab: Ehrenfreund et al. 1997

- Shape of ice band depends on ice environment (polar or apolar)
- CO_2 ice develops double peak structure upon heating → ice segregation (irreversible!) => temperature (history) diagnostic

Different ice phases in YSO envelopes

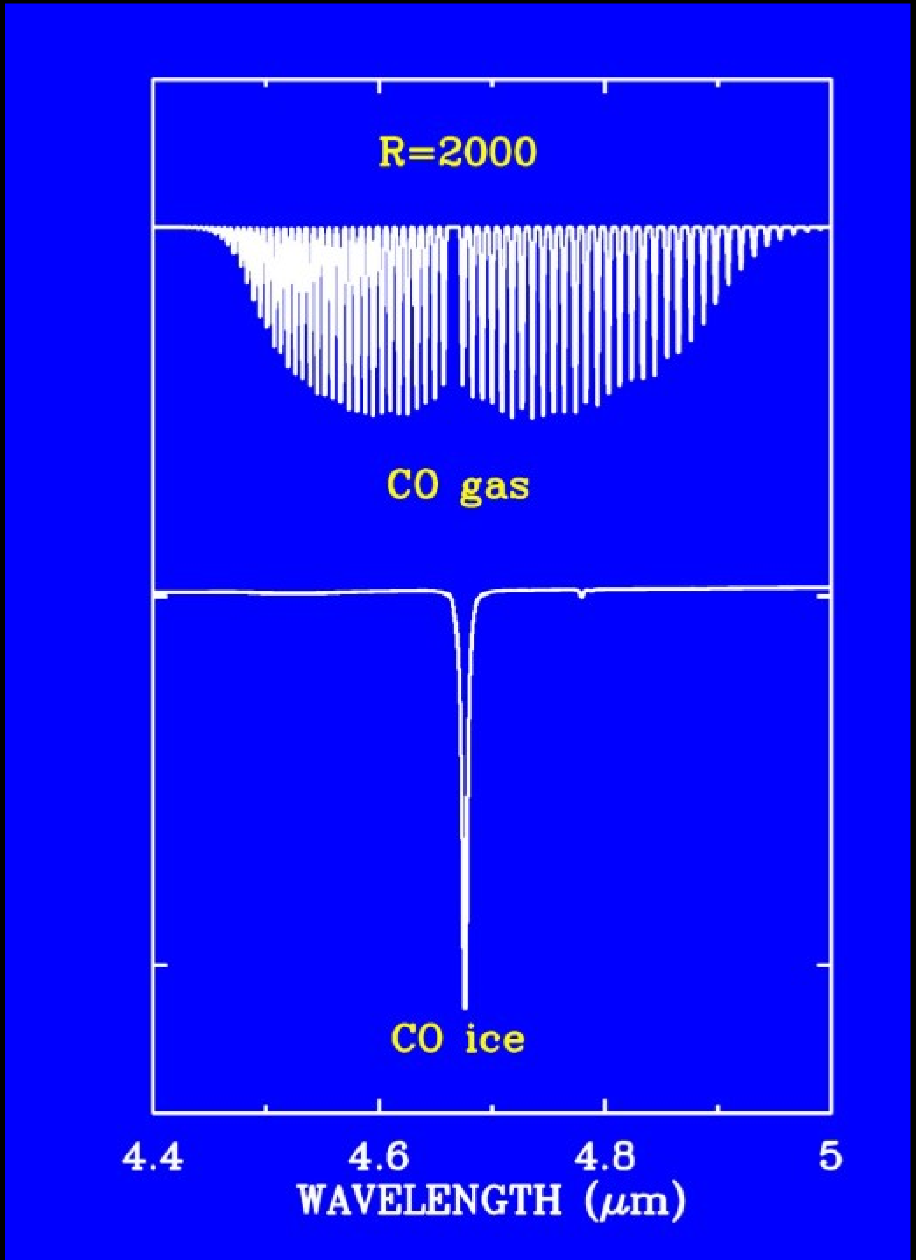


Ehrenfreund et al. 1997

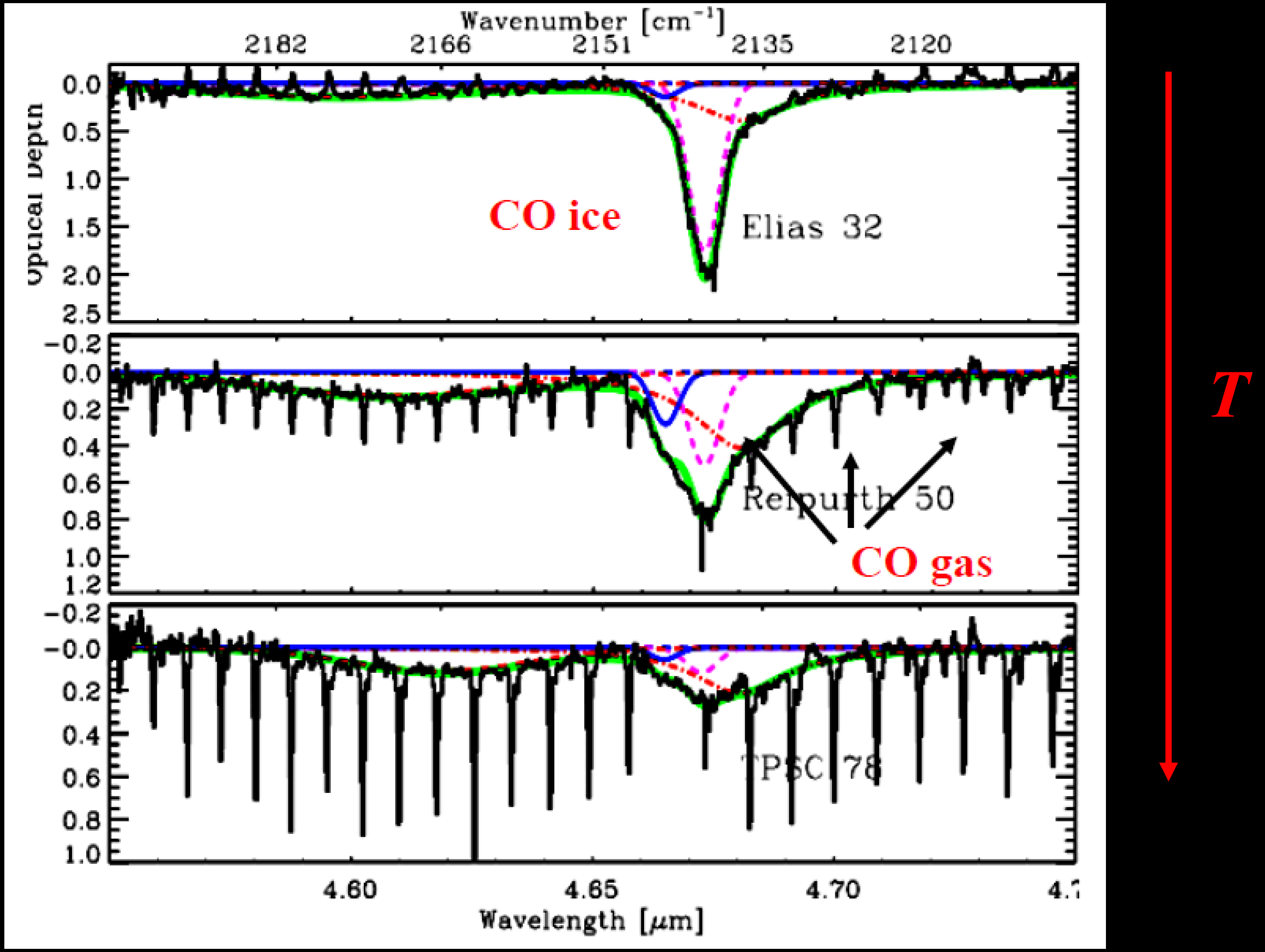
7.5 Warm inner envelope: ice sublimation

- Evaporation of ices directly observed in IR spectra
- Indirectly inferred from sub-mm data as a jump in abundance in inner envelope

Gas vs ice: IR

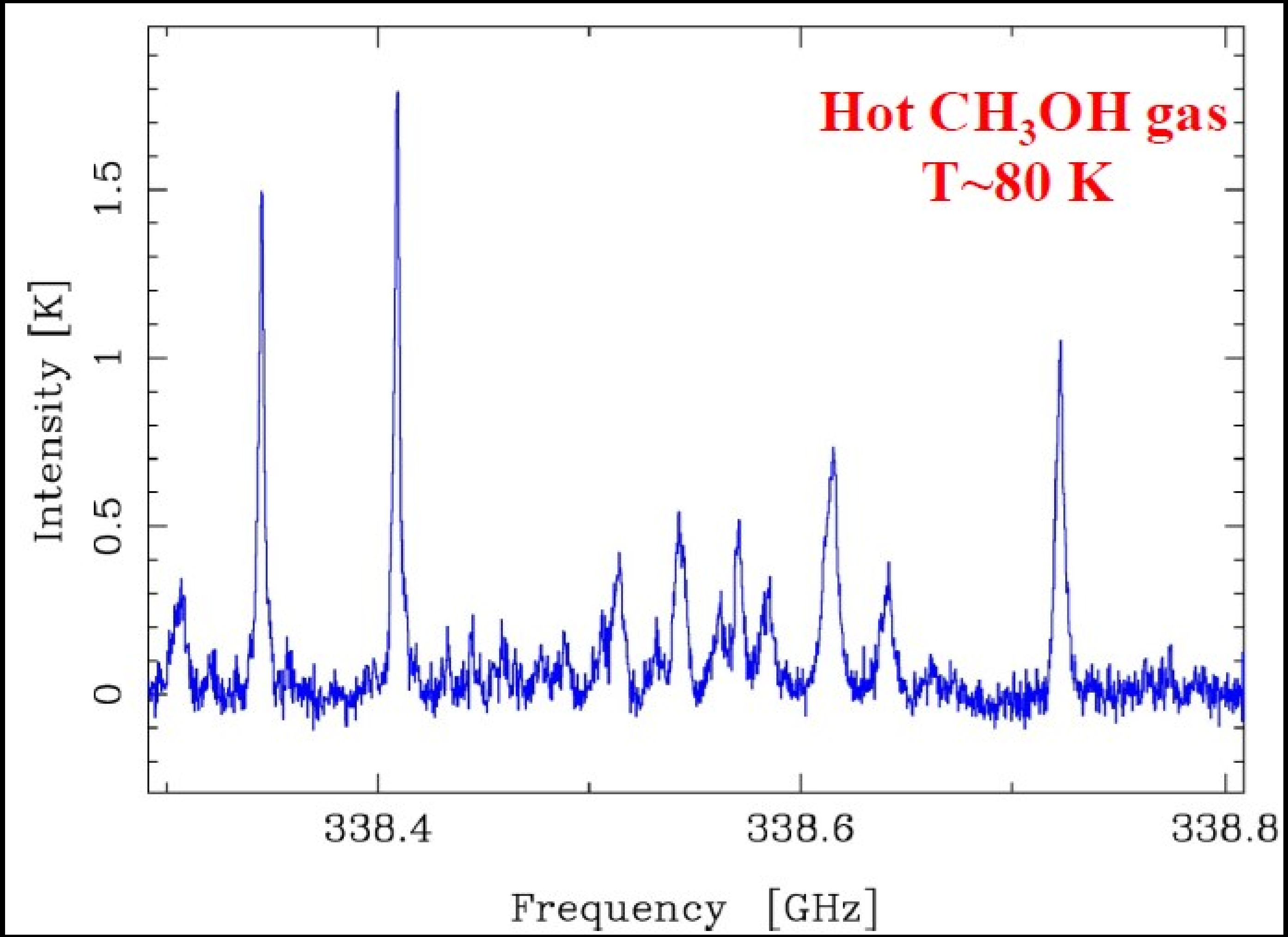


Ice sublimation low-mass YSOs



Pontoppidan et al. 2003

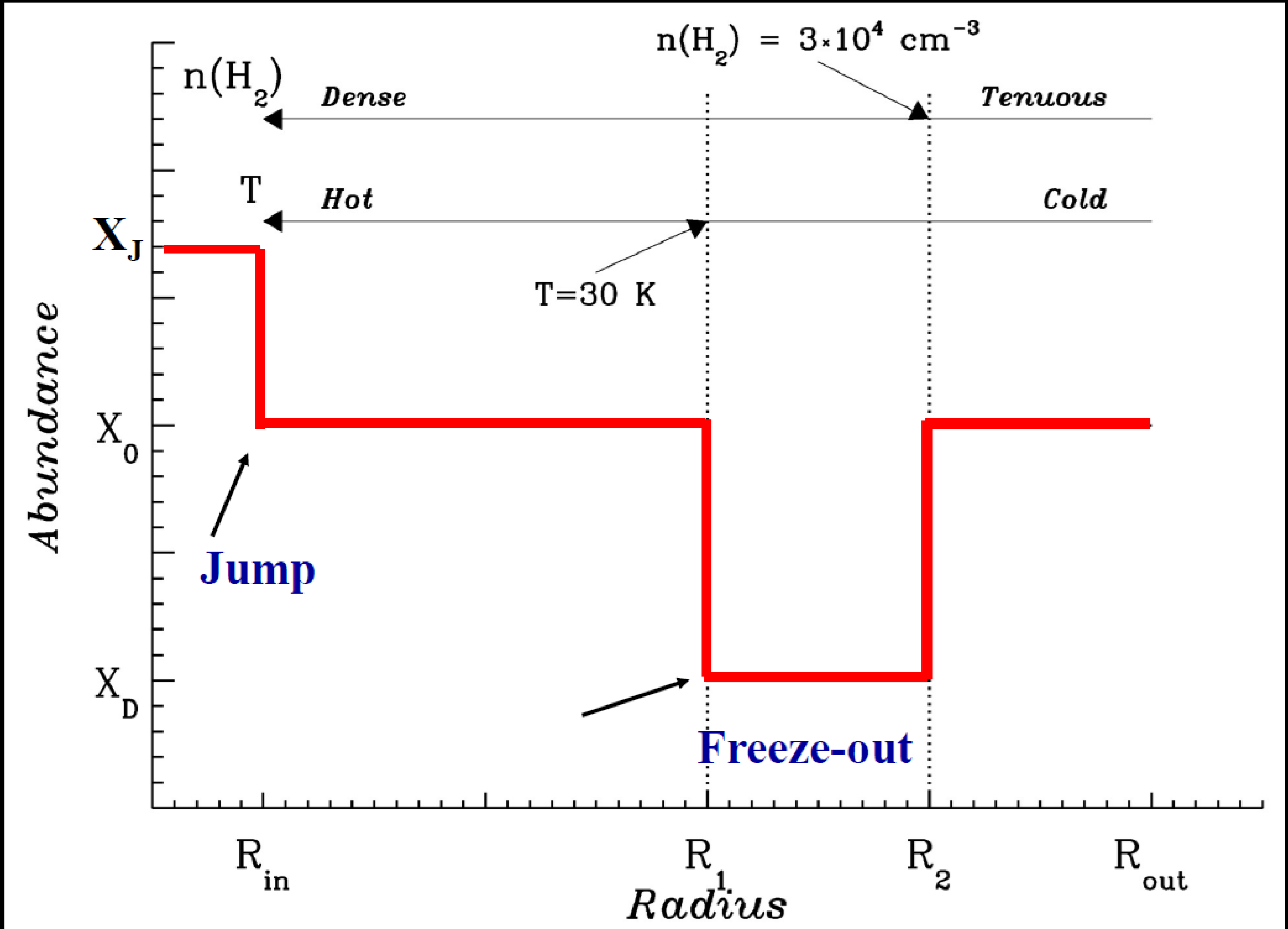
Hot methanol around solar-mass protostar

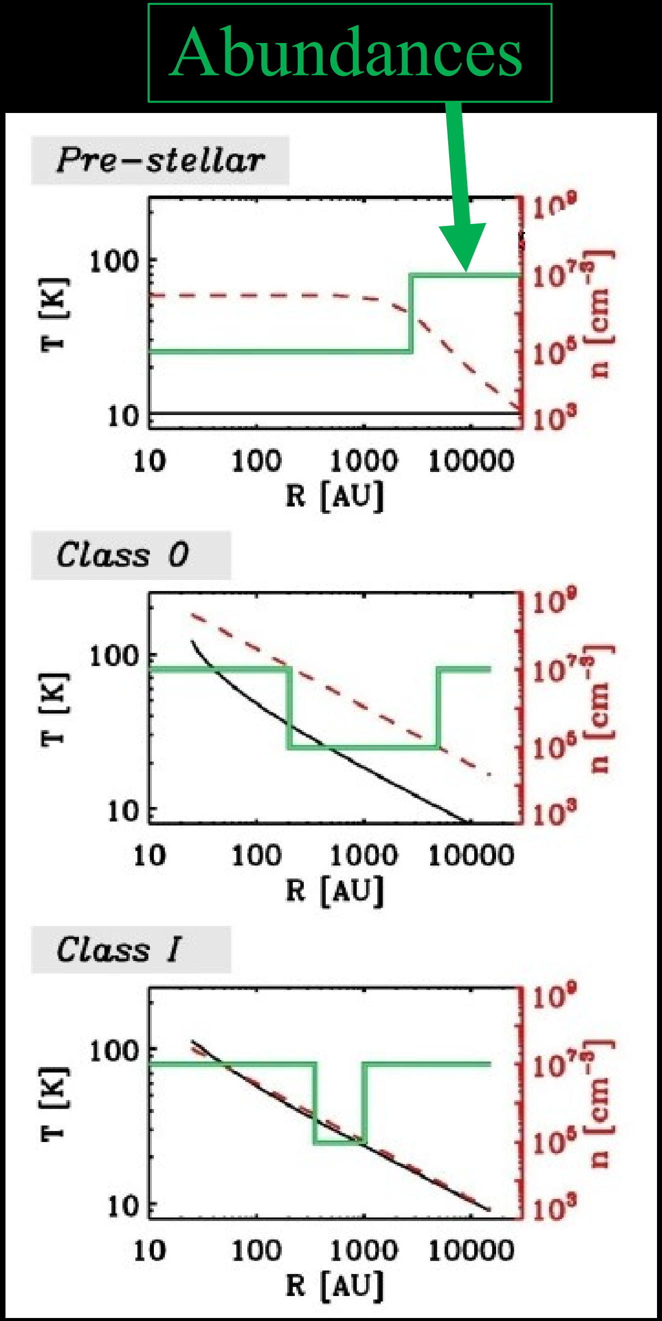


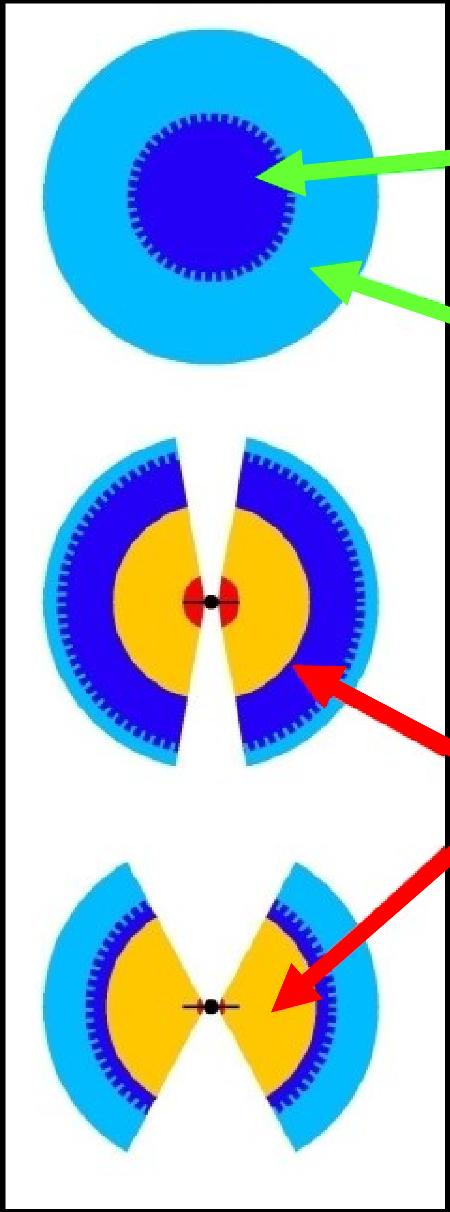
IRAS 16293-2422

van Dishoeck et al. 1995, Ceccarelli et al. 2000

Example: CH_3OH jump abundance structure







- ***Pre-stellar core:***
- Low temperature
- Depletion toward center
- …but not edge

- ***Protostellar core:***
- Central heating ~ temperature gradient
- Thermal desorption
- …outside (low *T*): depletion / no depletion regions as in pre-stellar stages

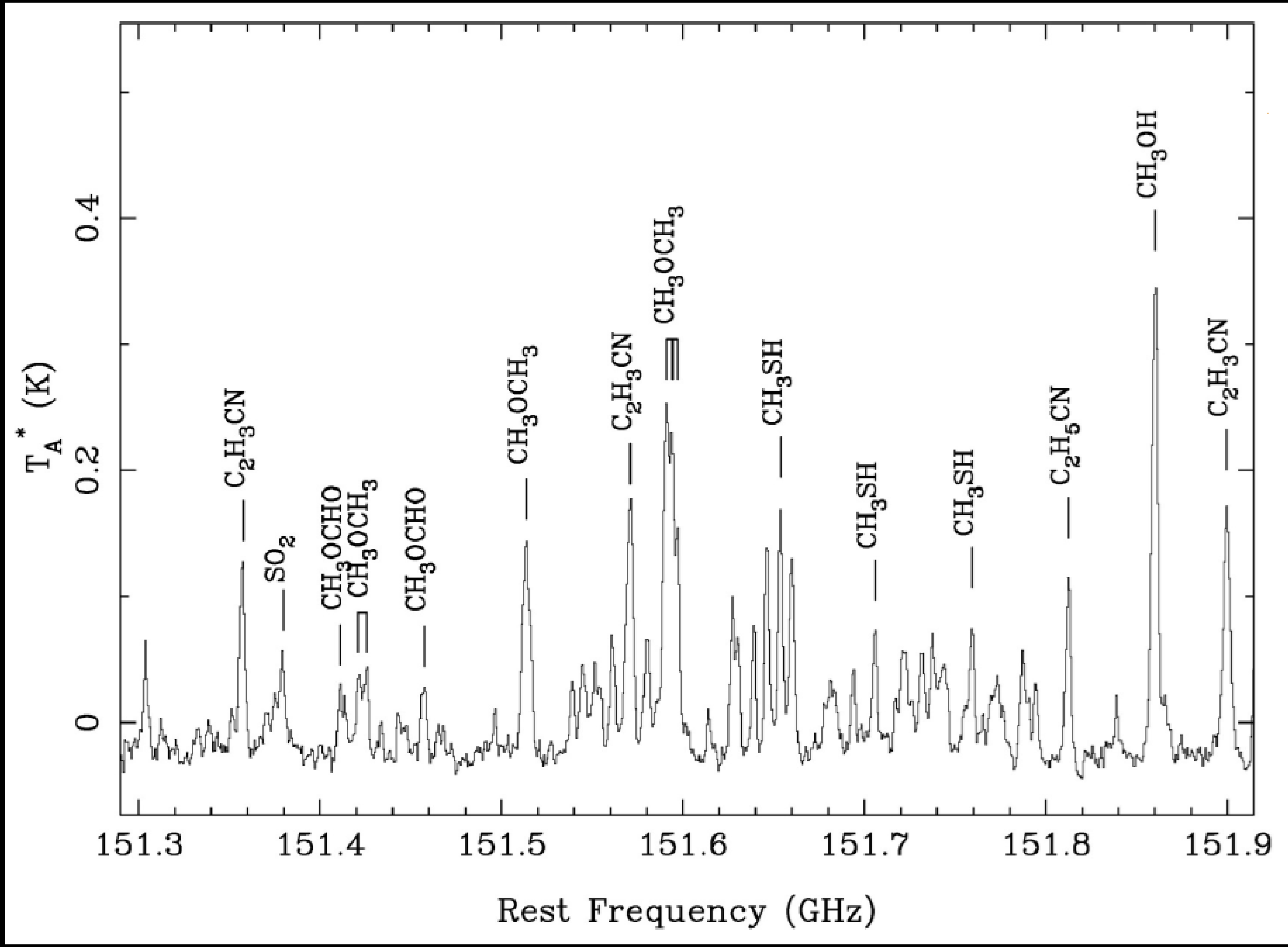
Jørgensen et al. 2005

Q: Can chemistry constrain timescales? Current data suggest phase of heavy depletions (pre+ protostellar) lasts only ~10^5 yr

7.6 Hot cores

- Observations of most high-mass YSOs such as *Orion-KL*, *Sgr B2*… show high abundances of complex saturated organic molecules
- These are called *'hot cores'* with characteristics $T \approx$ 100-200 K, $n \approx 10^7$ cm^{-3}, size < 0.1 pc
- Several low-mass YSOs show a similar chemical complexity
- Traditional view: molecules sublimated from grains into warm gas drive a rapid gas-phase chemistry for ~10^5 yr
  - Initial conditions: ice abundances, as constrained by observations

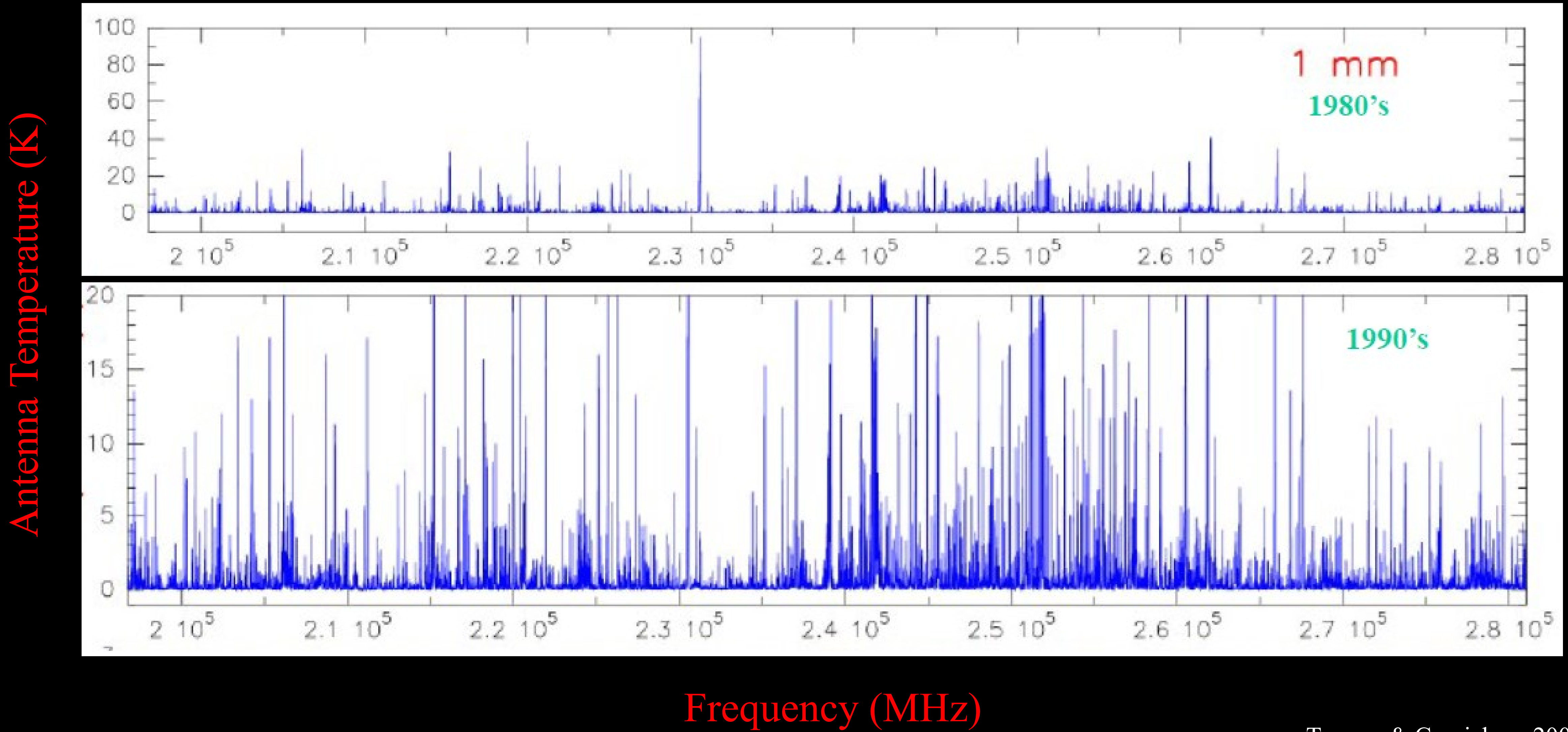
Typical hot core spectrum: Signpost of massive star formation



G327.3
Massive YSO

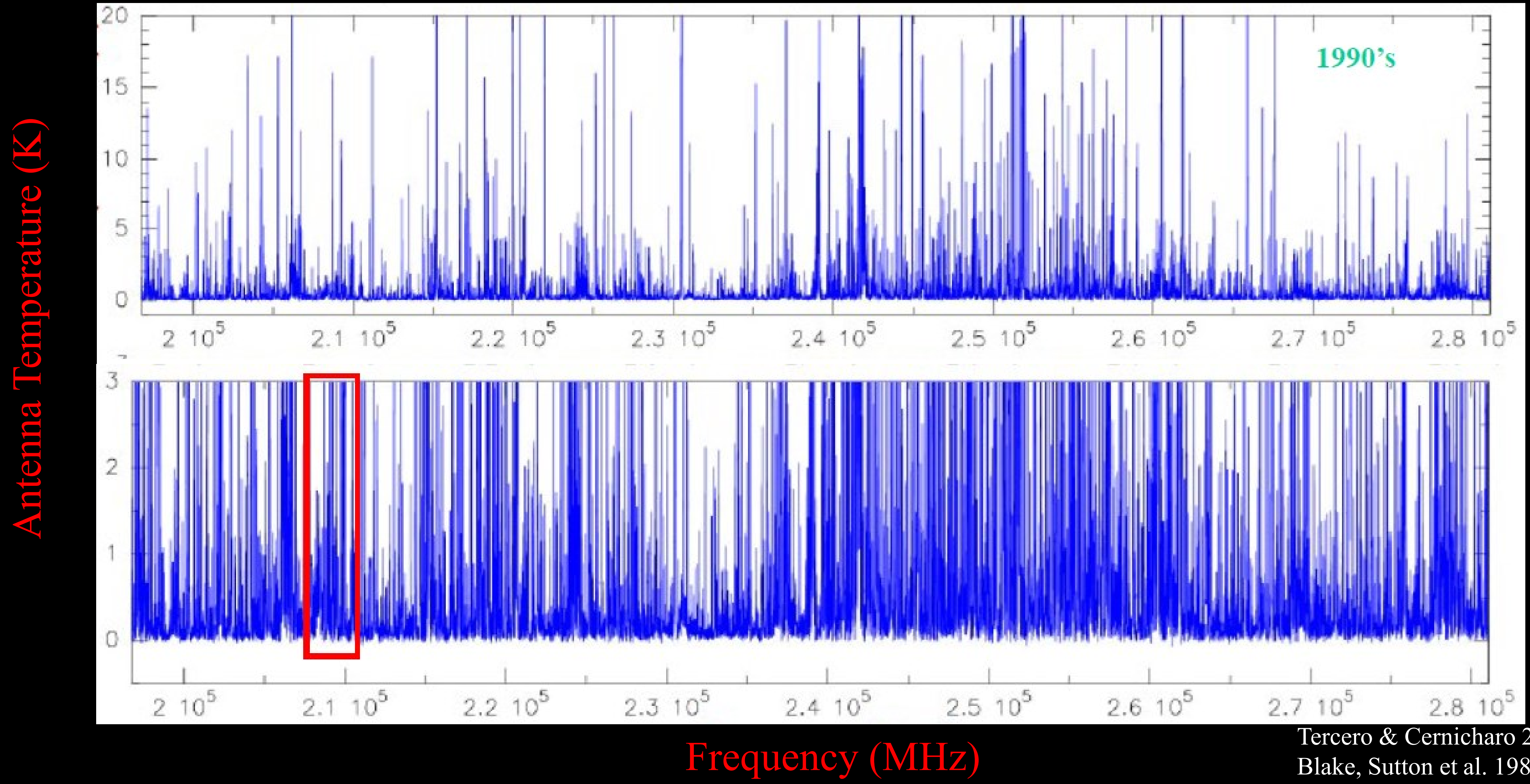
Gibb et al. 2000

Orion line surveys



Tercero & Cernicharo 2007
Blake, Sutton et al. 1985
Schilke et al. 1993, 1997
Crockett et al. 2014 Herschel HIFI

Orion line surveys



Tercero & Cernicharo 2007
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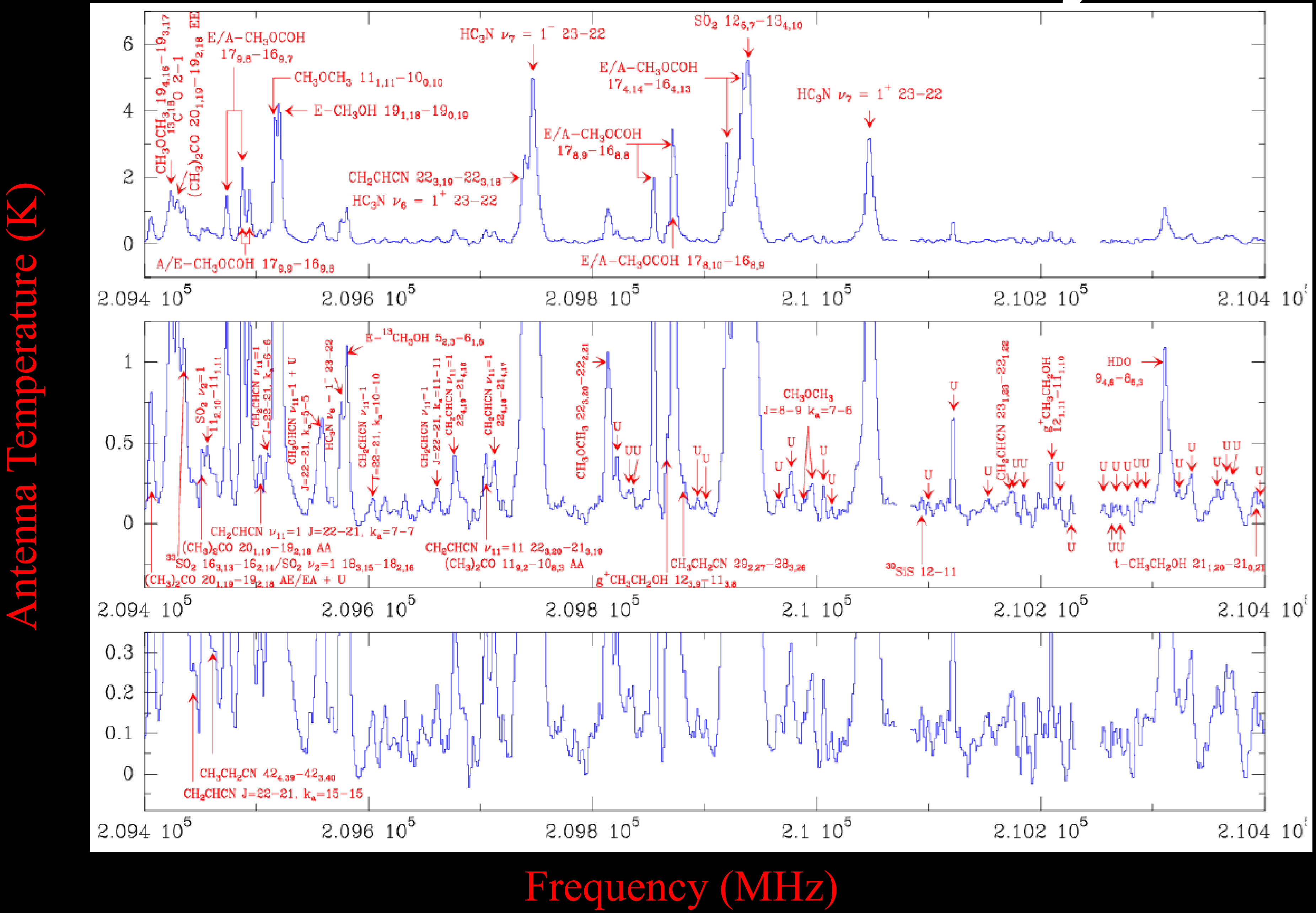
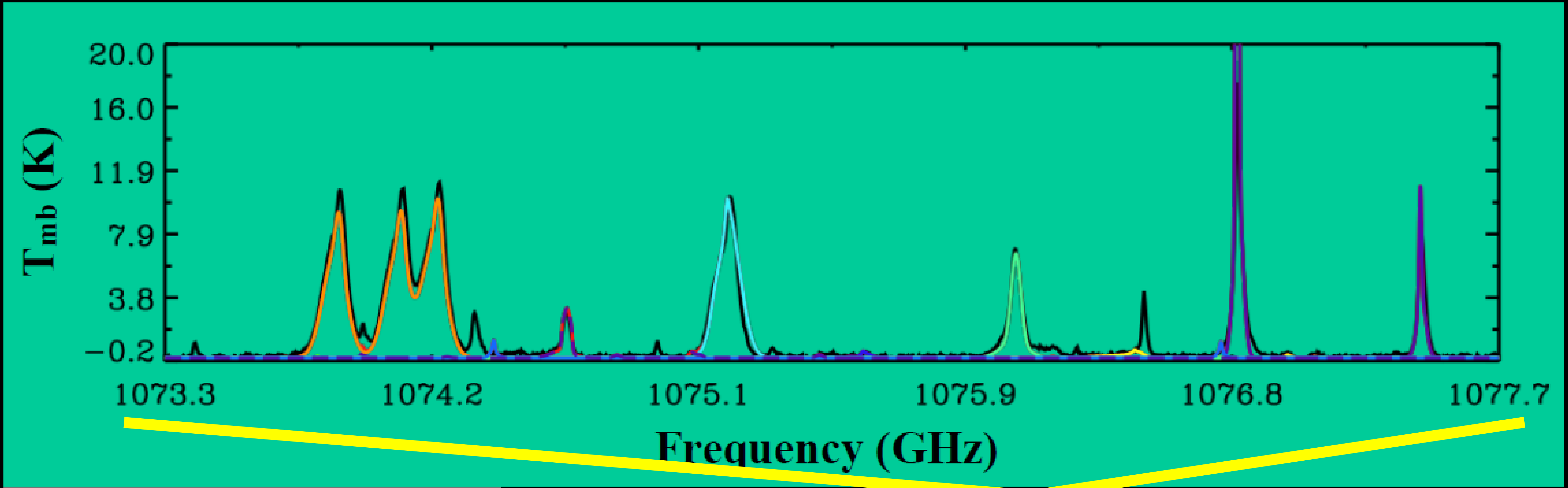
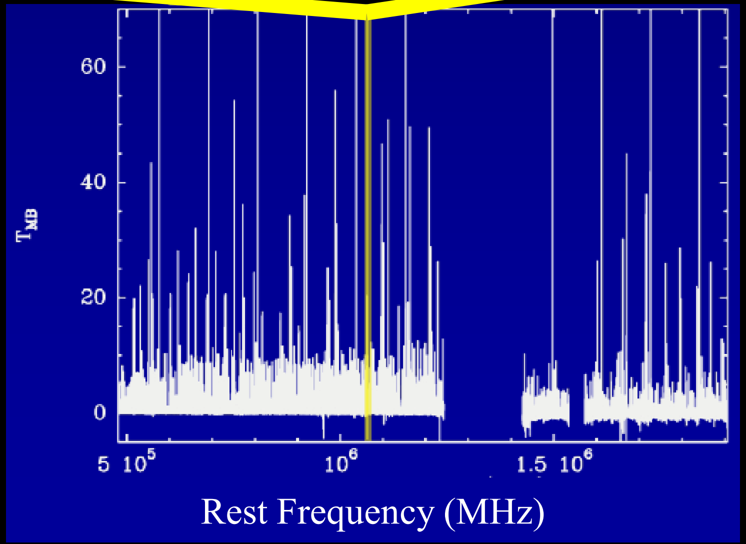
Orion line surveys



Q: How far does chemical complexity go? Prebiotic molecules?

Identifying and modeling emission



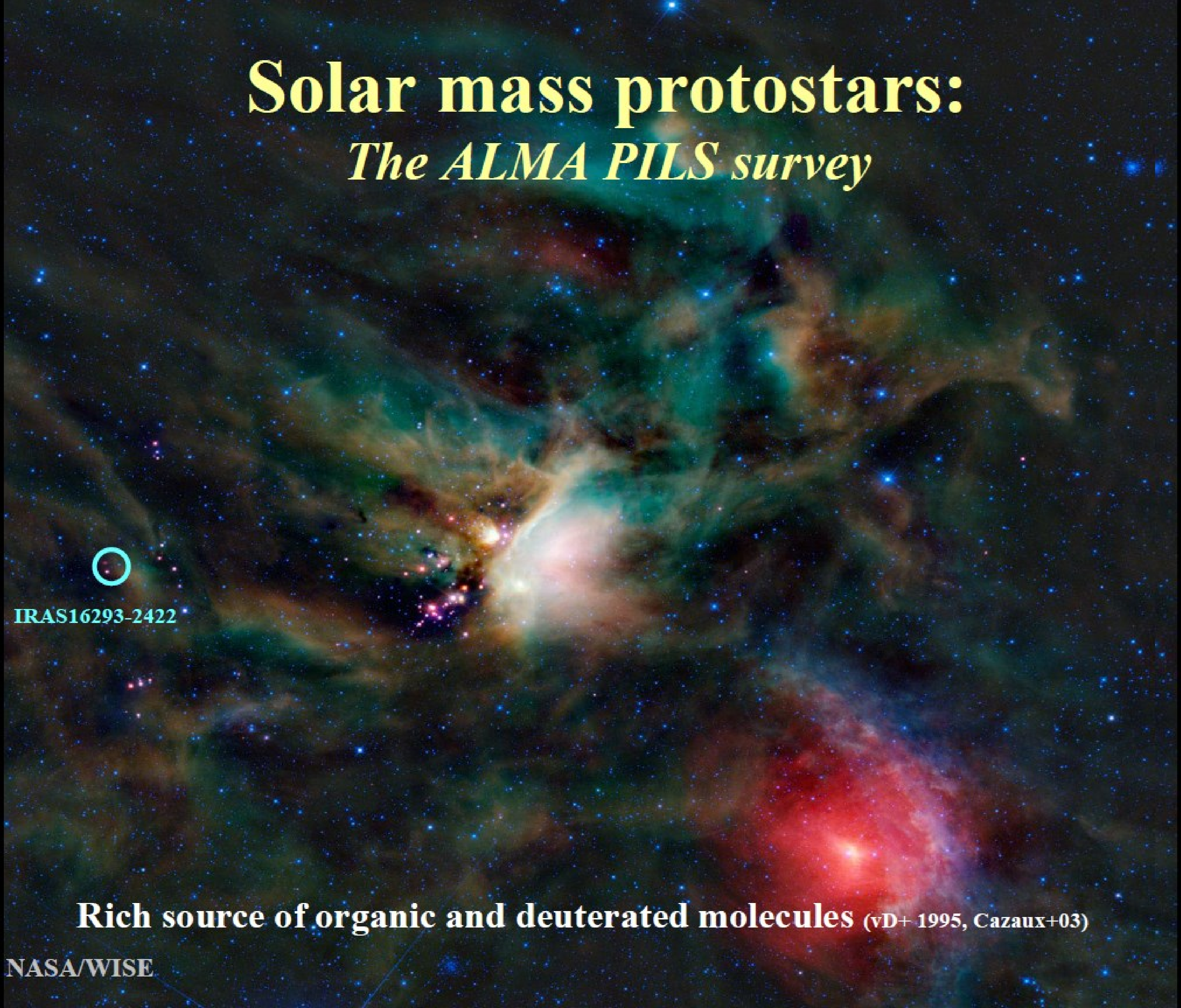


Crockett, Neill, Bergin et al. 2014, 2015

Solar mass protostars:

The ALMA PILS survey

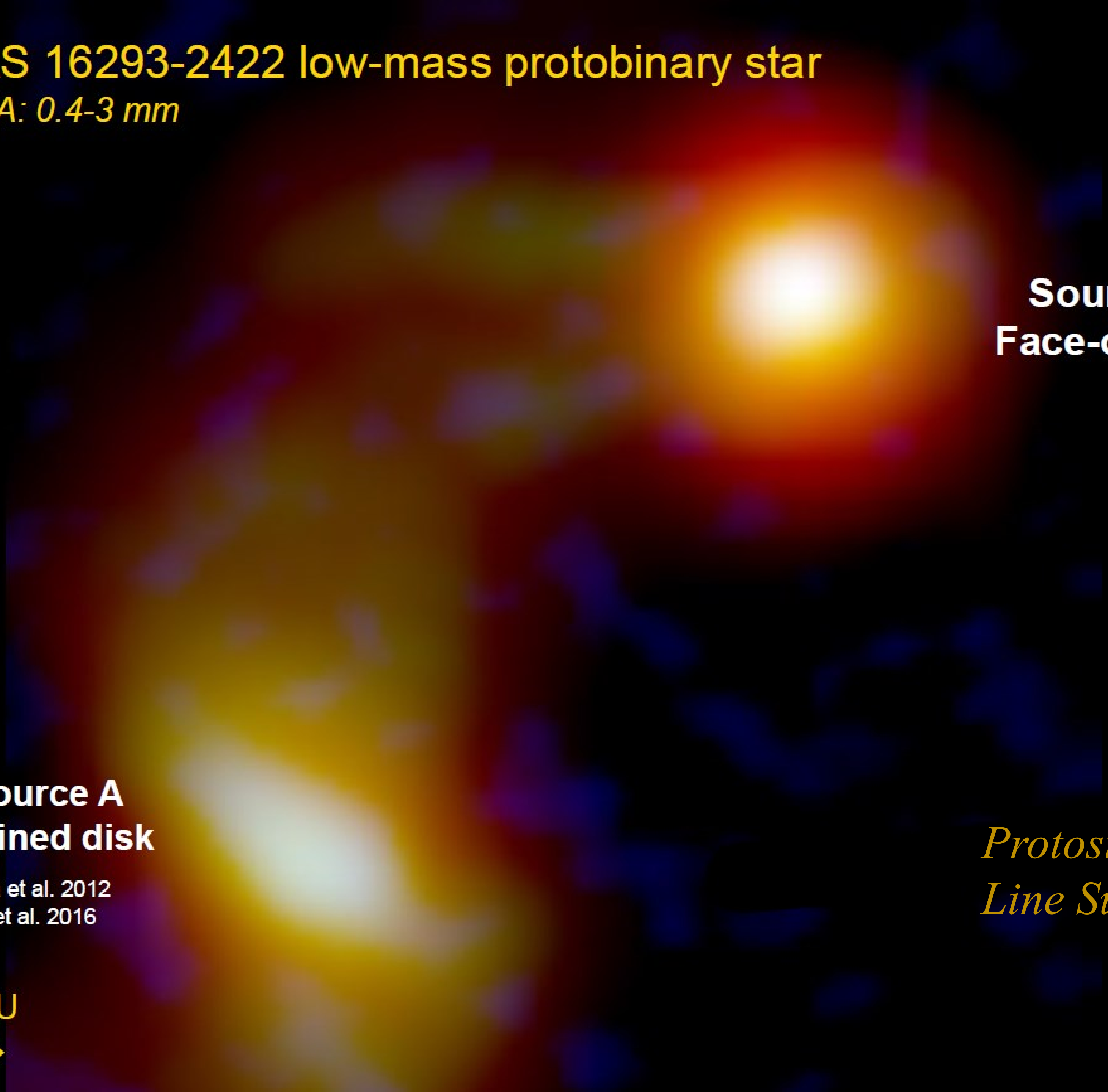
Ophiuchus d=125 pc low-mass star-forming region



Rich source of organic and deuterated molecules (vD+ 1995, Cazaux+03)

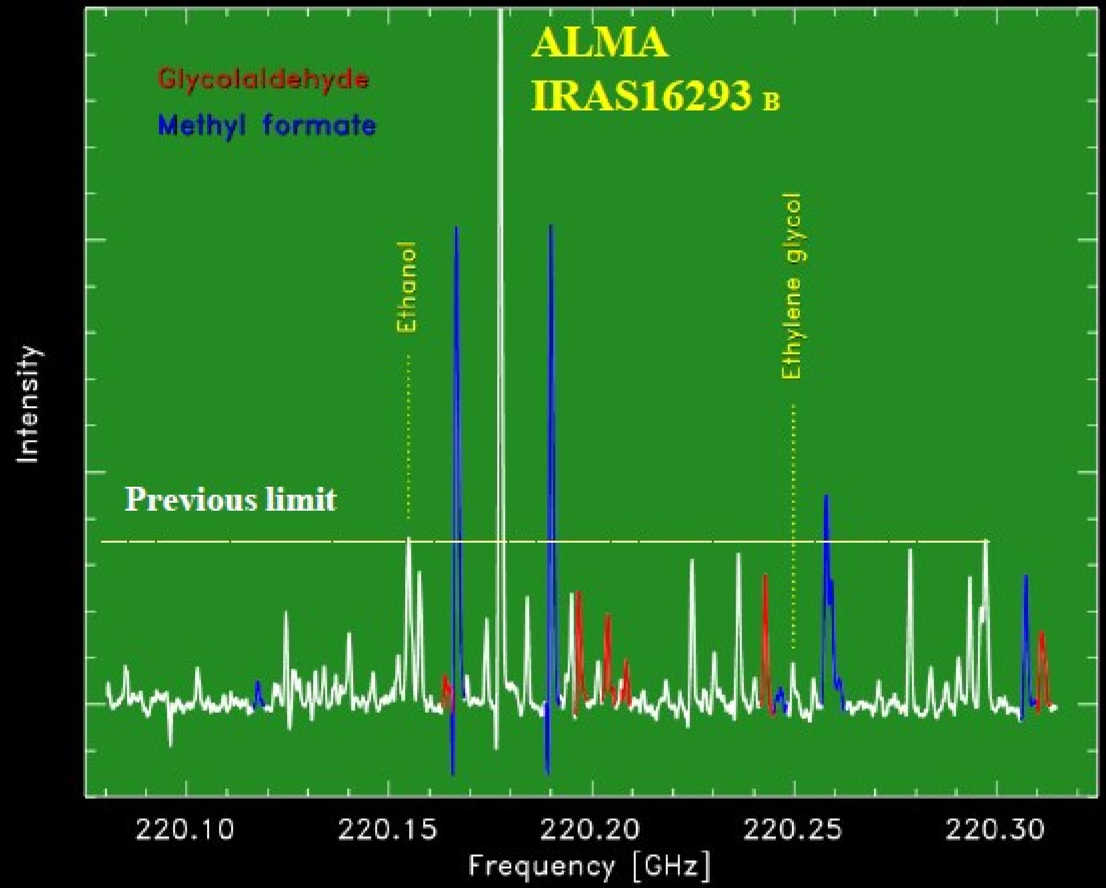
IRAS 16293-2422 low-mass protobinary star

ALMA: 0.4-3 mm



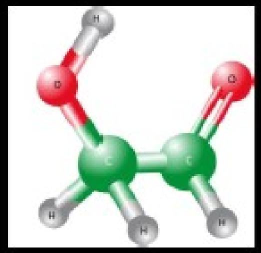
Protostellar Interferometric Line Survey (PILS)

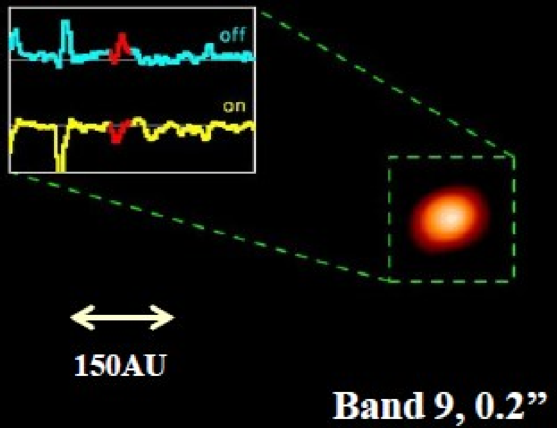
Detection of sugar near low-mass protostar



Detection of glycolaldehyde and ethylene glycol in first ALMA science verification data

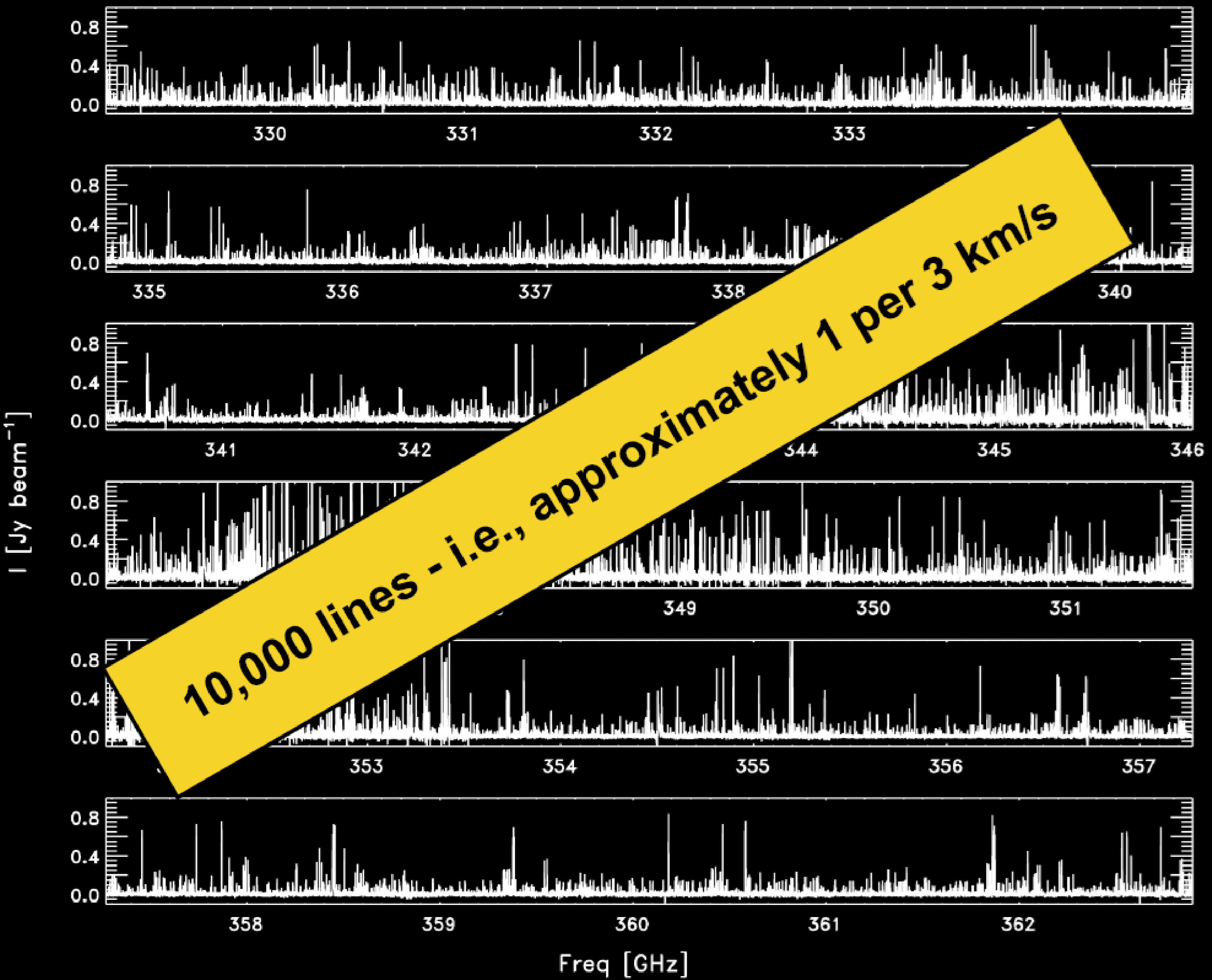
Jørgensen et al. 2012





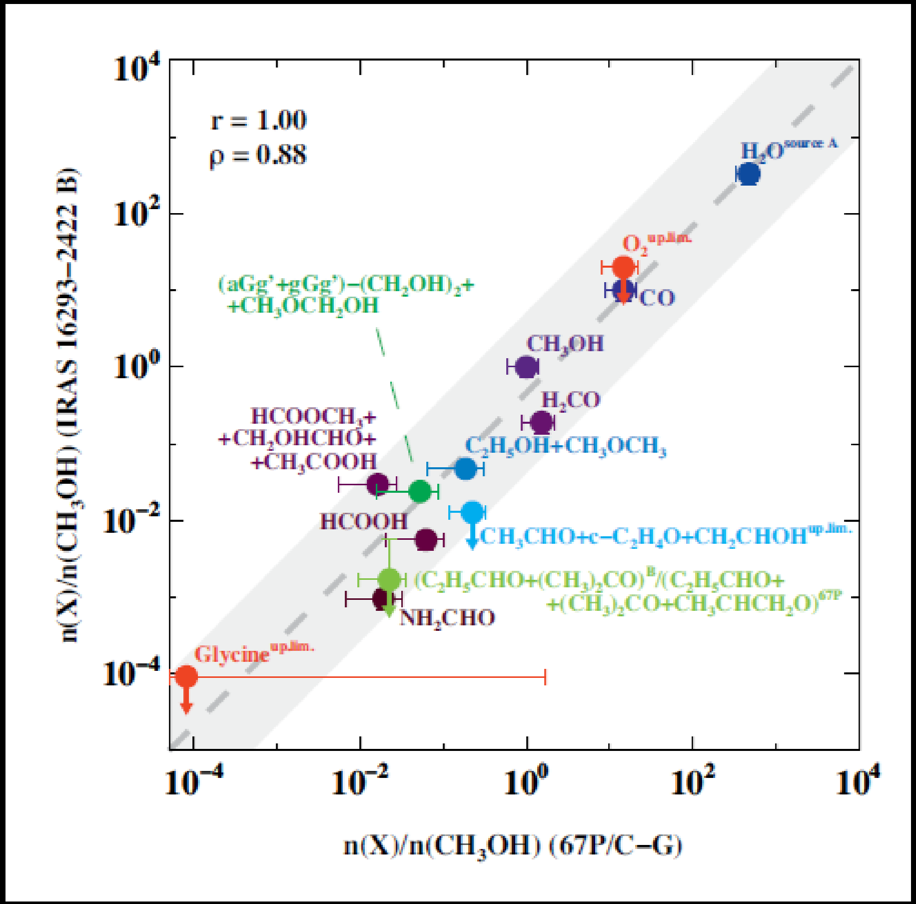
Complex molecules found on solar system scales (orbit of Uranus, 25 AU)

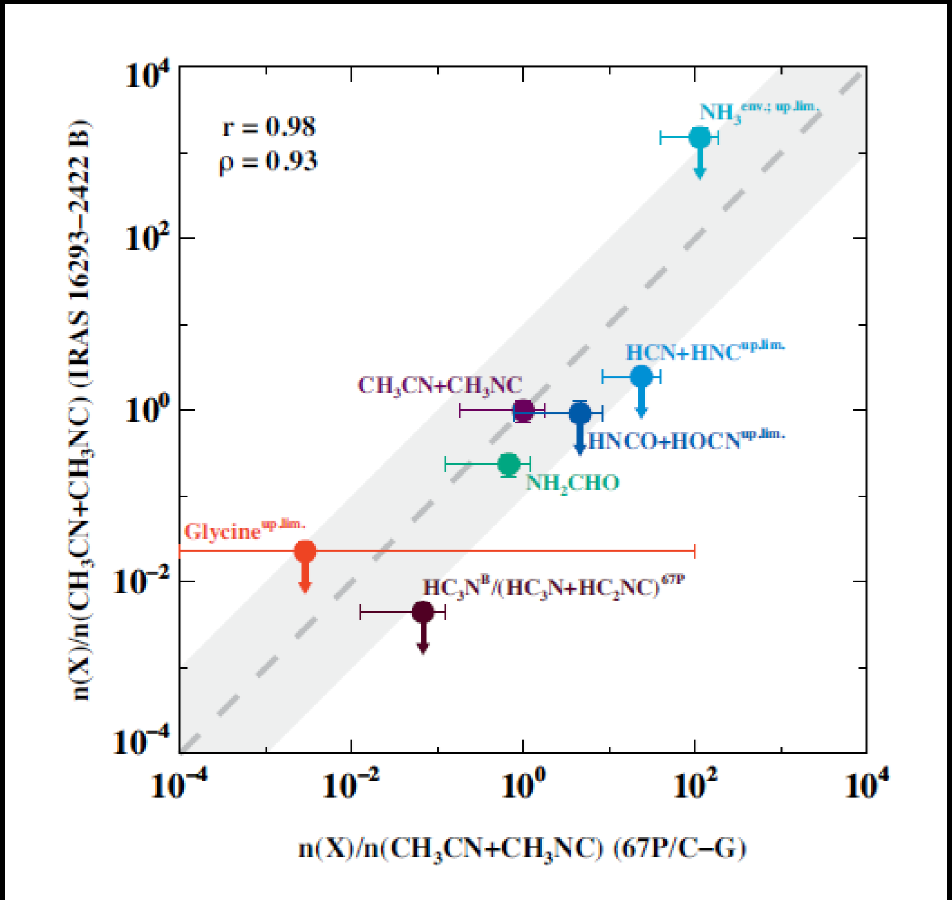
Full spectral survey of IRAS 16293-2422



Jørgensen et al. 2016

Protostellar chemical fingerprint

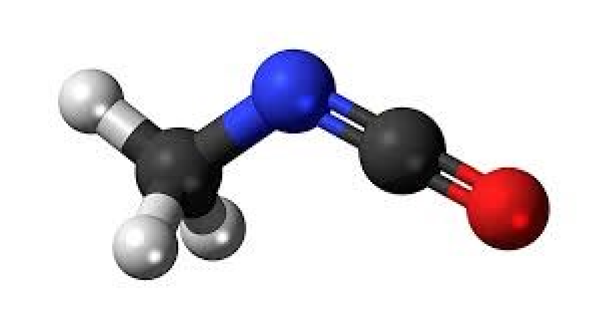




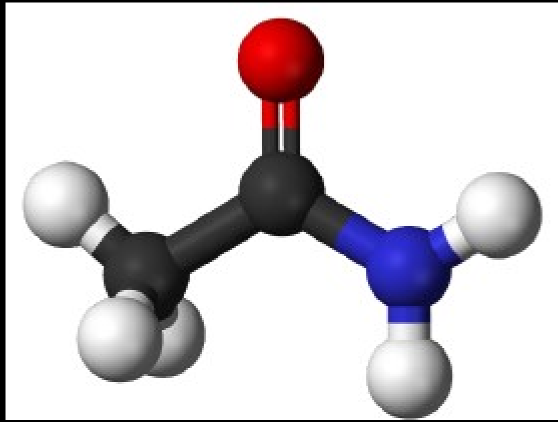
- More than 100 molecular species (including isotopologues)
- Dozens of new detections toward low-mass protostars (so far)
- Correlations with abundances from Comet 67P

Drozdovskaya et al. 2019

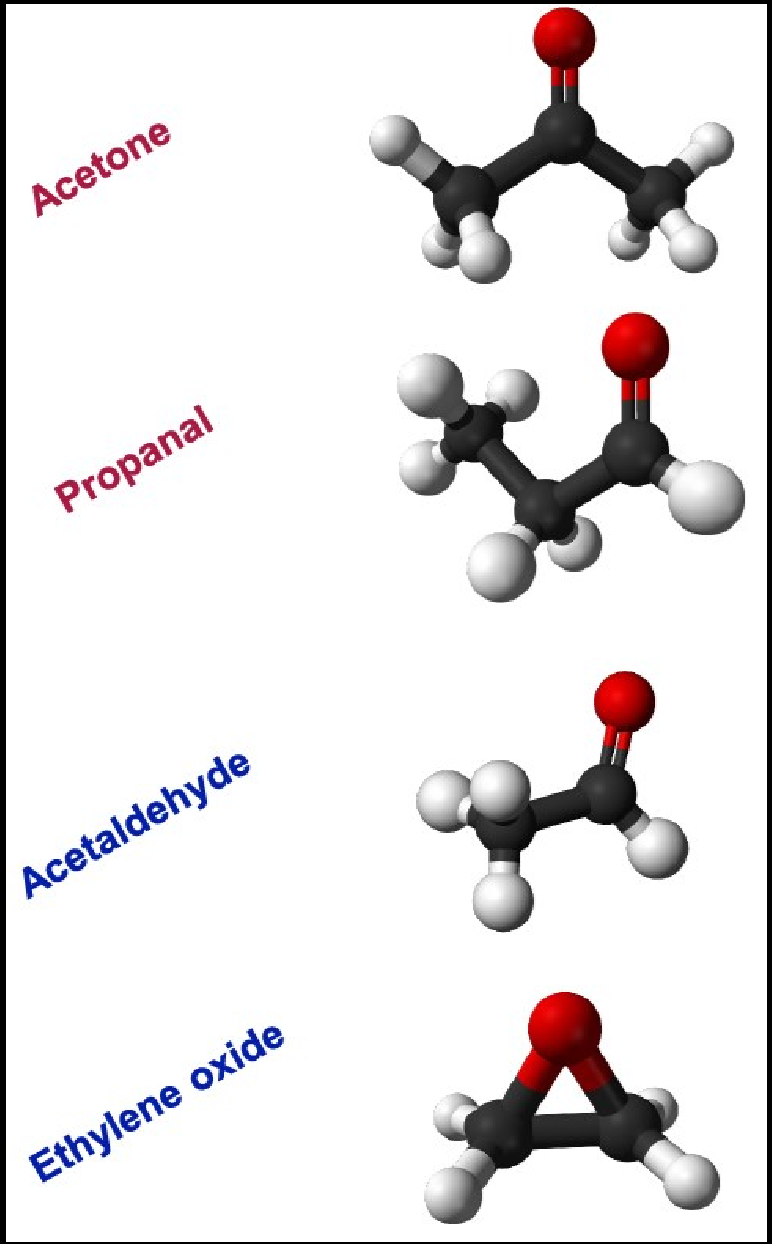
Complex molecules on solar system scales



Methyl isocyanate
'Prebiotic' molecule

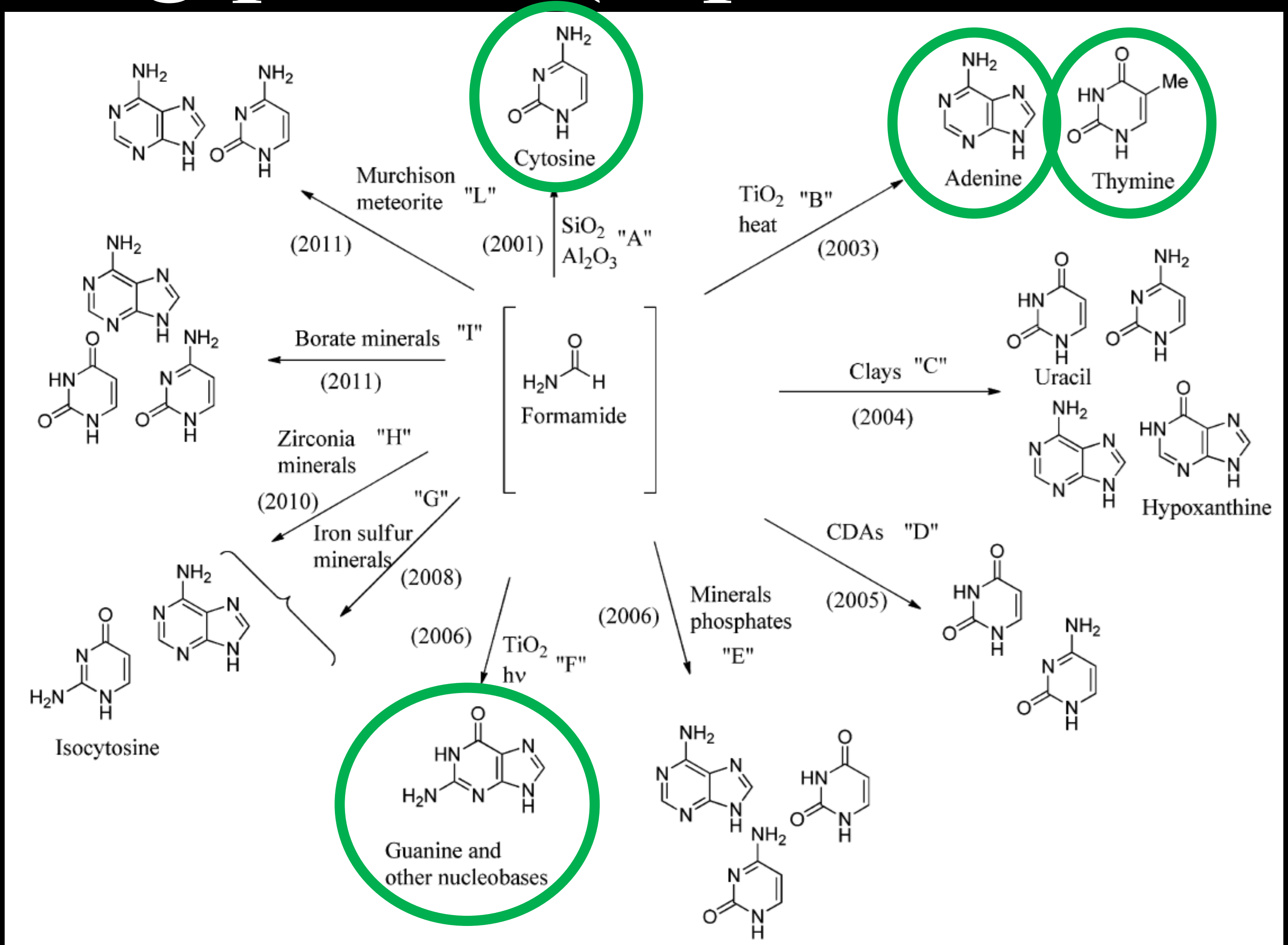


Acetamide
(but no glycine yet)



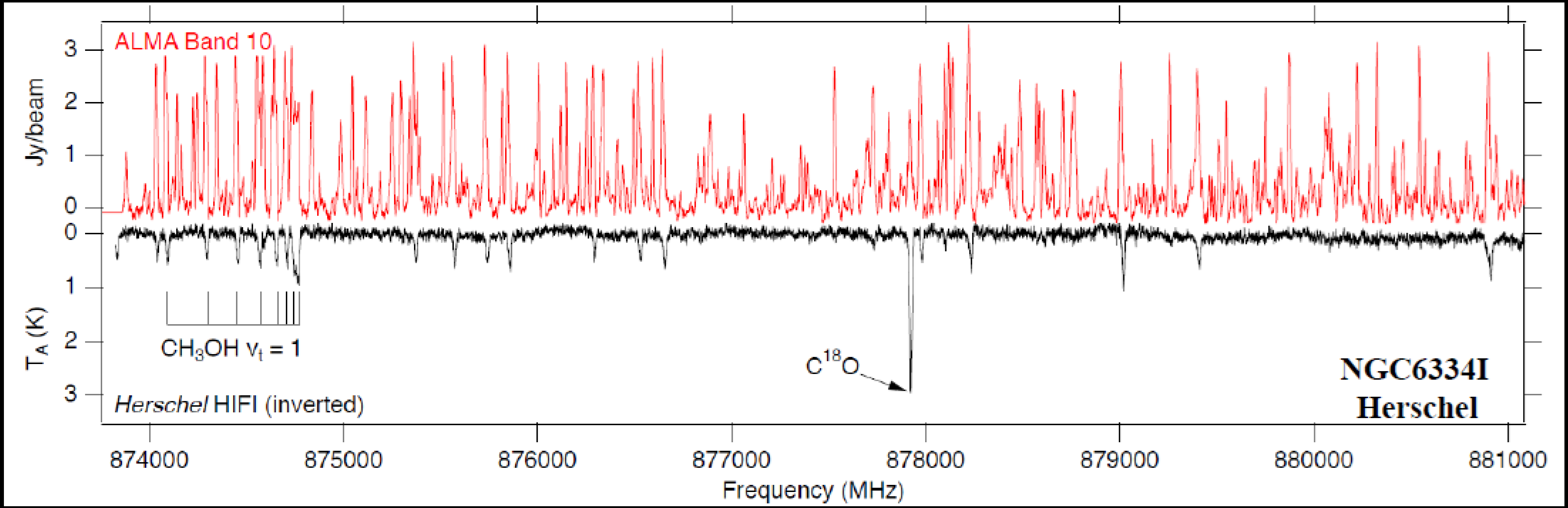
Lykke et al. 2017
Ligterink et al. 2017
Martín-Domenéch et al. 2017
Ligterink et al. 2018

From formamide to amino acids and bases on a young planet (liquid water, clays...)



Saladino et al. 2012

The ALMA revolution: sensitivity to small scale emission

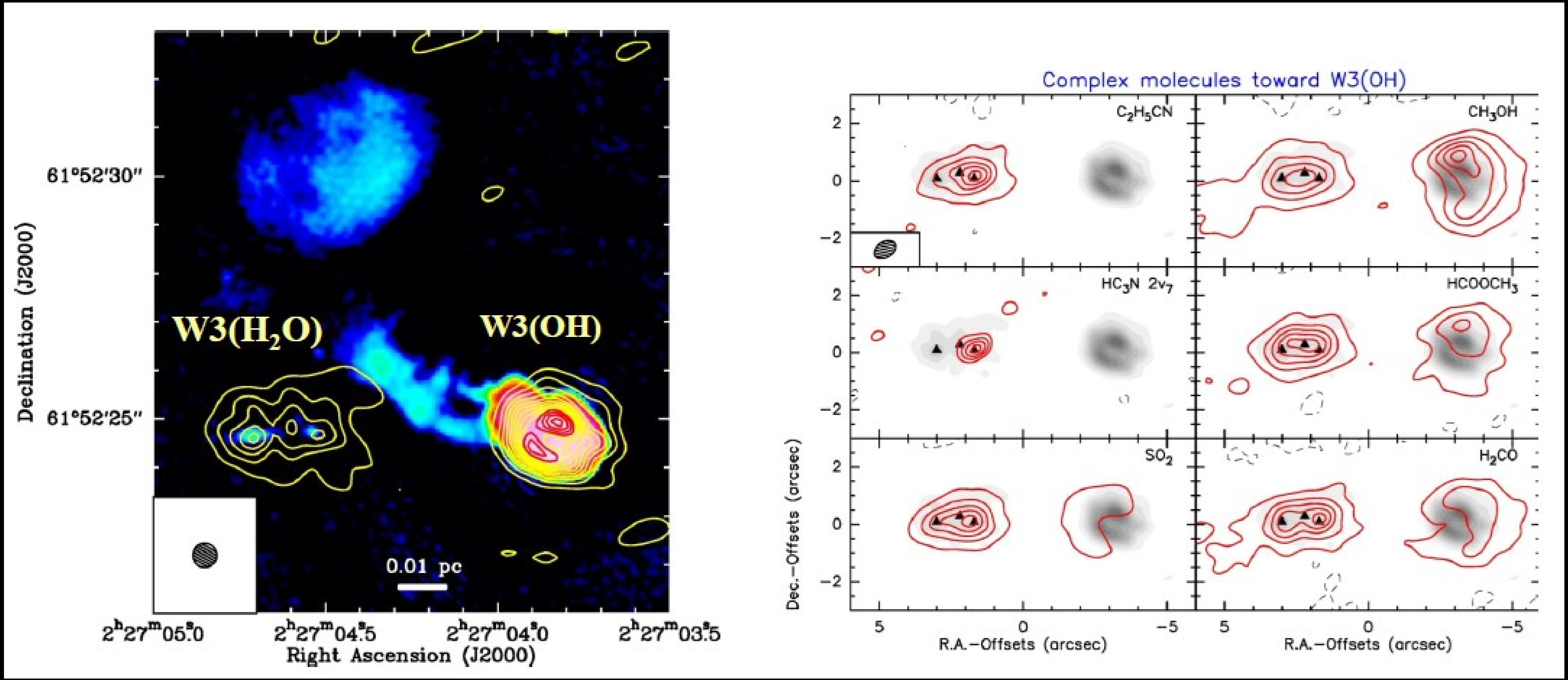


High-mass star-forming region

McGuire et al. 2019
Bogelund et al. 2019

Chemical differentiation on small scales

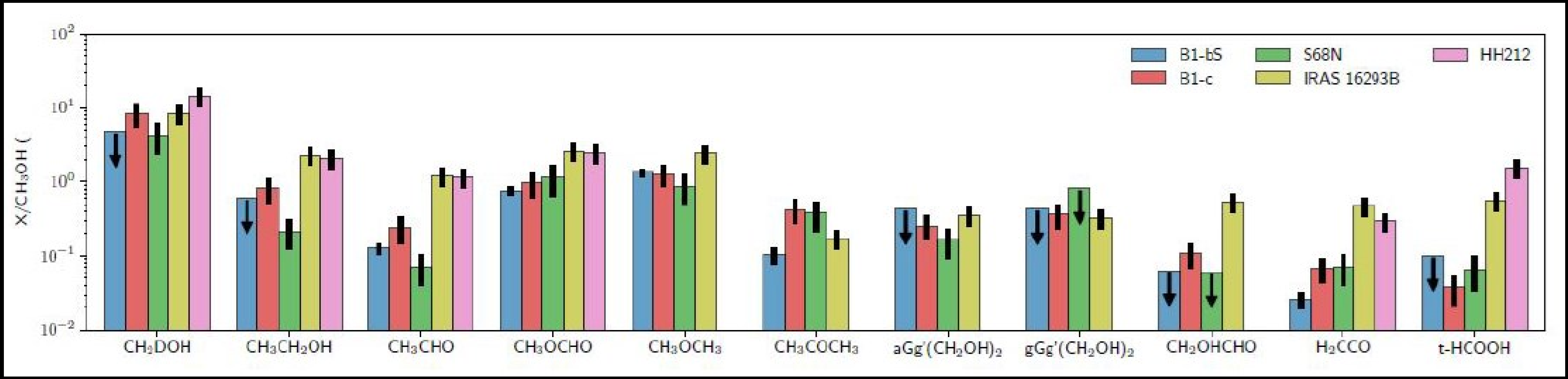
High-mass protostars



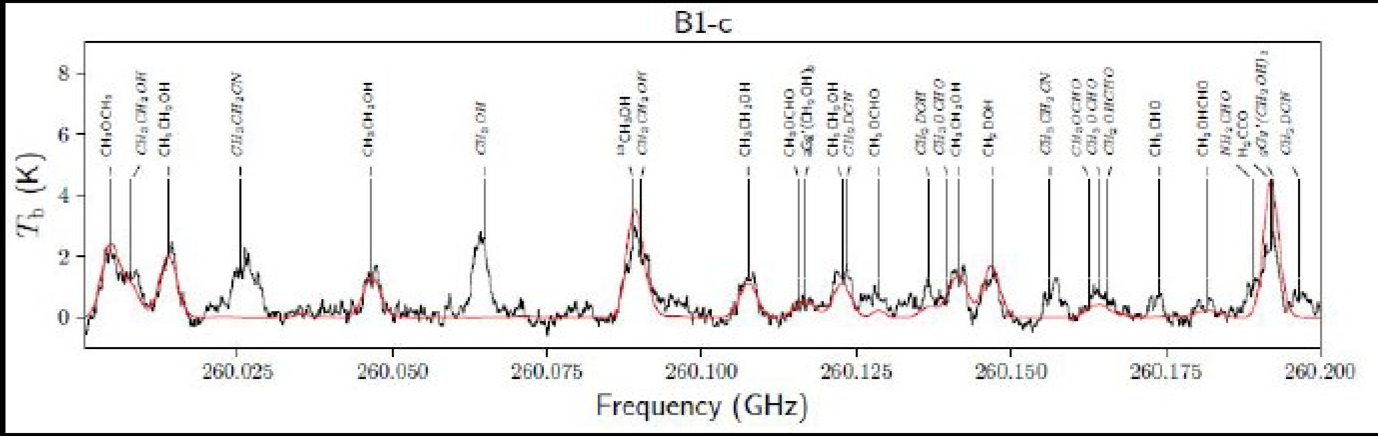
- Chemical differentiation between O- and N-rich complex organics on few arcsec scale (few hundred – few thousand AU) – different ages and formation

Wyrowski et al. 1999
Bisschop et al. 2007

Similar COM abundances among low & high mass stars



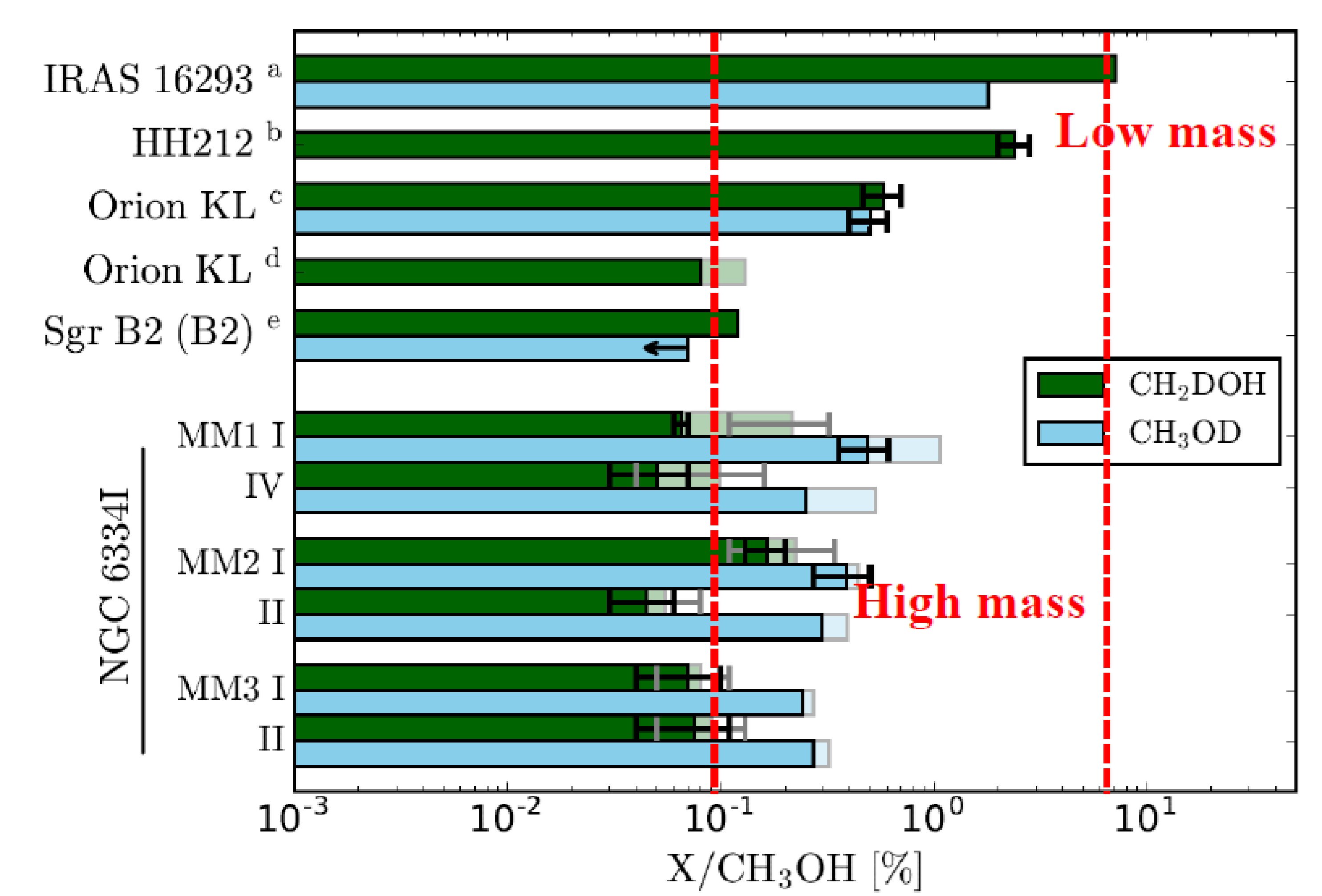
Perseus
Serpens
Ophiuchus
Orion



B1-c
Low-mass protostar

van Gelder et al. 2020
Bogelund et al. 2019

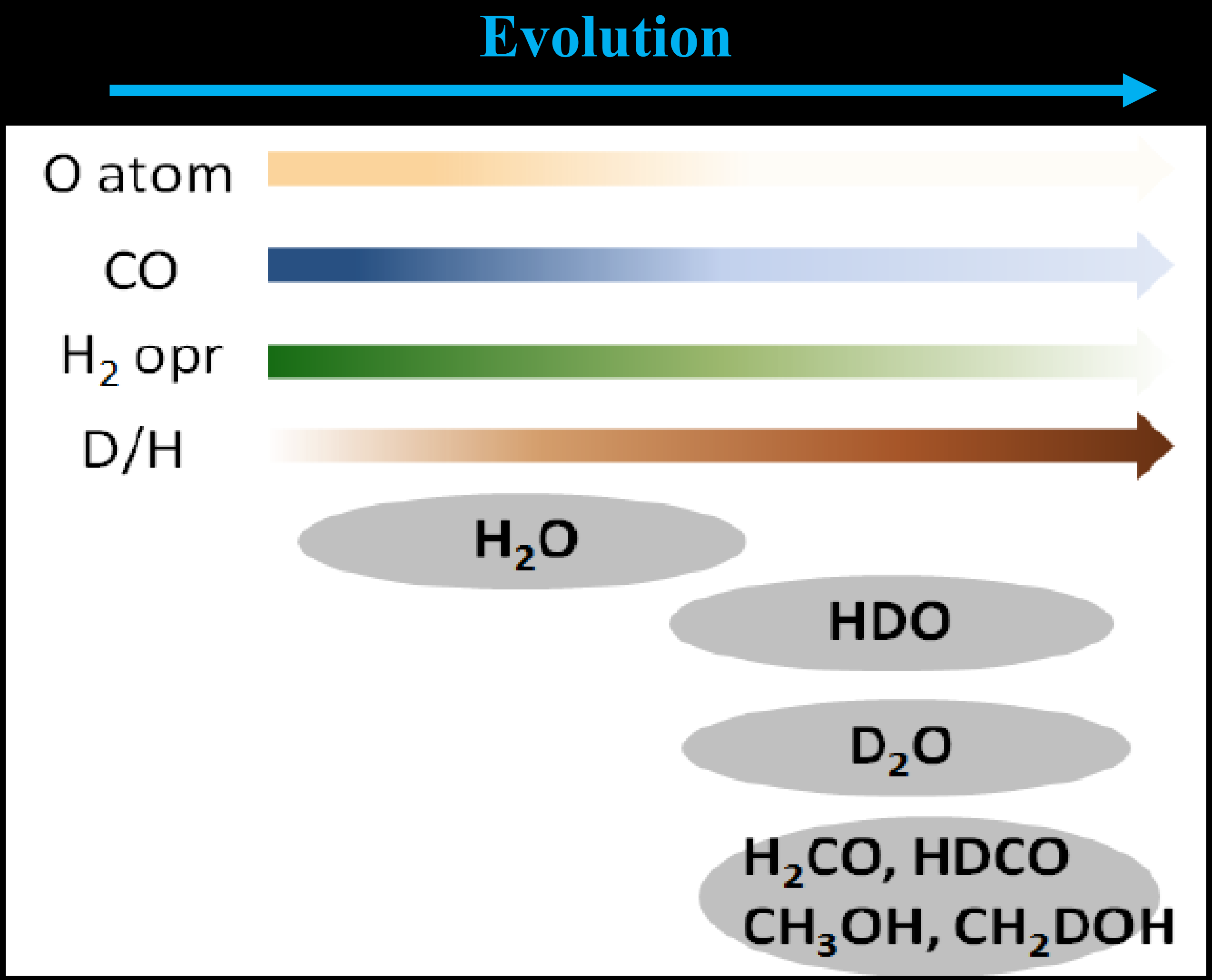
Low vs high mass deuteration



- Much lower deuteration in high mass sources
- Higher temperature effect?

Bogelund, Taquet, et al. 2018

Highly deuterated COMs



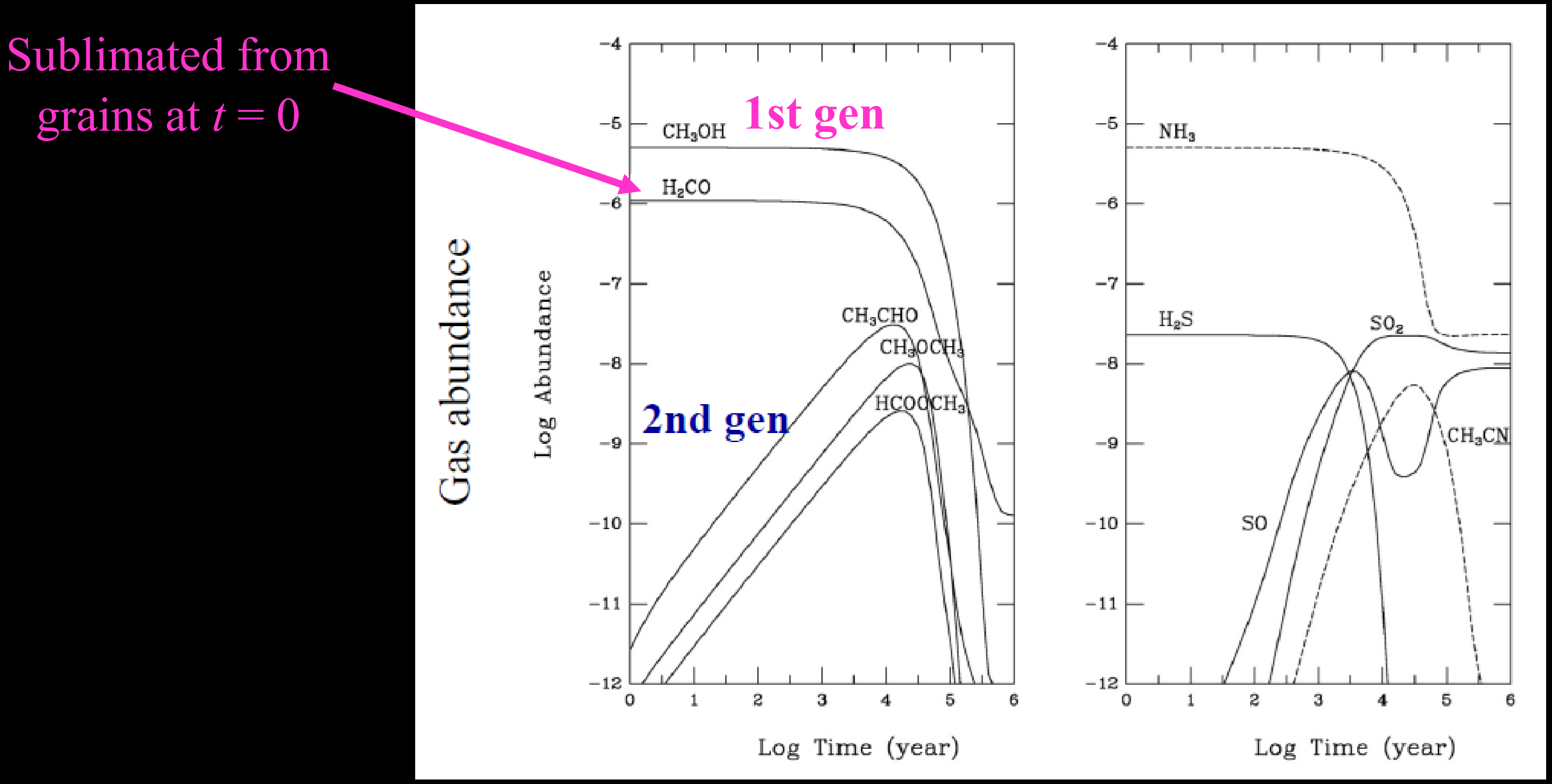
Time

Temperature

- COMs much higher level of deuteration than water

Taquet et al. 2014
Furuya et al. 2015

Traditional hot core chemistry



Charnley et al. 1992, 1997

- Hot gas-phase chemistry starting at $t = 0$ from sublimated ices
- Which complex organics are 'first generation' made in the ices, and which are 'second generation' produced in the gas?
- Can complex organics, e.g., CH_3OCH_3/CH_3OH be used as chemical clocks?
- In this scenario, differences between sources may be explained by different initial ice composition or different 'age' (evolutionary stage)

New insights

- Hot core gas-phase **'second generation'** models can no longer quantitatively reproduce observations of some complex organics because of new laboratory rates (e.g., DR branching ratios)
- Similarity in abundance *ratios* across wide range of sources requires a mechanism which does not critically depend on specific time or conditions
- Several complex molecules can already be formed in cold clouds at ~10 K.
- Ice processing by UV (=> produce radicals) at somewhat elevated temperatures (20-40 K) also produces many complex molecules
  - Radicals become mobile at higher *T*

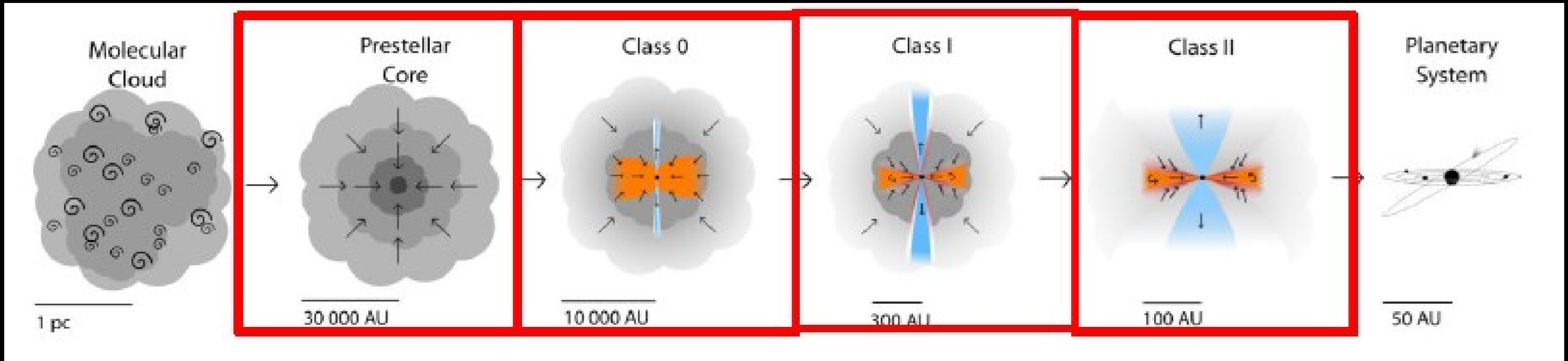
Origin of complex organics

- *Zeroth generation:* formed on ices in cold (~10 K) dark clouds: CH_3OH + more?
- *First generation:* formed in ices by reaction with radicals at slightly elevated temperatures (20-40 K)
  - Needs a little UV to produce radicals, e.g., by cosmic-ray induced photons
- *Second generation:* formed in hot (> 100 K) gas from reactions with sublimated species

Herbst & van Dishoeck 2009

Complex organic molecules

- Seen at all stages (pre-ALMA) !
  - Complex molecules found at *all* stages: in pre-stellar cores, protostars, shocks, disks
- New era with ALMA
  - ALMA can *image* each line
  - Sensitivity to solar-mass protostars, not just Orion-like

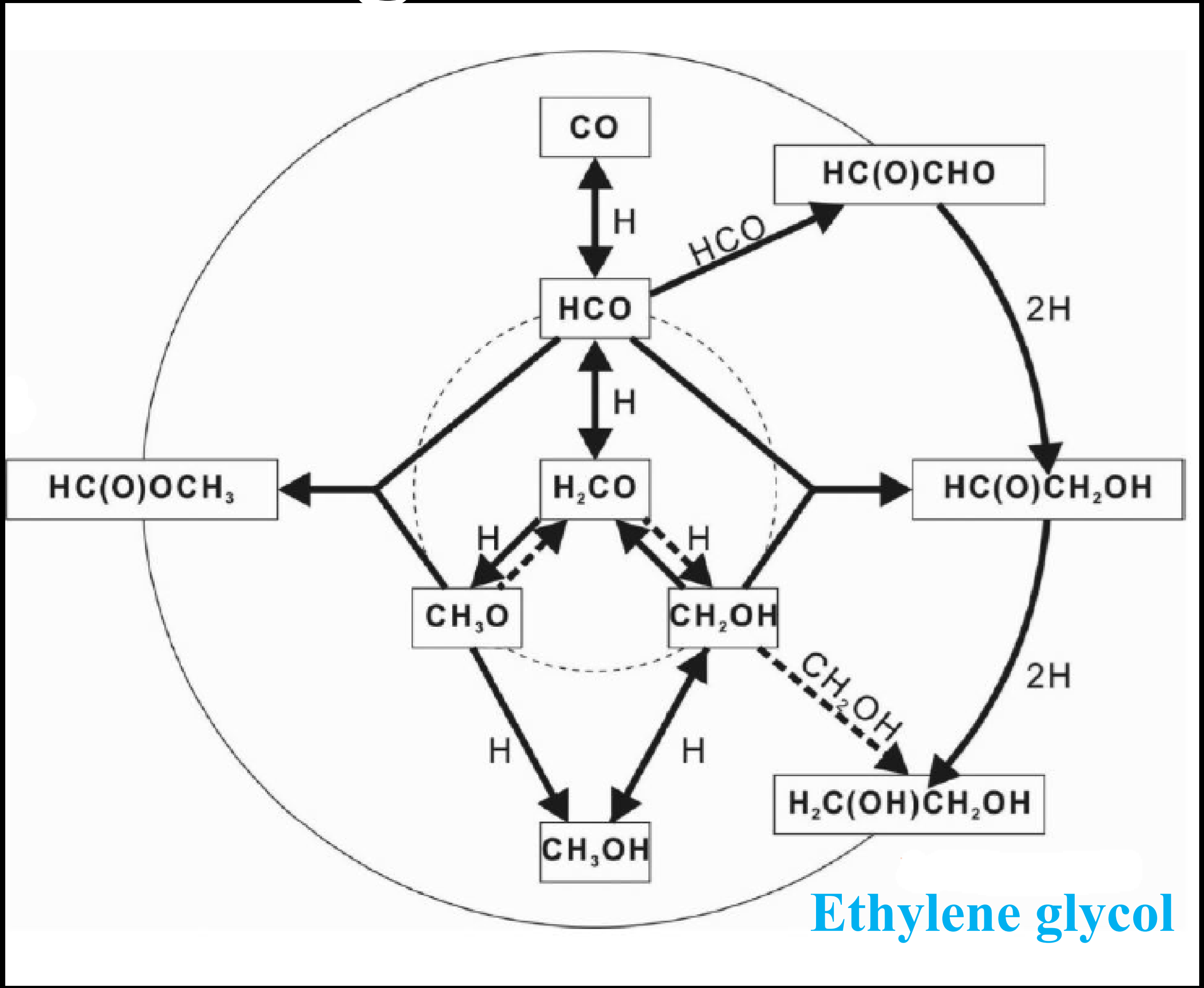


Forming complex organics on cold grains

Watanabe et al. 2005
Fuchs et al. 2009
Öberg et al. 2009
Fedoseev et al. 2014, 2015

- CO freeze-out in dense cores → HCO → ... → CH_3OH
- Radical – radical reactions at low *T*
- UV-induced chemistry
- Heating by protostar → Thermal desorption → Observe with ALMA

Making COMs at low *T*

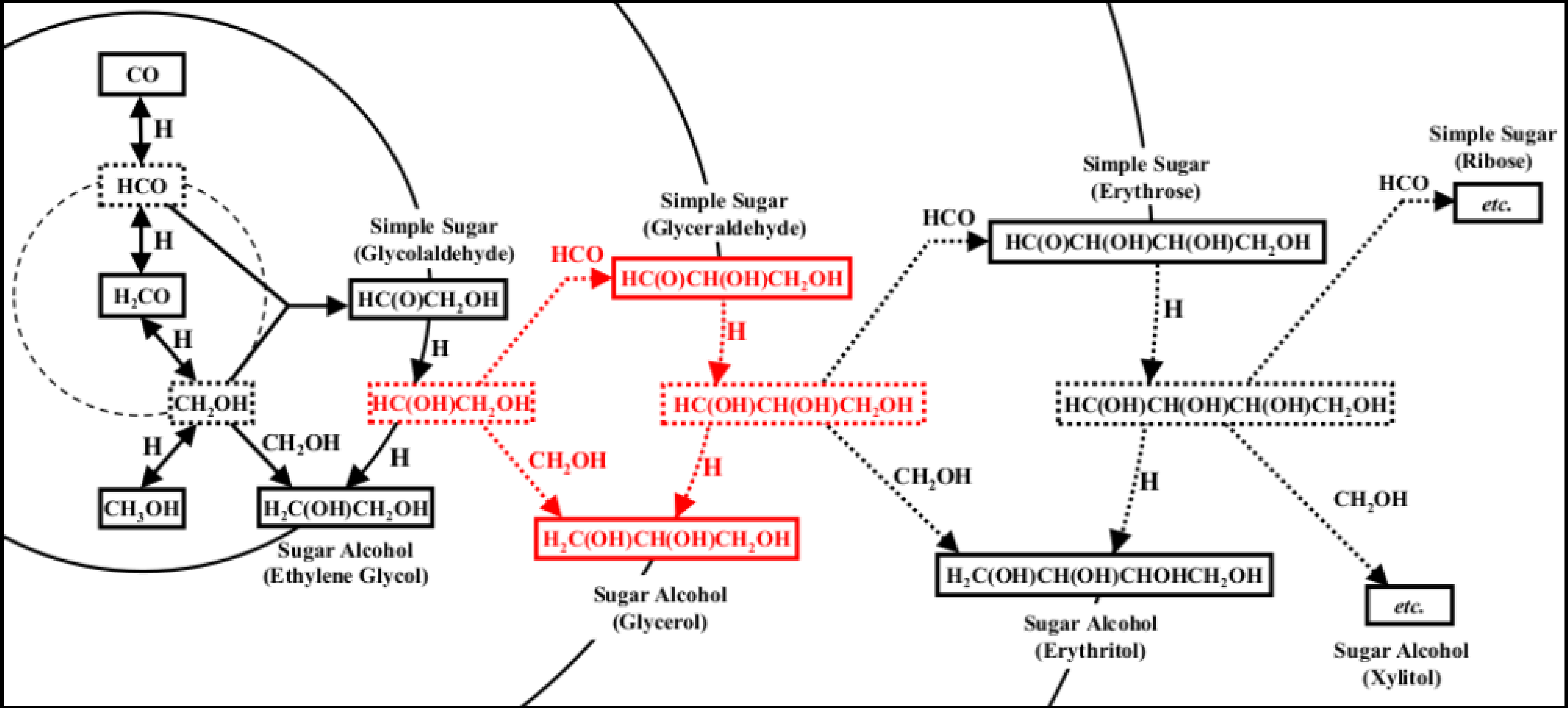


Fedoseev et al. 2015
Chuang et al. 2016, 2017

- Reactions proceed at 15 K, even without need for UV

How far can complexity go?

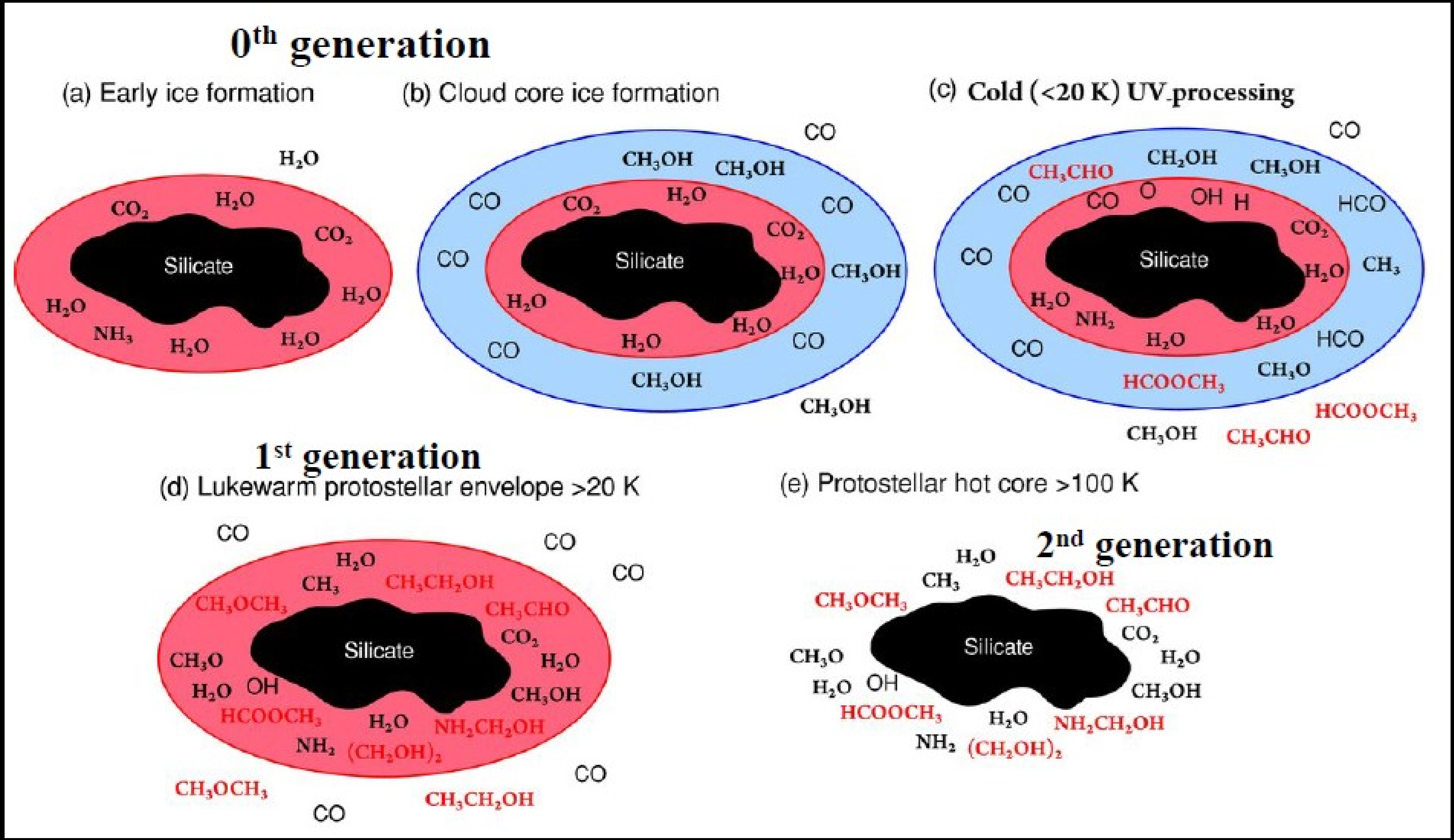
Starting from CO hydrogenation



- ***Can even make glyceral and real sugars without heating or UV!***

Fedoseev et al. 2017

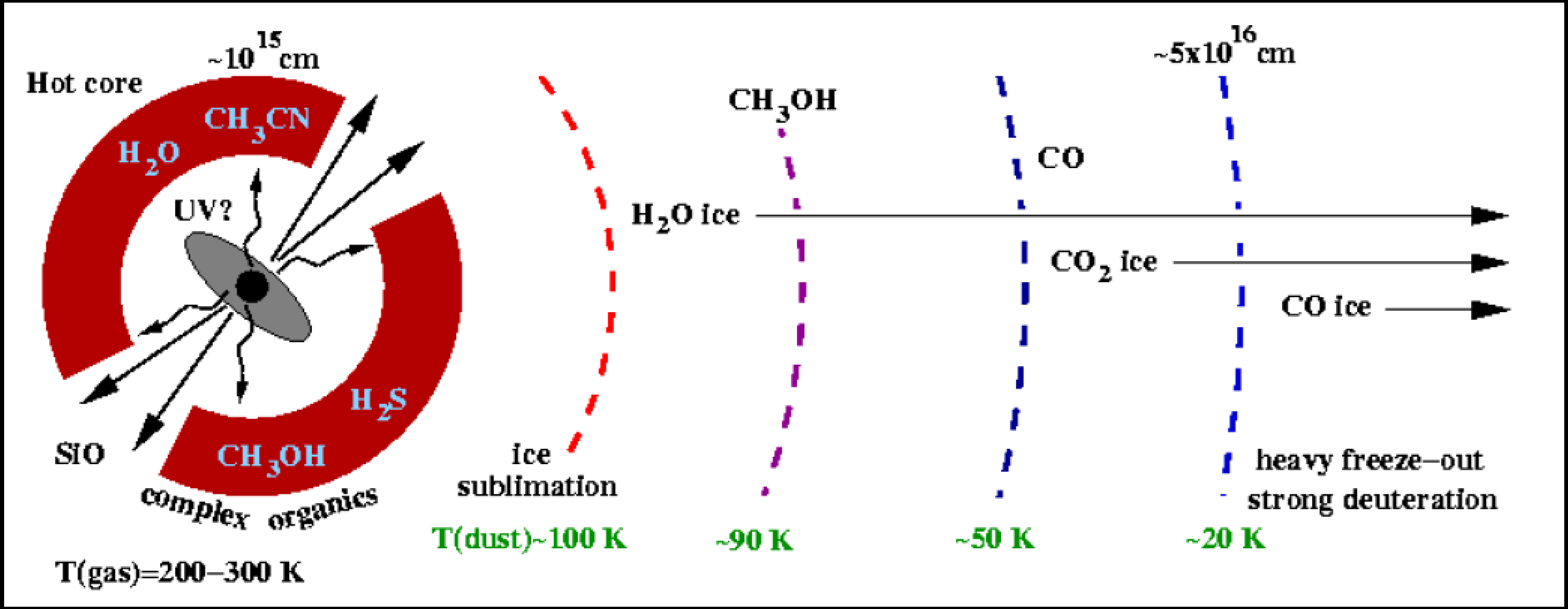
Complex ice chemistry



- Differences in 0th and 1st generation COMs no longer so clear

Öberg et al. 2010
Herbst & van Dishoeck 2009

Chemical structure of envelope



2nd generation

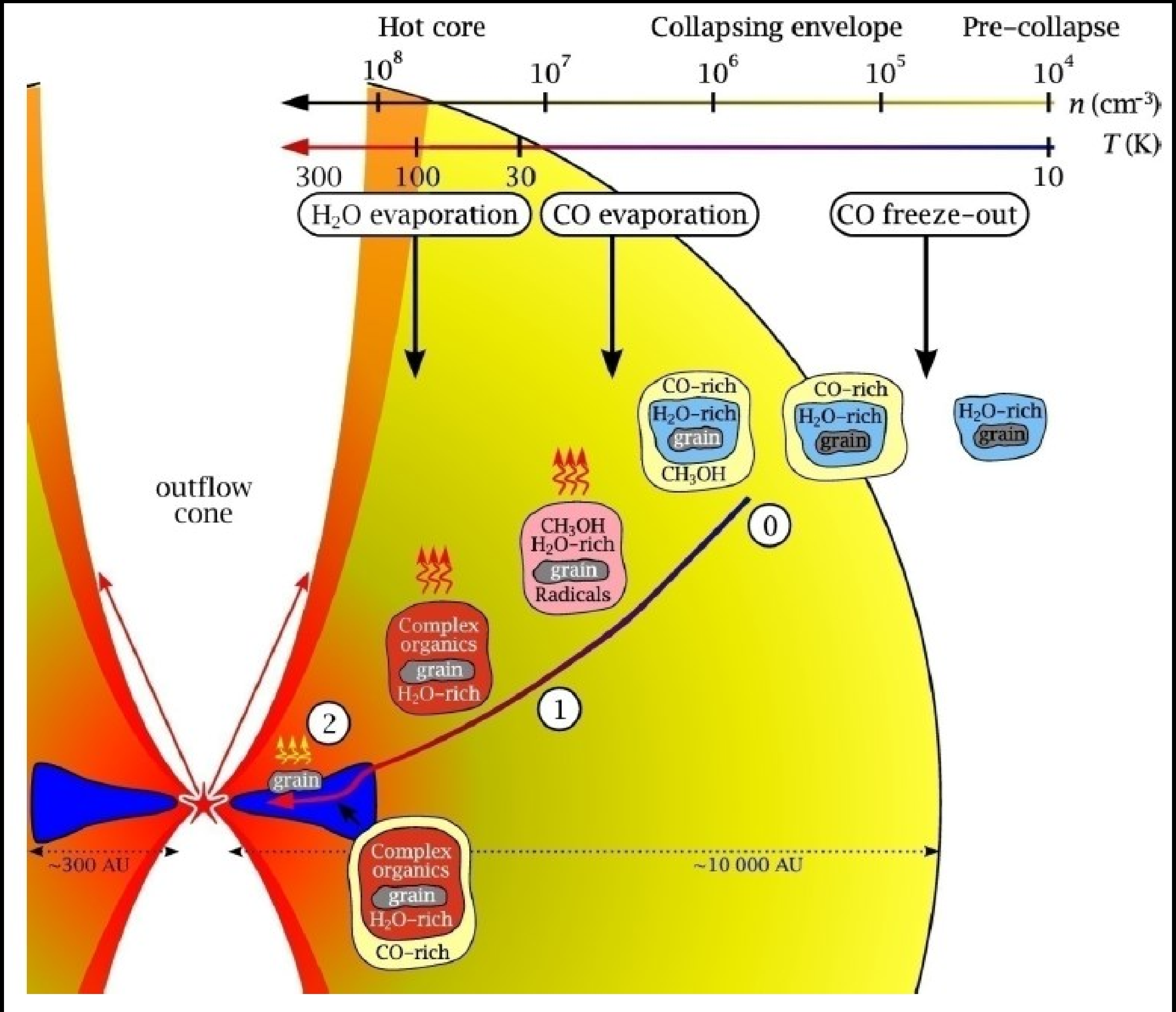
0th-1st generation

van Dishoeck & Blake 1998

Chemical scenario

- Heavy freeze-out of molecules onto grains in cold pre-stellar phase
- Grain-surface reaction produce new species
- Protostar heats surroundings
  - Ice sublimation
  - Hot core chemistry
- Fraction of ices and gas ends up in disks; remainder dispersed

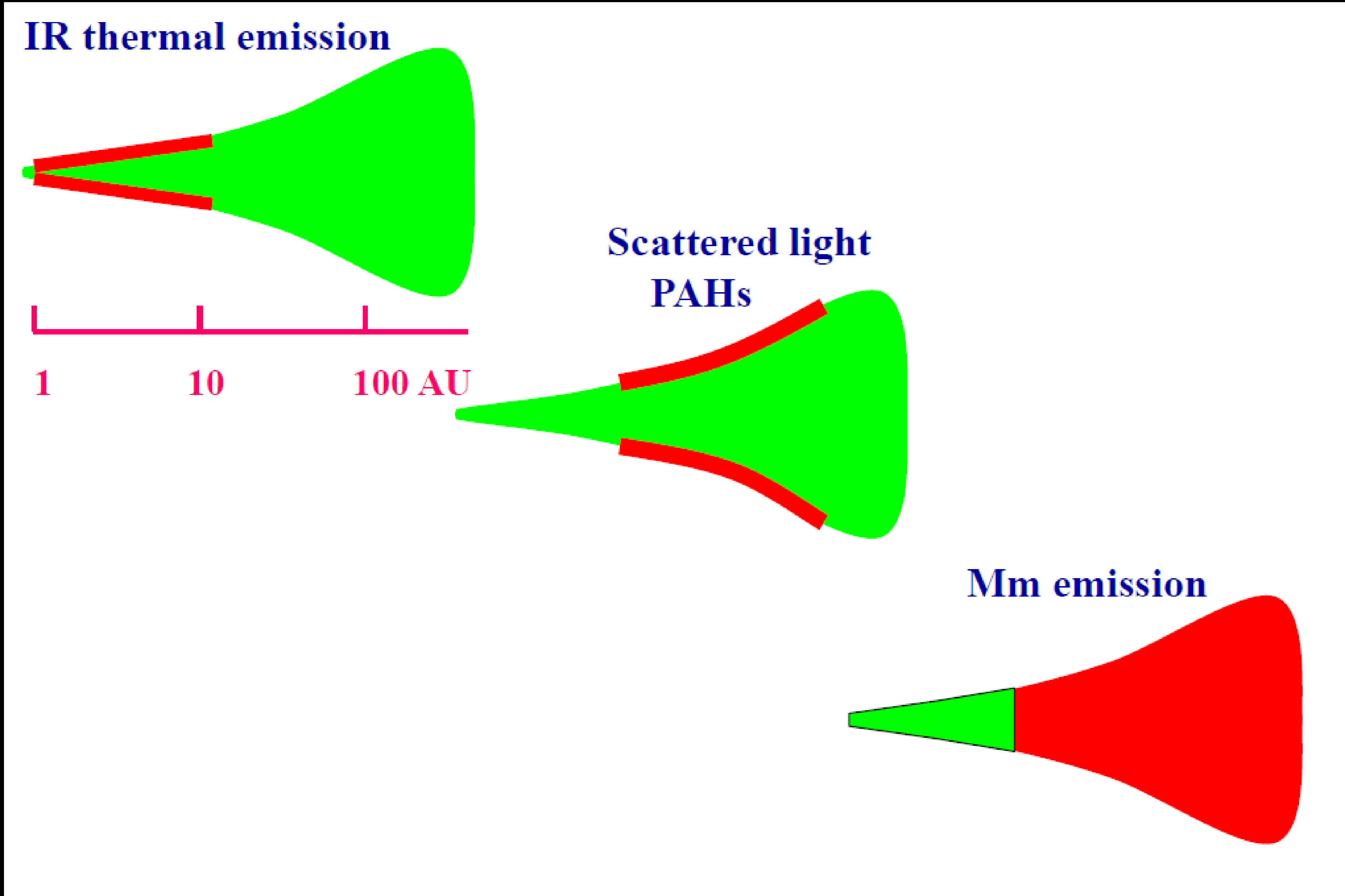
Follow journey of parcel from cores to disk



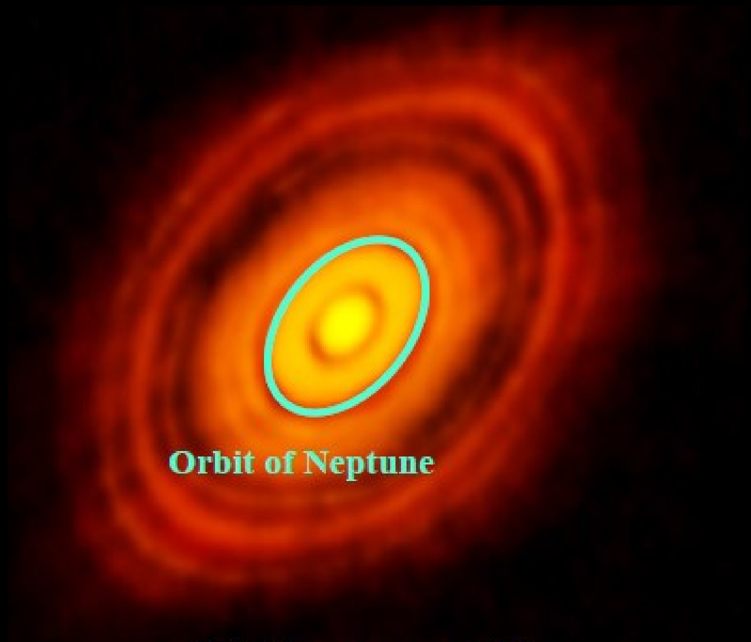
Herbst & van Dishoeck 2009

Visser et al. 2009, 2011

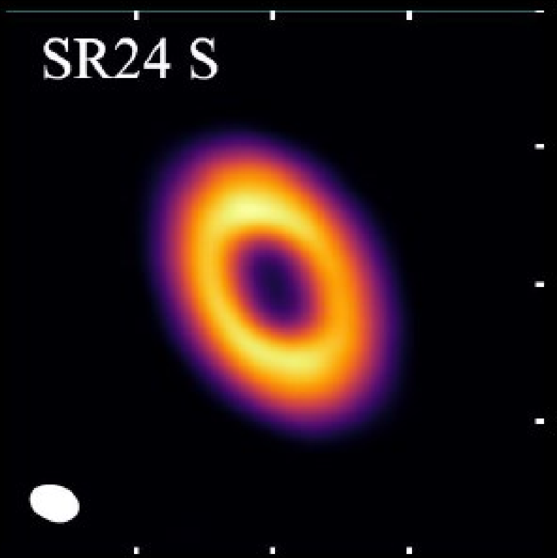
7.7 Outer disk chemistry – probing different parts of disks



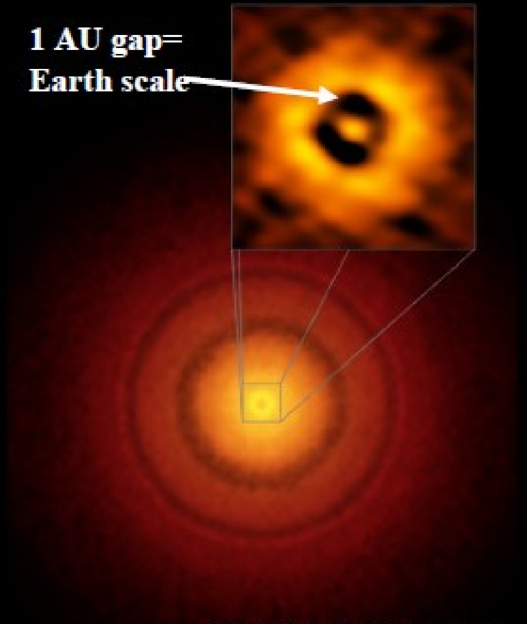
New era of observational planet formation



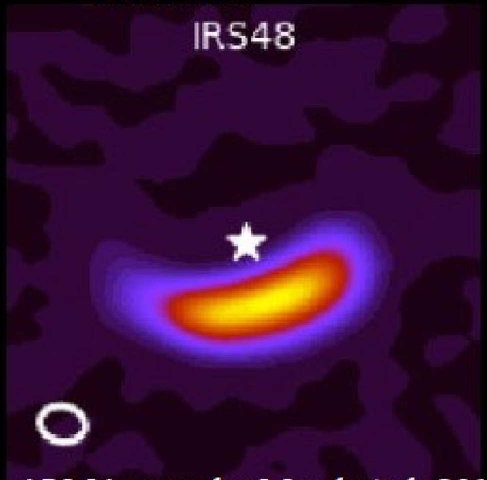
HL Tau young disk
ALMA partnership
et al. 2015



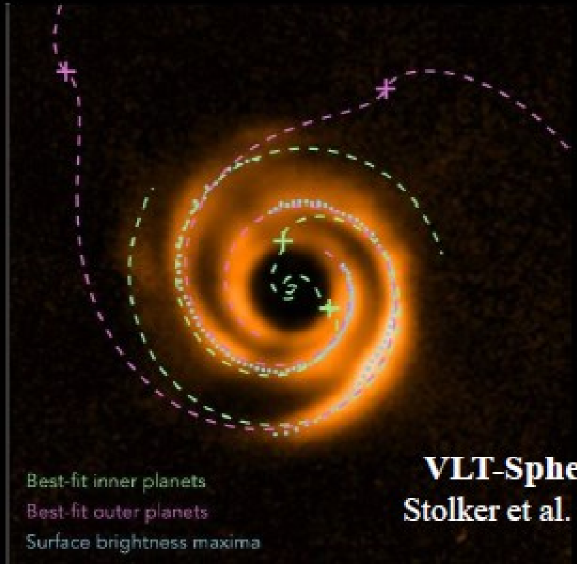
ALMA: Pinilla et al. 2017



ALMA TW Hya
Andrews et al. 2016



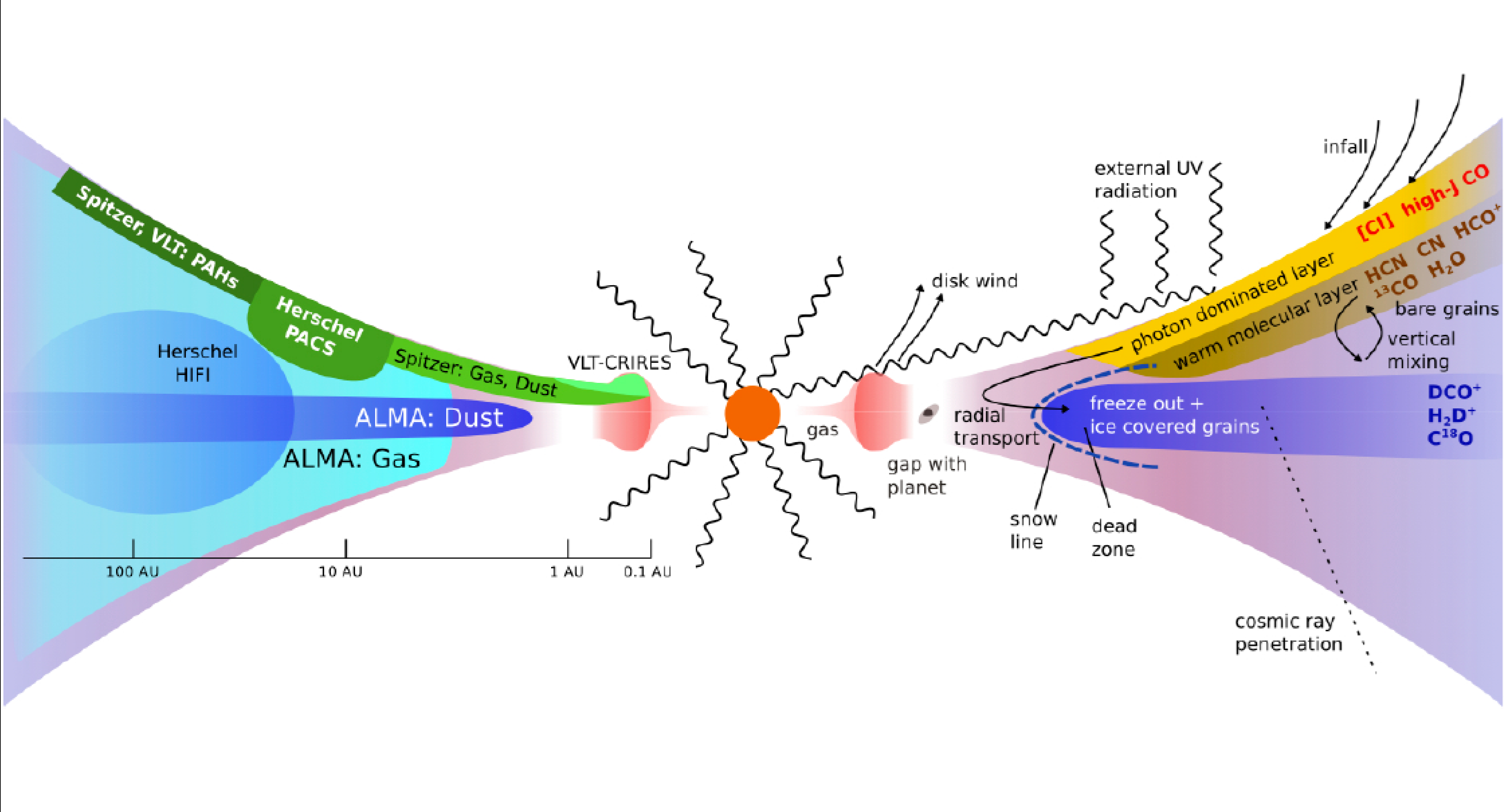
ALMA: van der Marel et al. 2013, 2016



VLT-Sphere, Gemini-GP…
Stolker et al. 2016

ALMA:
Fedele et al. 2017

IR inner disk, mm outer disk

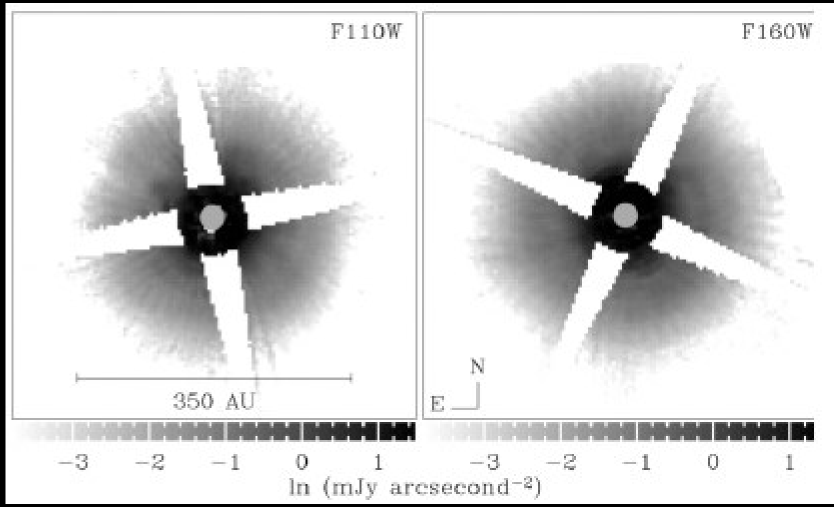


Bruderer 2011

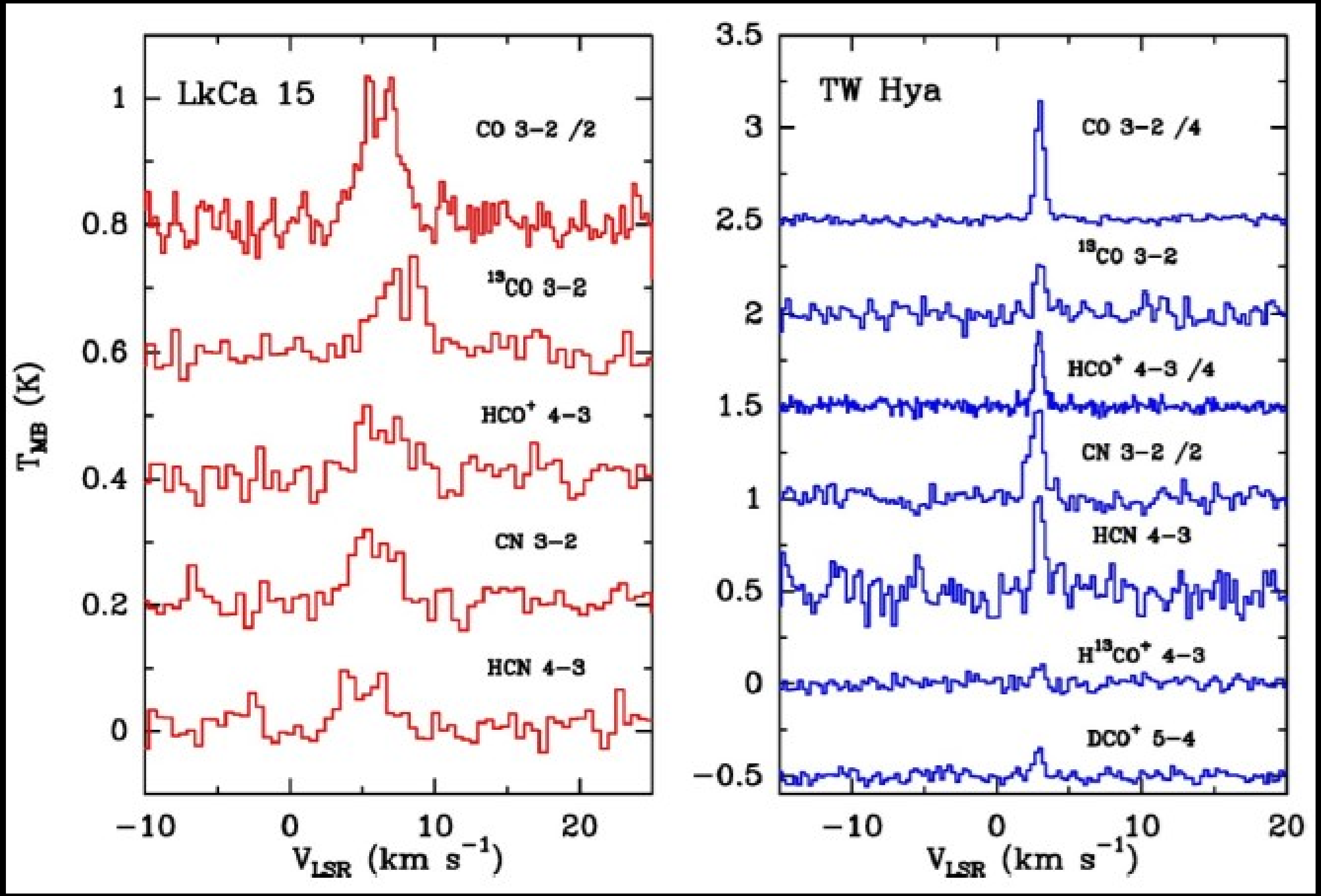
Chemistry in outer disks: mm data

TW Hya face-on disk

1.1 µm **1.6 µm**



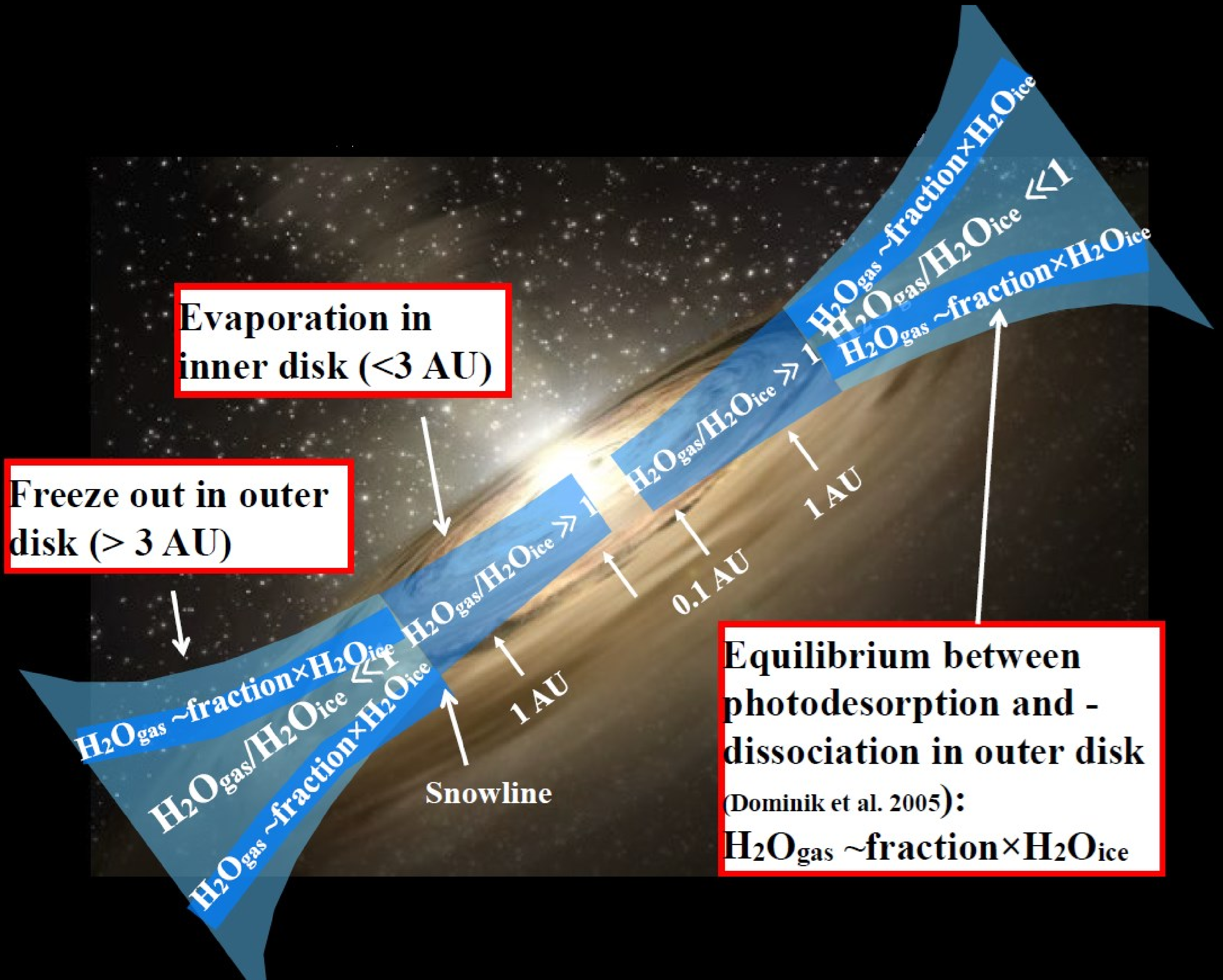
Scattered light => radius 200 AU



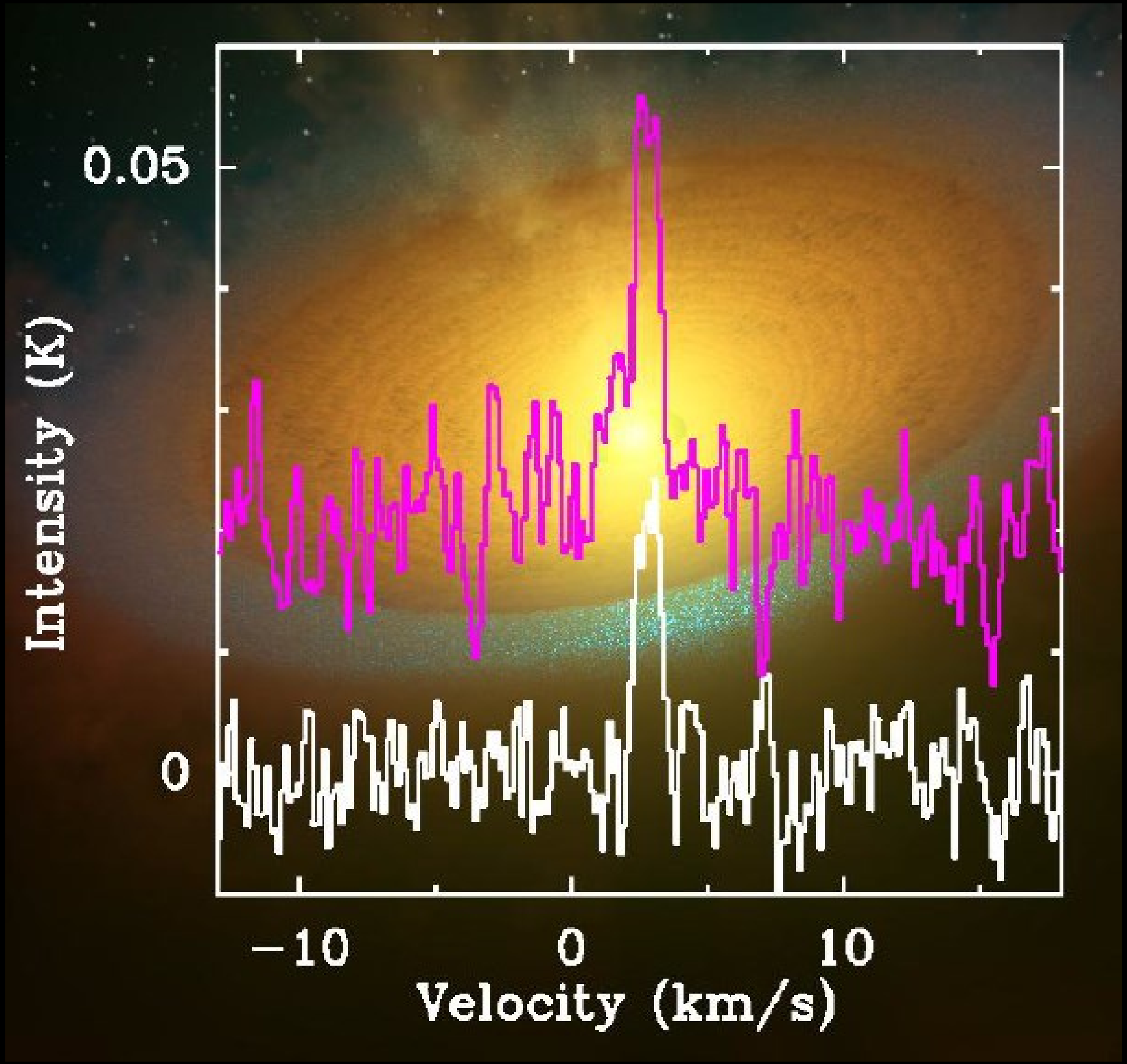
van Dishoeck et al. 2003
Thi et al. 2004
Kastner et al. 1997
Weinberger et al. 2002

- Small molecules detected, including deuterated species
- Instruments prior to ALMA did not have sensitivity to search for complex molecules

Snowlines in disks



Cold H_2O reservoir in disks



TW Hya

Herschel-HIFI

p-H_2O 1_{11}-0_{00}

1113 GHz

o-H_2O 1_{10}-1_{01}

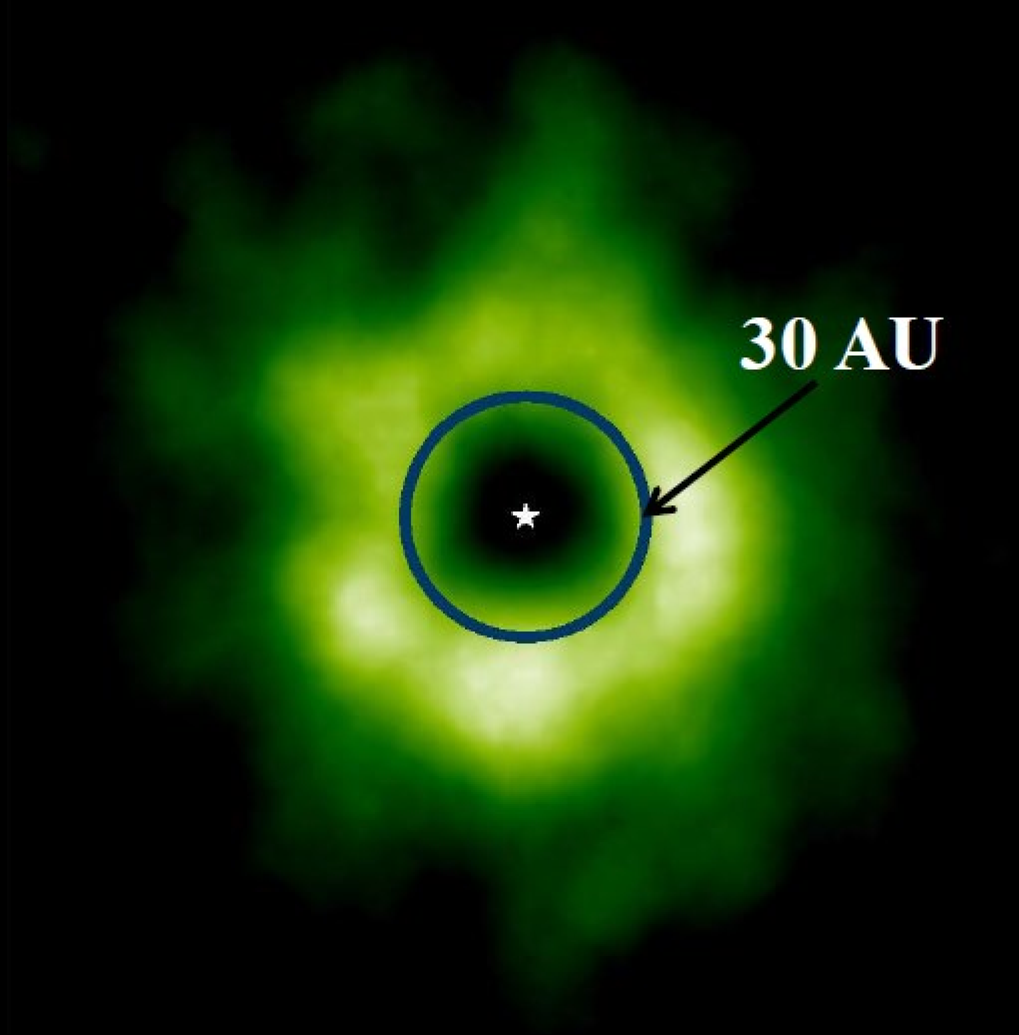
557 GHz

Elevated o/p ratio in H_2O compared to comets

Hogerheijde et al. 2011

6000 oceans of water ice in disk

Imaging the CO snowline



TW Hya

Face-on disk

d = 68 pc

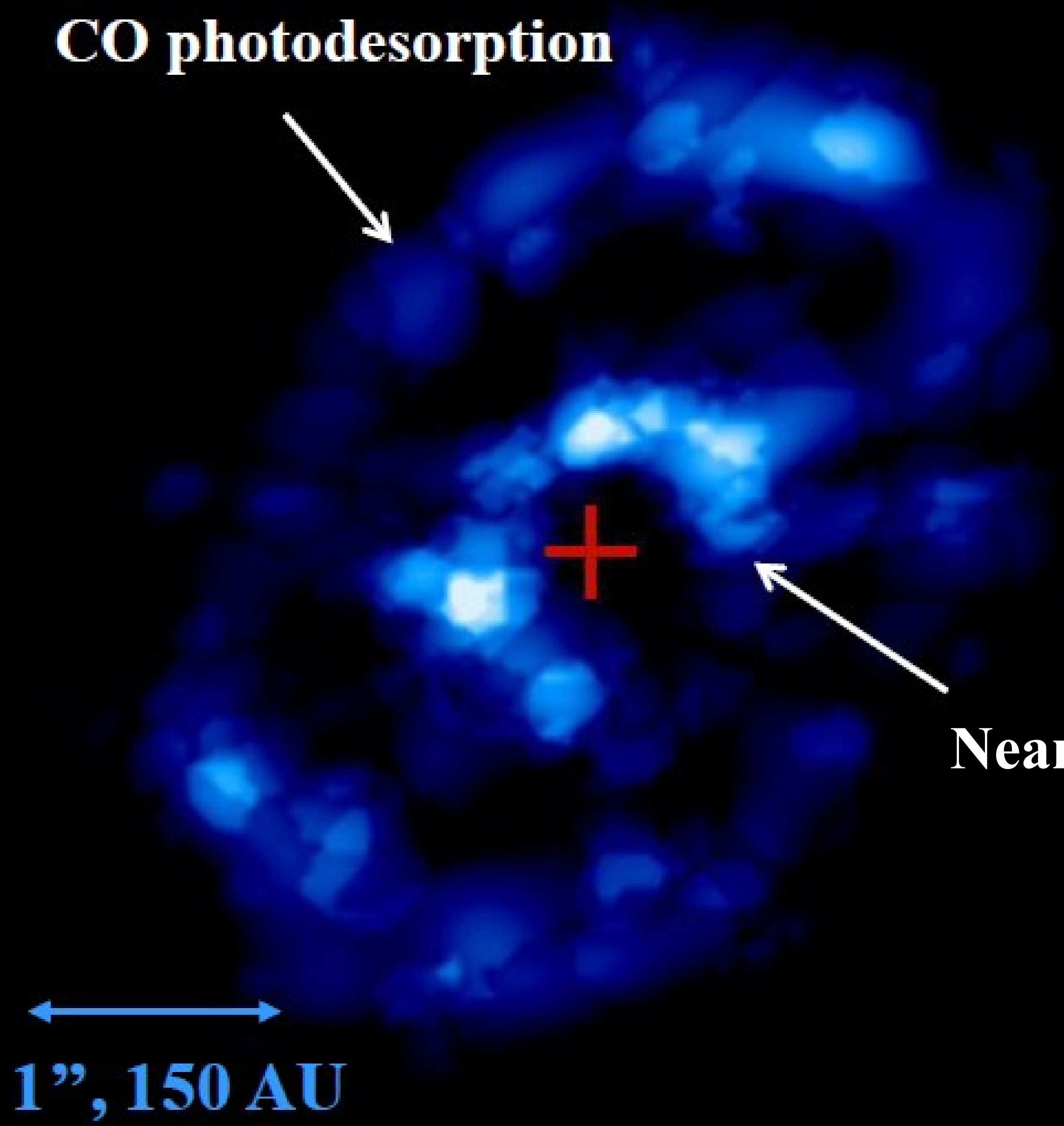
N_2H^+ 4-3

Qi, Öberg, et al. 2013

N_2H^+ appears when CO freezes out

→ Tracer of snowline

Tracing the CO snowline



IM Lup

ALMA

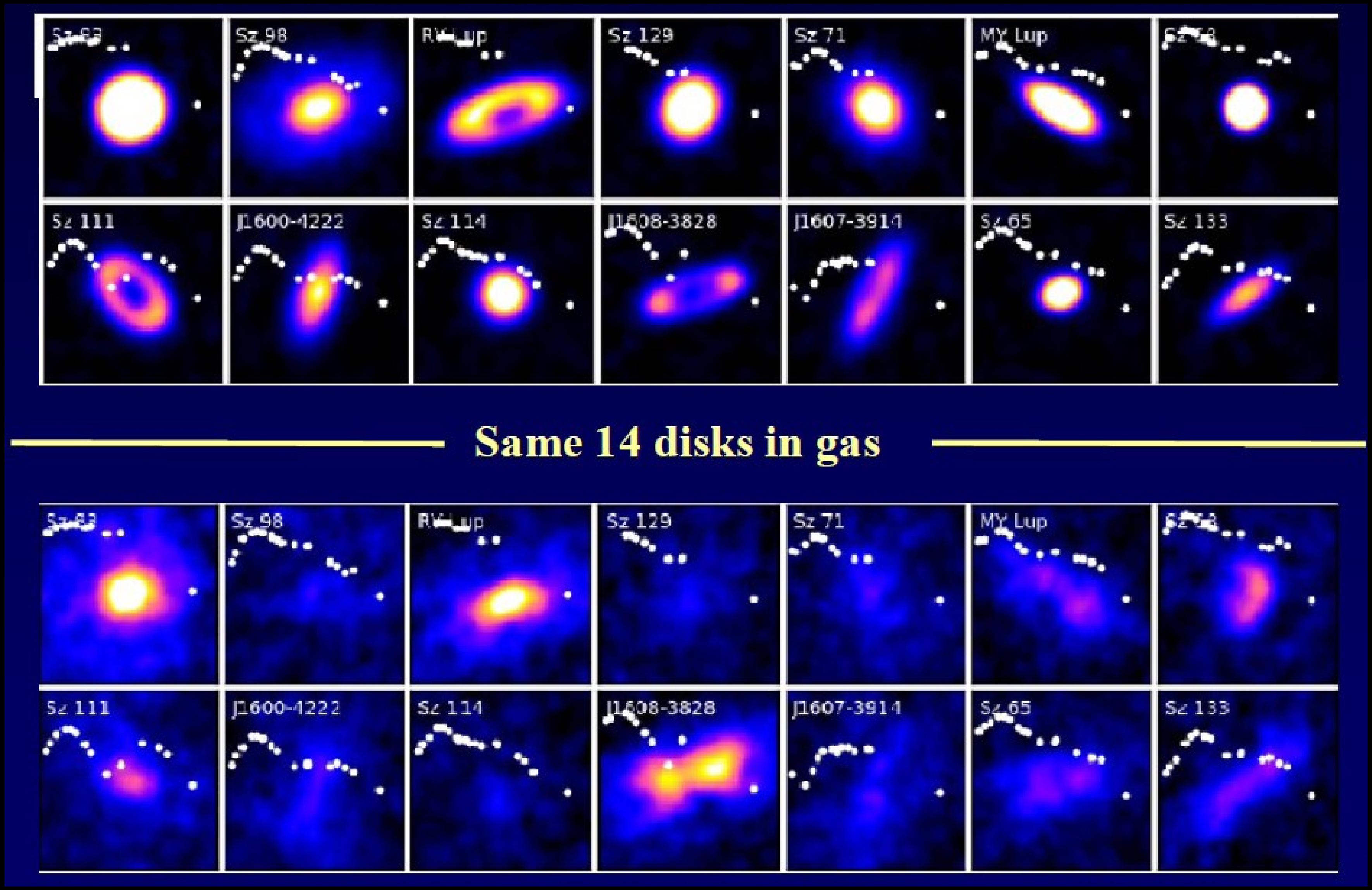
Double rings!

DCO^+ 3-2

Near CO snowline

Öberg, et al. 2015

Puzzle: CO much weaker than expected



Dust

1.3 mm continuum

Gas

CO 2-1

Ansdell et al. 2016, 2018
Miotello et al. 2017

Why is CO weak?

- CO frozen out Included
- CO (isotope-selective) photodissociation Included
- CO locked up in large bodies in midplane Possible
- CO / volatile carbon transformed ???
  - Gas-phase chemistry
  - Ice chemistry → CH_3OH, CO_2, CH_4, C_2H_6

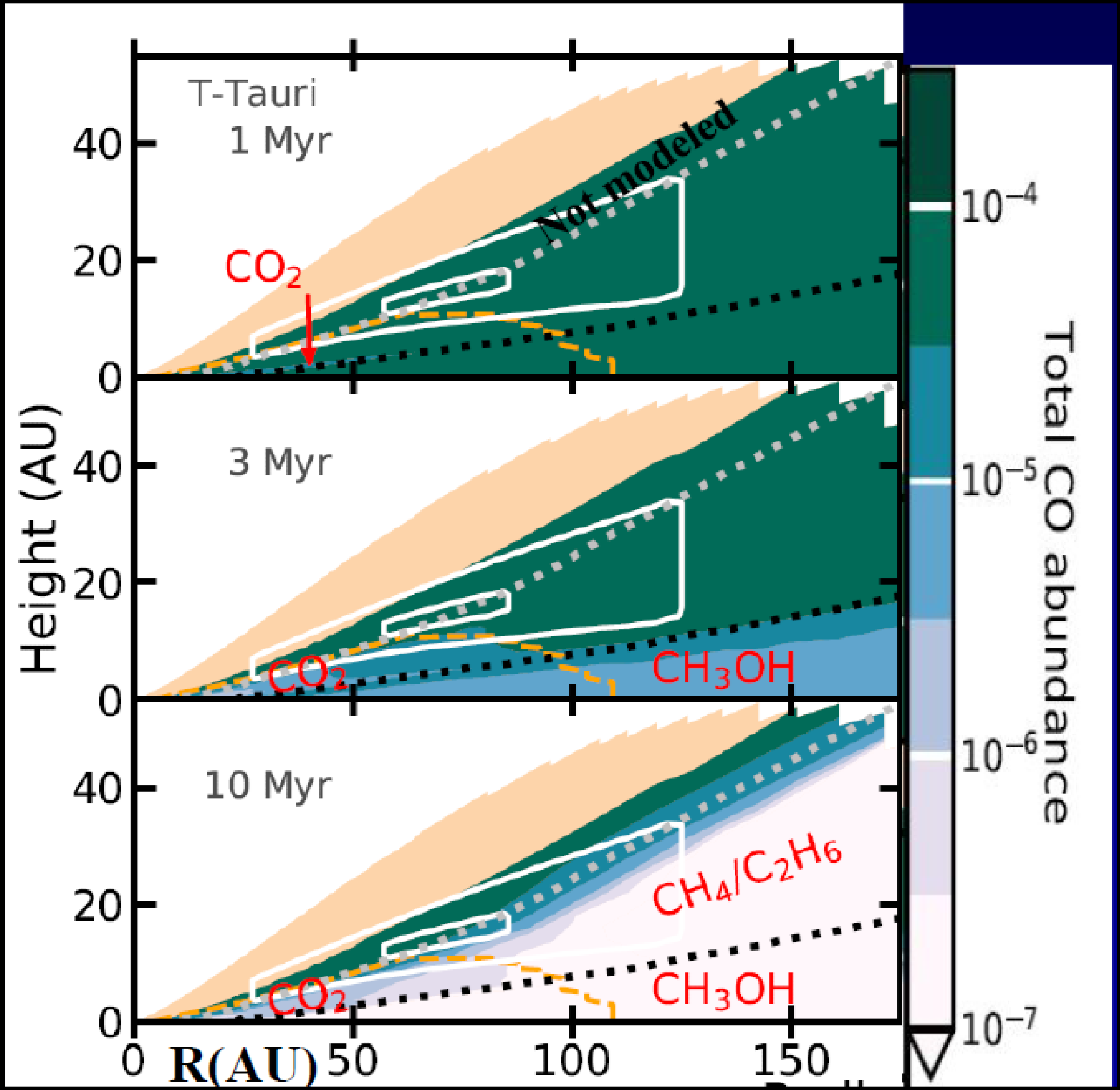
Key parameters: temperature, time, cosmic ray ionization rate ζ

Aikawa et al. 1999
Eistrup et al. 2016, 2018
Wu et al. 2016, 2017
Molyarova et al. 2017
Schwarz et al. 2018
Bosman et al. 2018

CO depletion models

Young disk

Old disk



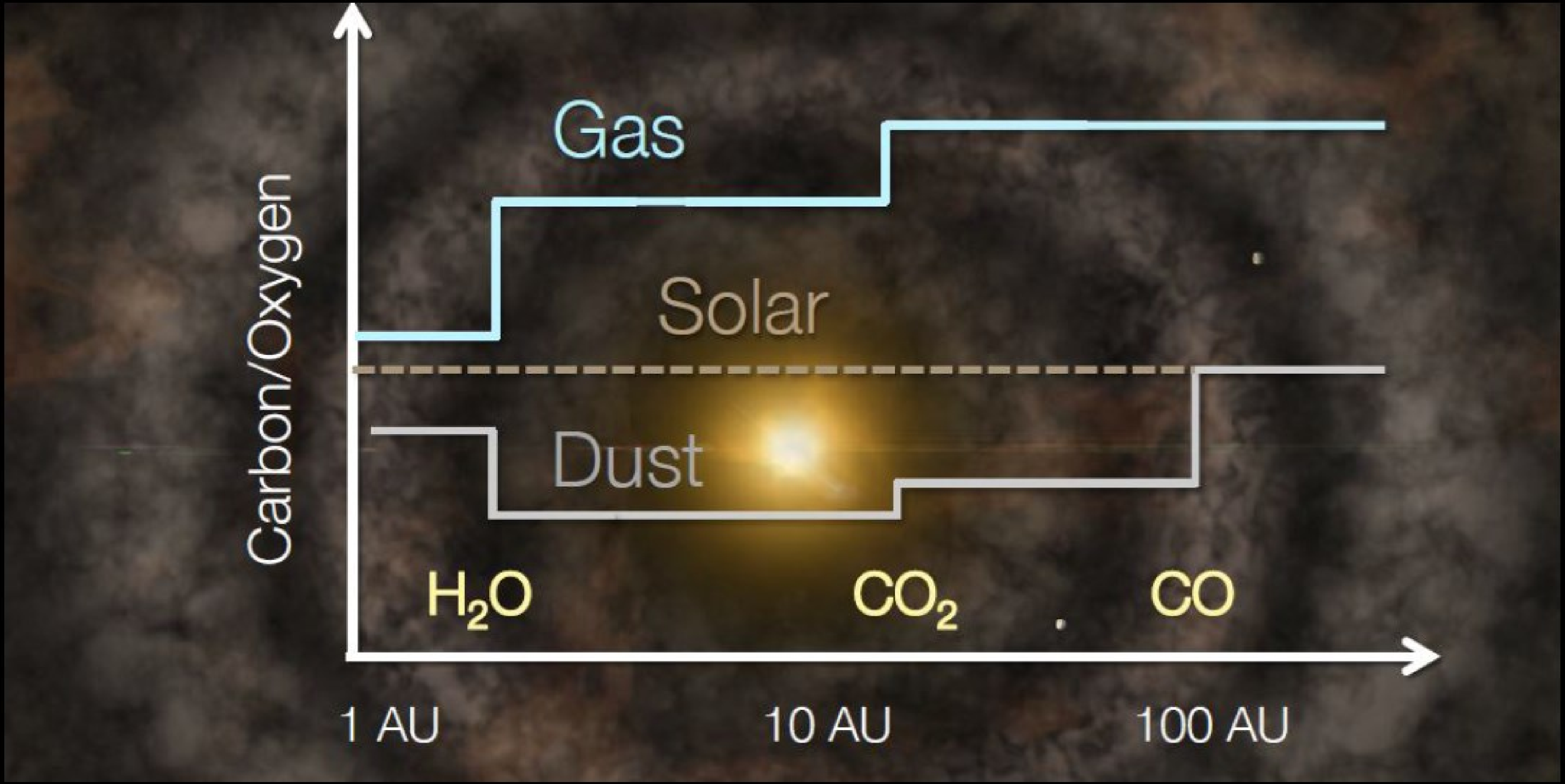
$\zeta = 10^{-17}\ s^{-1}$

White contours: 25-75% emission

Bosman et al. 2018

- Young disks show little CO transformation, in old disks most CO is missing

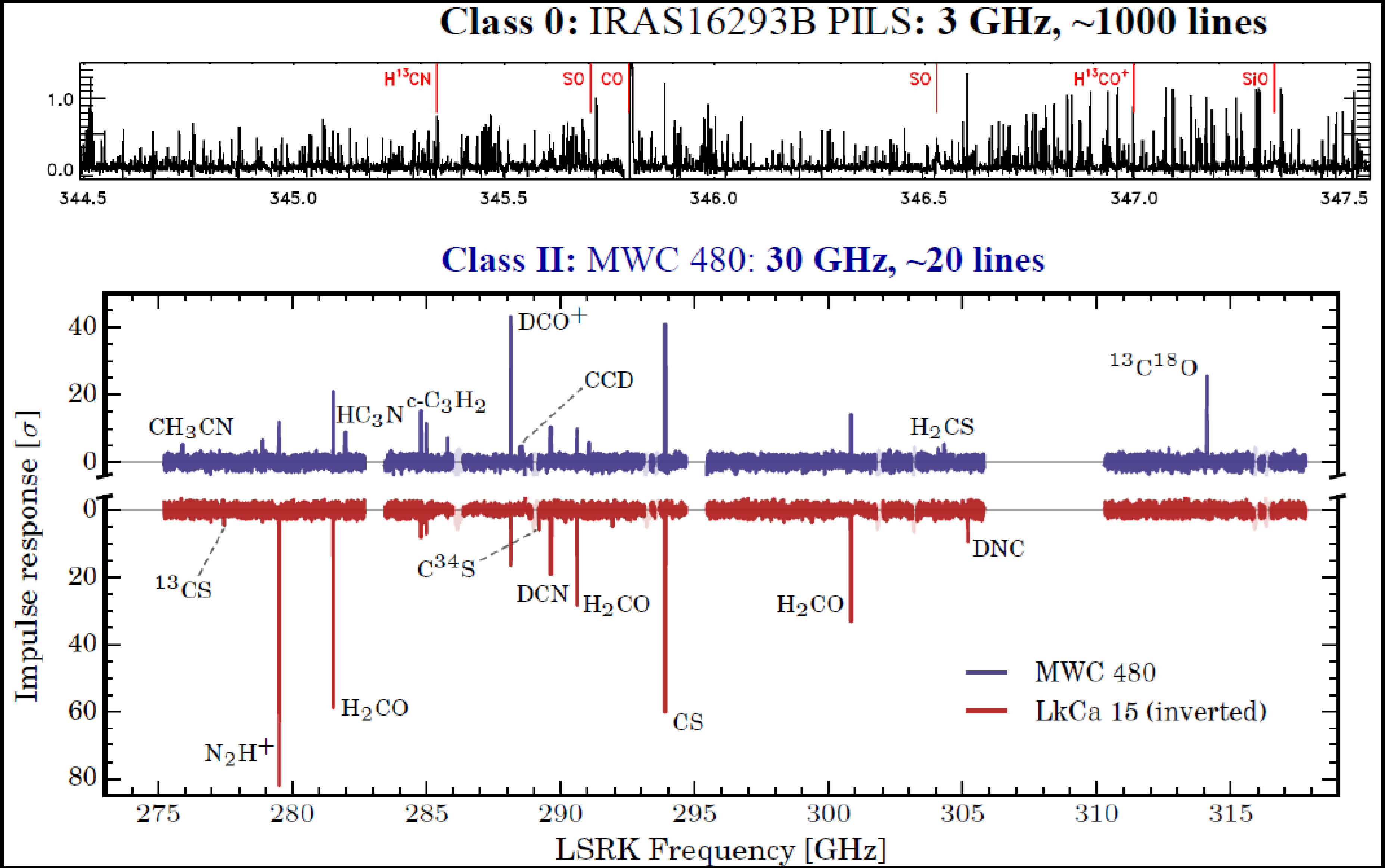
Changing C/O ratio with radius



- Ices are oxygen rich
- Gas is carbon rich
- But both C and O are depleted

Öberg et al. 2011
Walsh et al. 2015

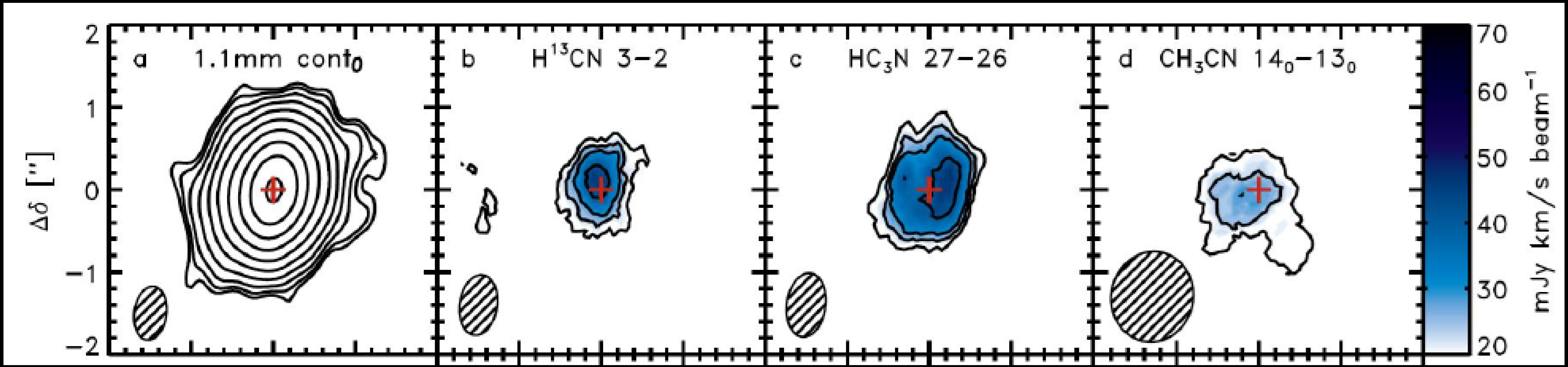
Mature disks have few COMs



Loomis et al. 2020

Complex molecules in disks

MWC 480 Herbig disk with ALMA: CH_3CN

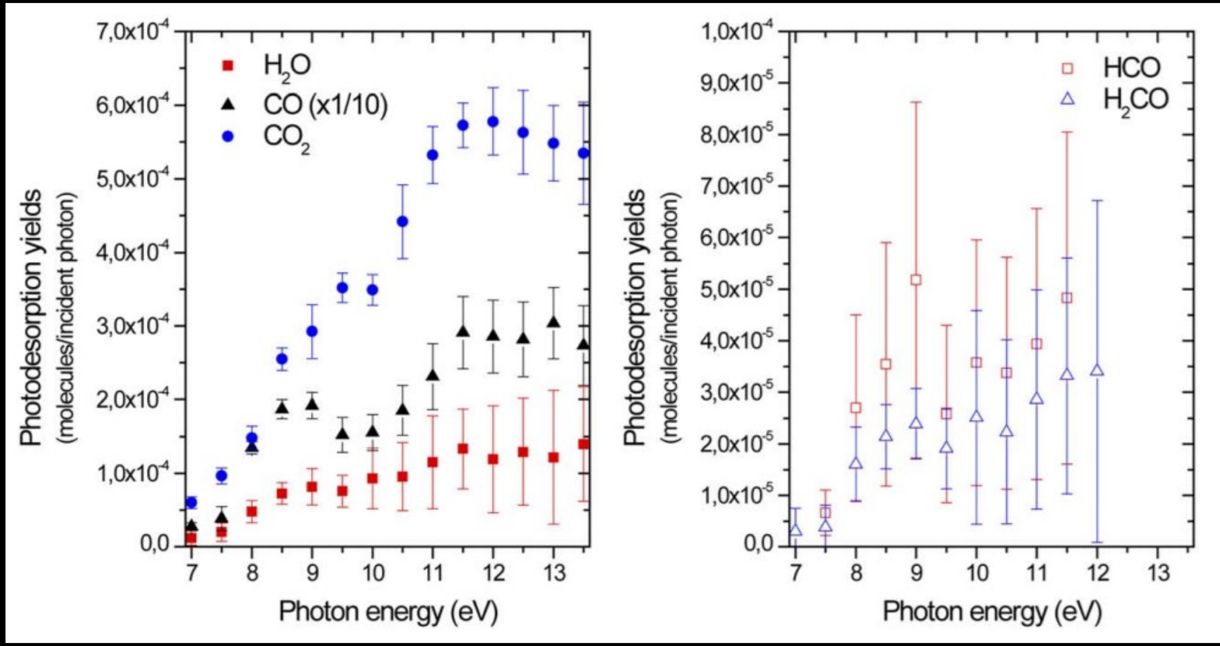


- HC_3N/HCN ~0.4, CH_3CN/HCN ~0.05 at 30 AU
- CH_3OH detected in TW Hya disk, but weak

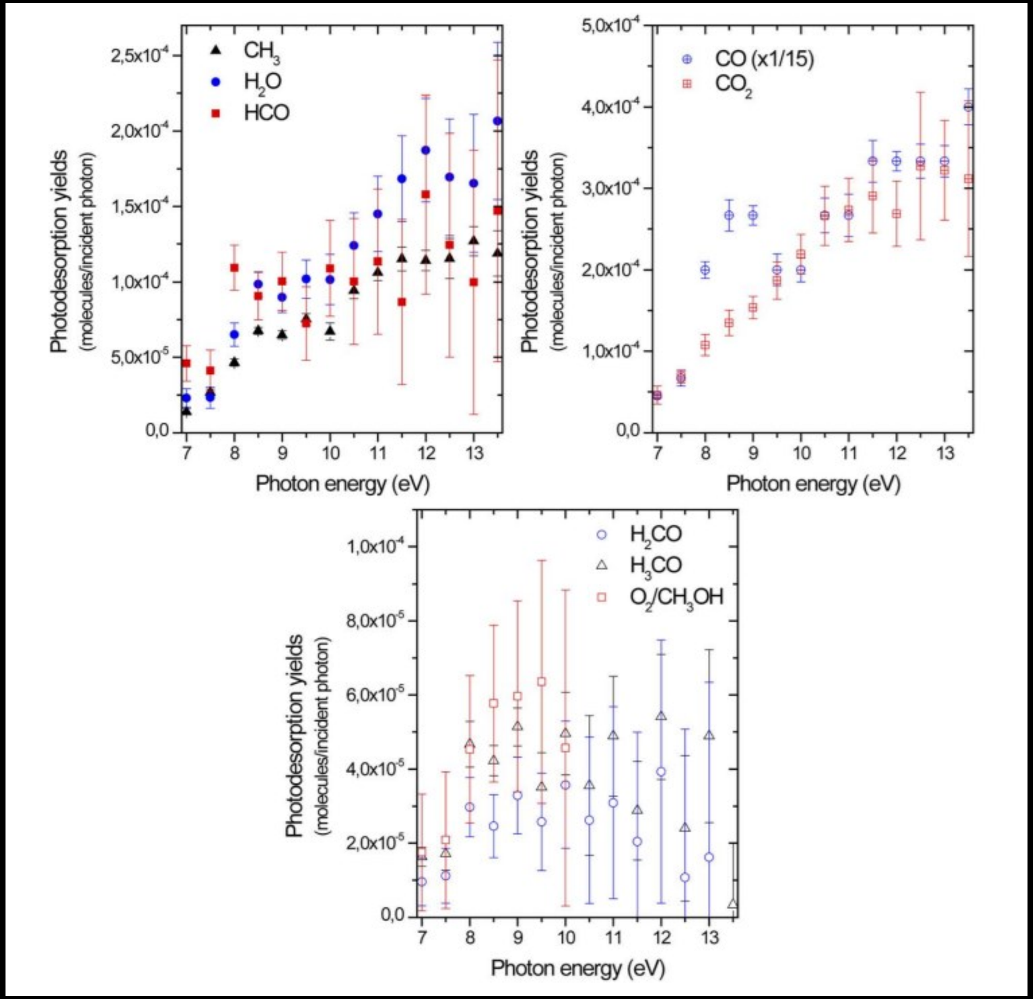
Öberg et al. 2015
Walsh et al. 2016

Insight from ice experiments

UV photodesorption destroyed O-bearing COMs but retains cyano-COMs



Bertin et al. 2023



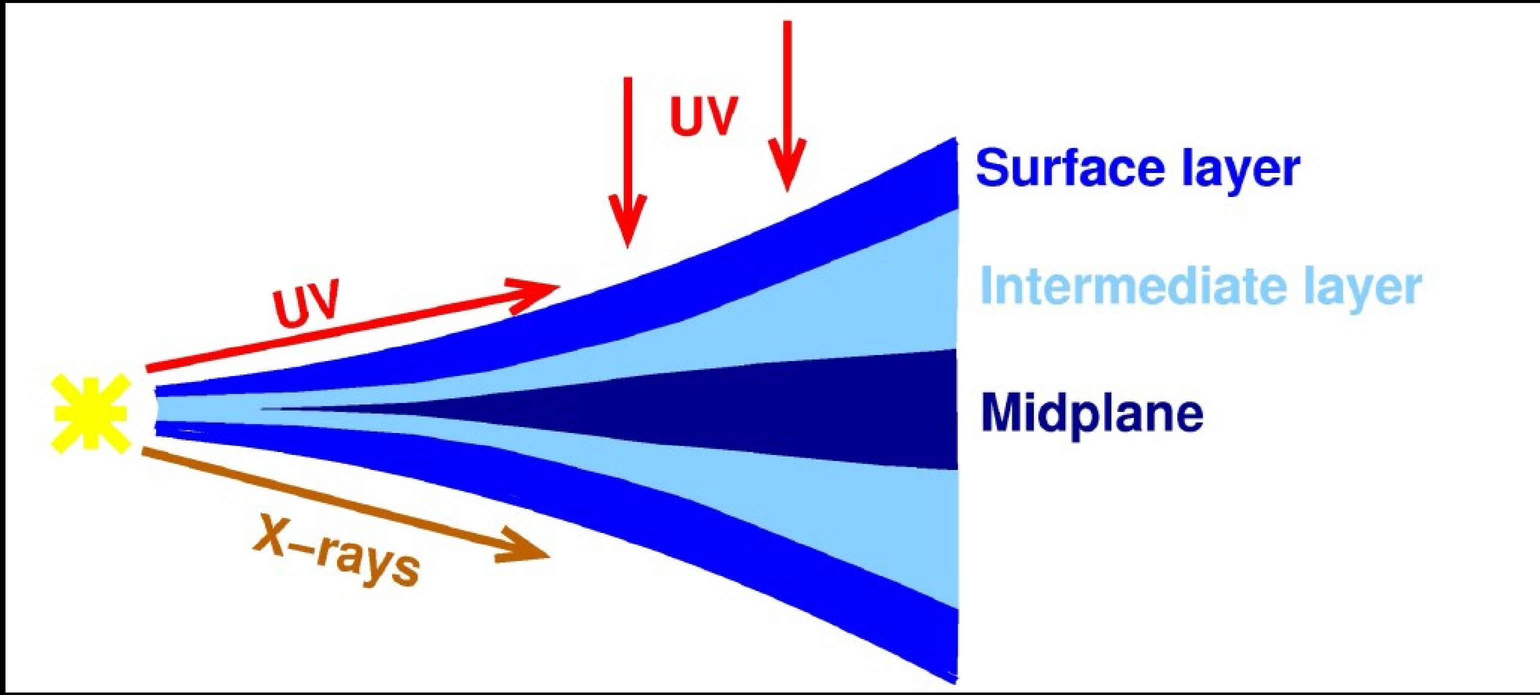
- Pure HCOOH and $HCOOCH_3$ ices – only fragments desorb
- CH_3CN photodesorbs intact!

Observational findings

- Simple gas-phase molecules observed (>50 AU)
  - Ion-molecule reactions (HCO^+)
  - Photon processes (high CN/HCN)
  - High deuterium fractionation (DCO^+)
  - Low abundances of complex species (H_2CO)
- Disk-averaged abundances are “depleted” by factor of 5-100 (using mass from dust continuum and assuming gas/dust = 100) due to freeze-out in cold midplane and photodissociation at the surface
- Transformation of CO to CO_2, CH_3OH, hydrocarbons at low T
- Solid CO and H_2O detected in edge-on disks
  - Not yet CH_3OH ice
- Absence of PAHs – now confirmed with JWST! (Arulanantham et al. 2024)
  - Most T Tauri disks do not show PAH emission, abundances < 0.1 ISM

Chemical structure of 2D flaring disks

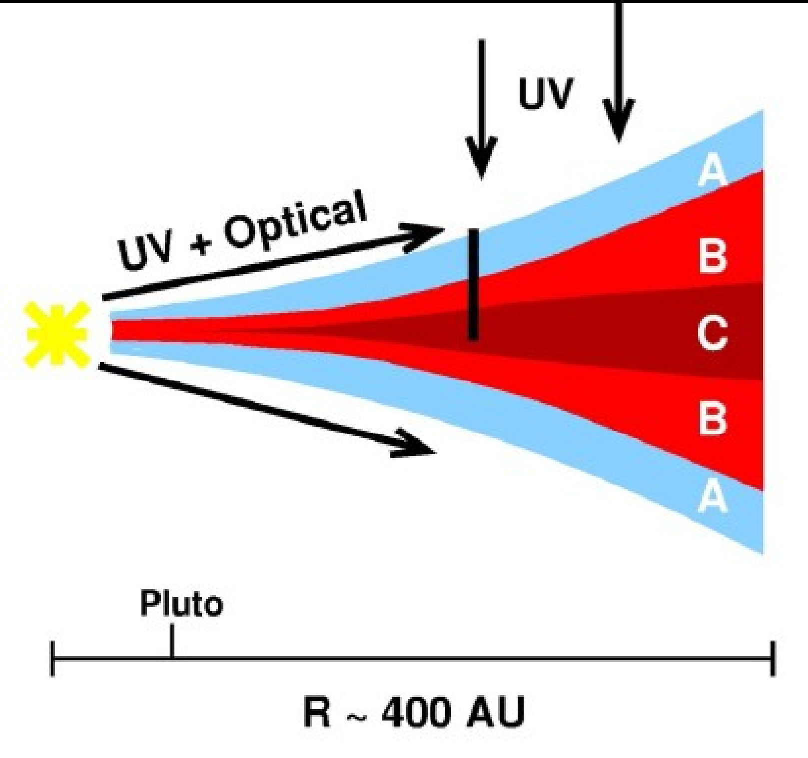
- Surface layer: molecules dissociated by UV photons
- Warm intermediate layer: molecules not much depleted, rich chemistry
- Cold midplane: molecules heavily frozen out

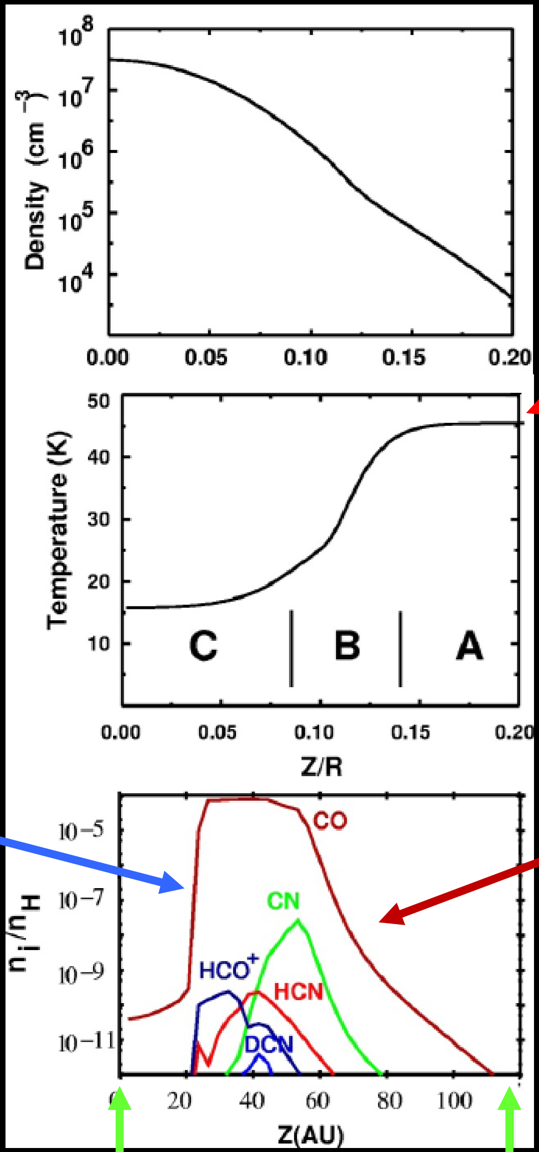


- PDR-like structure but with large density gradients and very intense UV (up to 10^6 x ISM)

Aikawa et al. 2002
Bergin et al. 2007, PPV +
many other groups

Vertical structure





R = 200 AU

T_{gas} is larger

Freeze-out

Photodissociation

midplane

surface

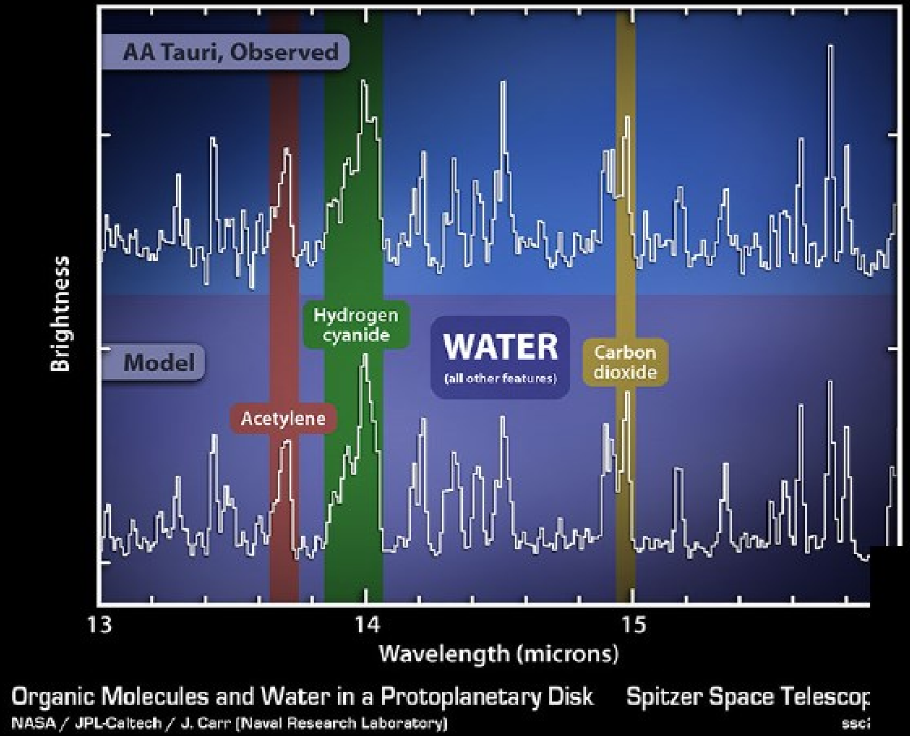
Ionization fraction:

- Surface: 10^{-4} (C^+)
- Intermediate: 10^{-9} (HCO^+)
- Midplane: ~10^{-11} (H_3^+, H_2D^+)

7.8 Inner disk (<10 AU)

- Surprising detections of mid-IR observations of CO, H_2O, OH, HCN, C_2H_2, ...
- Many sophisticated thermo-chemical models being developed
  - Hollenbach & Gorti, Glassgold, Meyerink et al., Woitke, Kamp & Thi (PRODIMOO), Agúndez et al., Bruderer (DALI), ...

Hot water and organics in inner few AU of disks

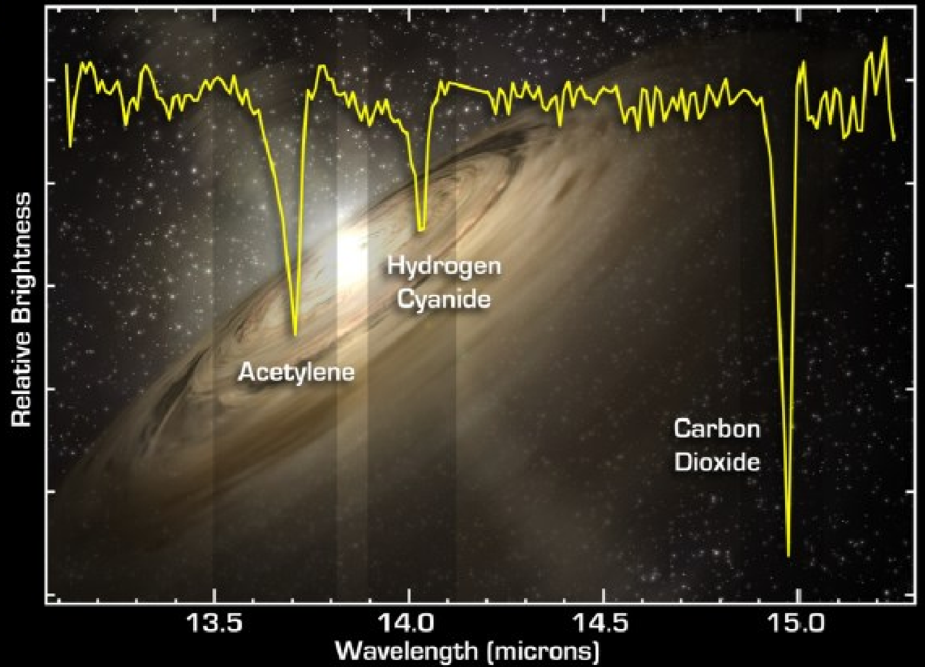


Carr & Najita 08
Salyk + 08, 11
Pontoppidan+10

T_{ex}=300-700 K

Spitzer observations of T Tauri stars show rich spectra of simple molecules H_2O, HCN, C_2H_2, CO_2

Lahuis +06

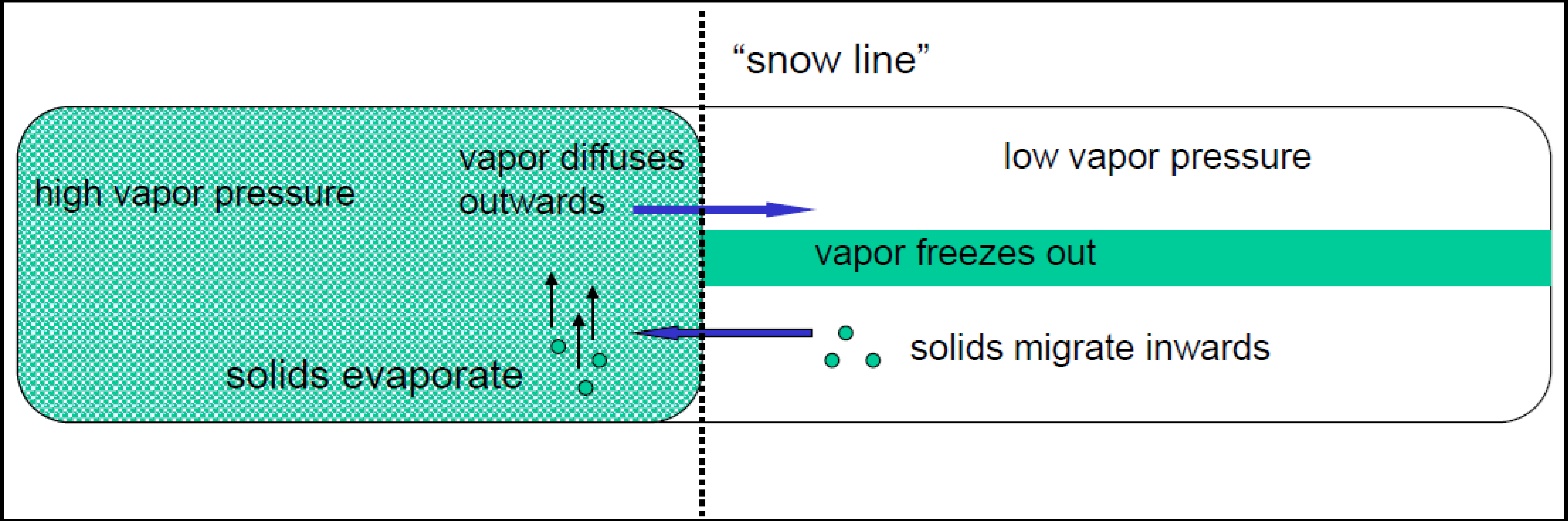


Implications

- Water gas is found well inside the ‘snow’ line (estimated at ~3 AU)
- Inward radial migration or upward mixing of icy grains and planetesimals, followed by evaporation?

How does disk water vapor depend on disk location and time?

- Water vapor contents may be set by a balance between vapor diffusion and icy planetesimal migration



Ciesla & Cuzzi 2006

- Inner disk water vapor content may reflect disk evolution

7.9 Cometary chemistry

- Comets are thought to have formed in the outer part of the disk which formed our solar system
- Comets contain the least-modified original interstellar material
- Early optical observations probed mostly daughter molecules (CH, CN, C_2, CO^+, OH, OH^+, ...)
- IR and (sub)mm observations provide direct information on parent molecules, i.e., ***original composition of ices***
- Lots of data from comets Halley, Hyakutake, and Hale-Bopp

Parent-daughter model

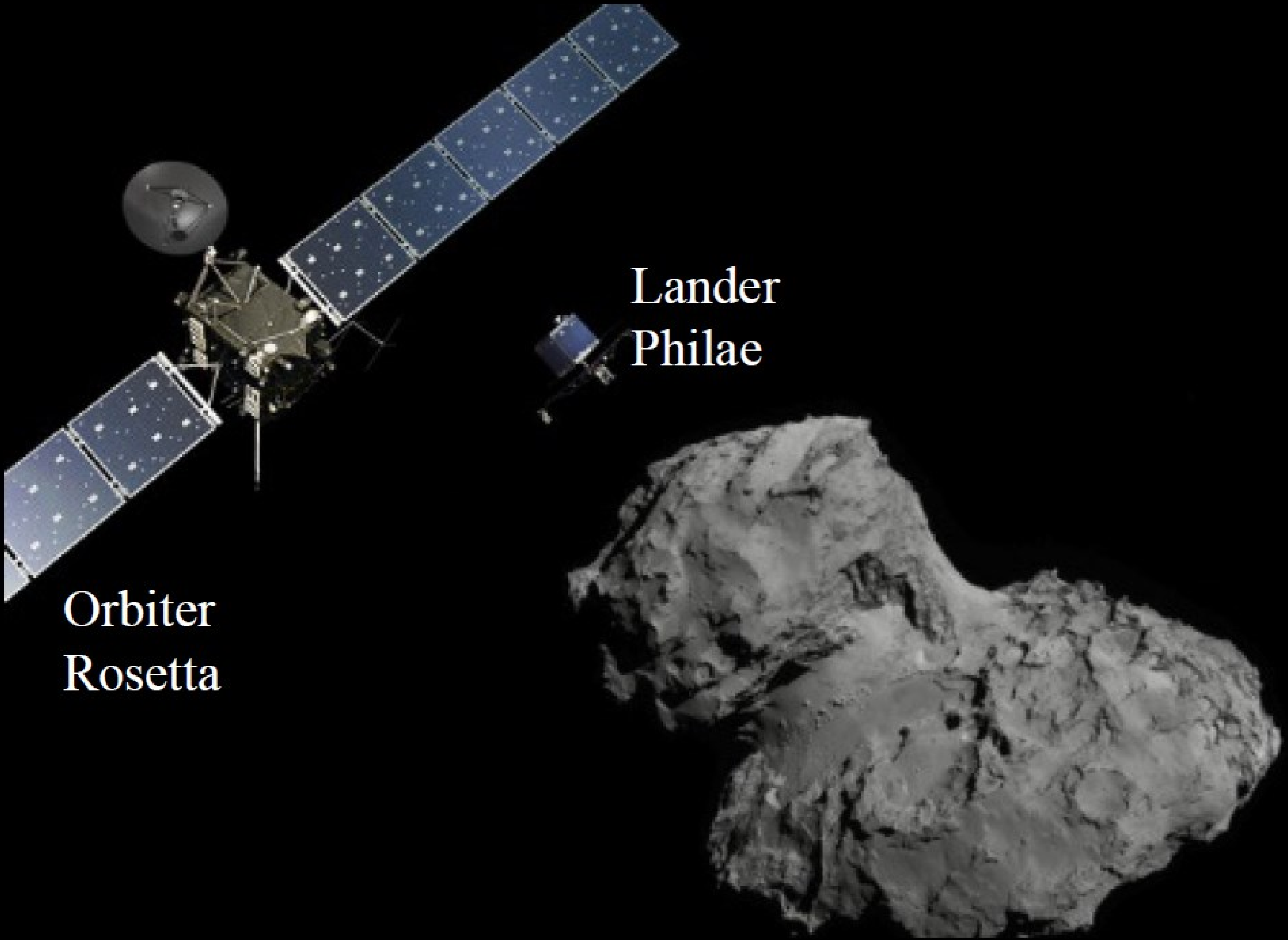
- As comet approaches Sun, ices heat up and evaporate. Radiation from the Sun photo-dissociates molecules:
  - $H_2O \rightarrow OH \rightarrow O$
  - $NH_3 \rightarrow NH_2 \rightarrow NH$
  - $CH_4 \rightarrow CH_2/CH_3 \rightarrow CH$
  - $HCN \rightarrow CN$

Ice abundances

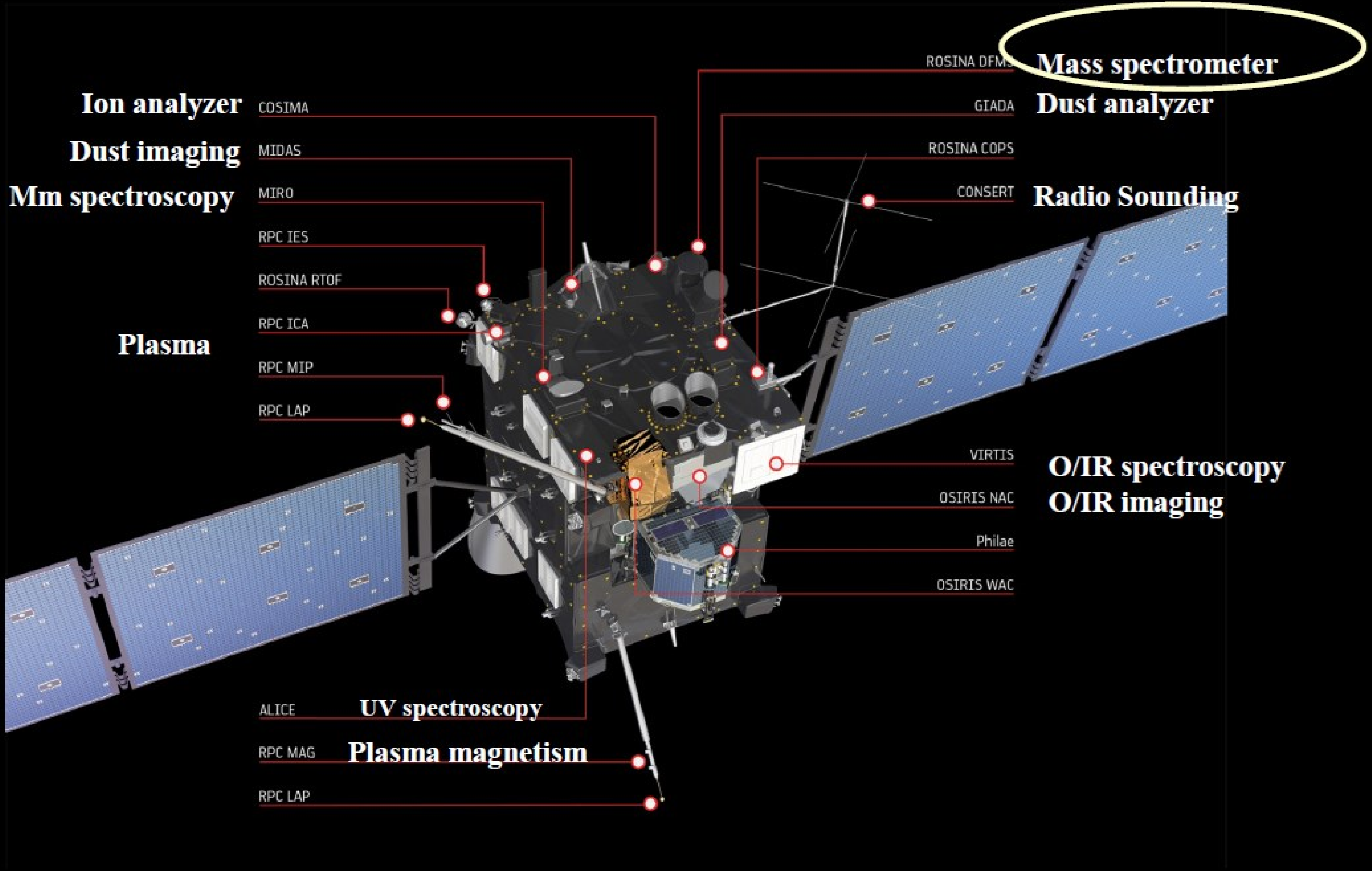
Species	Protostar ices	Comets
H_2O	100	100
CO	3-10	6-30
CO_2	10-35	2-20
CH_3OH	1-25	2
H_2CO	1-7	0.2-1
HCOOH	0.4-2	0.1
NH_3	1-10	0.5-2
CH_4	0.5-2	1

Similar abundances => some fraction of cometary ices are unaltered ISM ices?

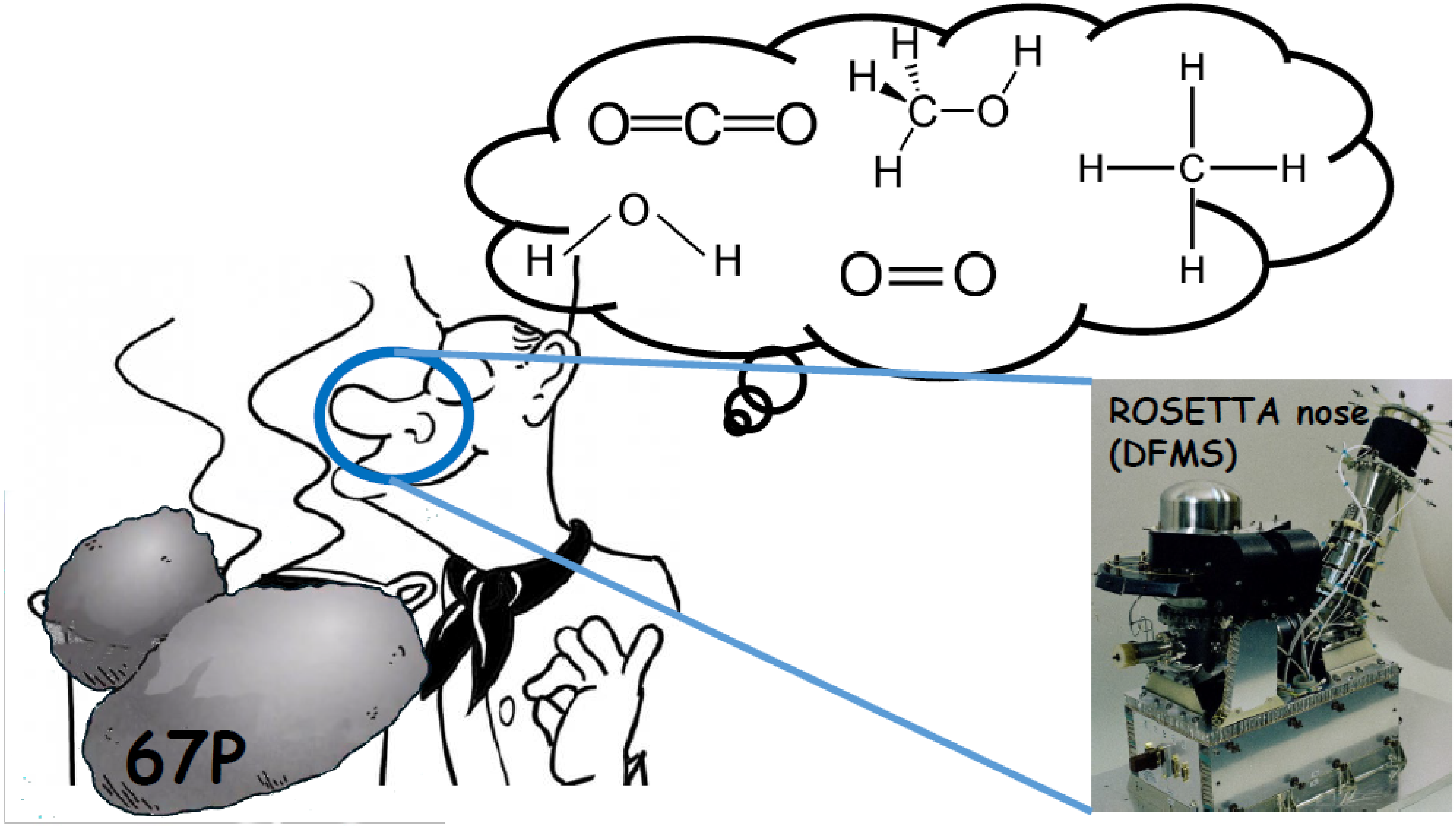
Rosetta and the origin of our solar system



Instruments on orbiter

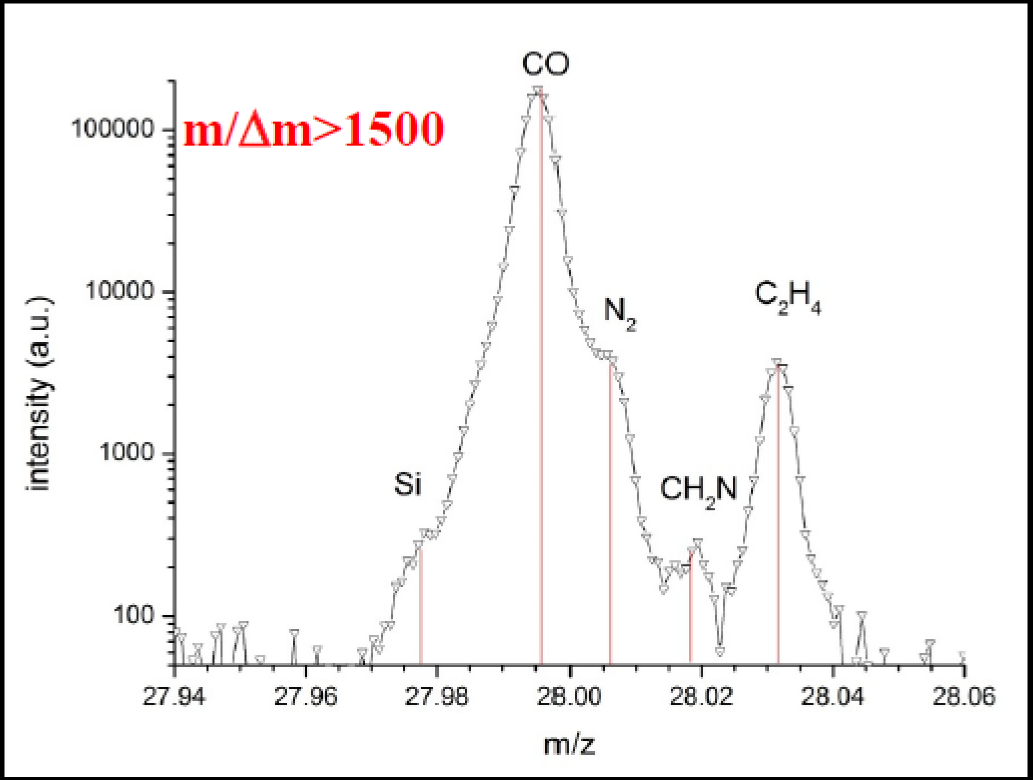


ROSETTA has a very good nose (DFMS)

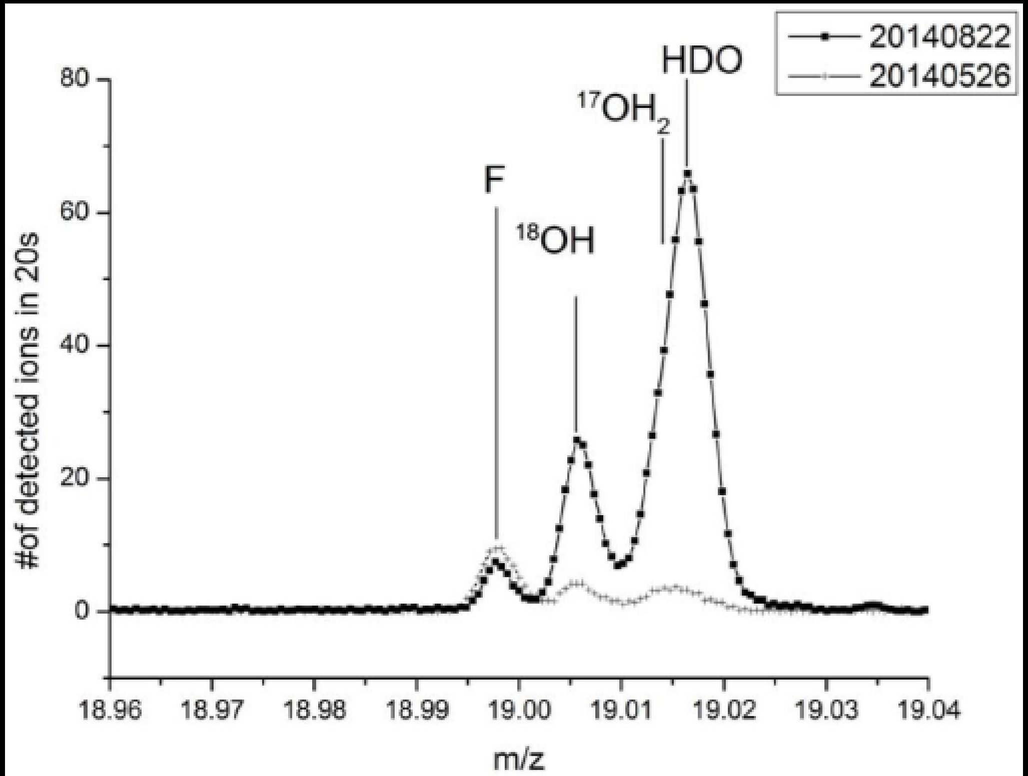


High mass resolution → unique identification

m/z 28: CO vs N_2

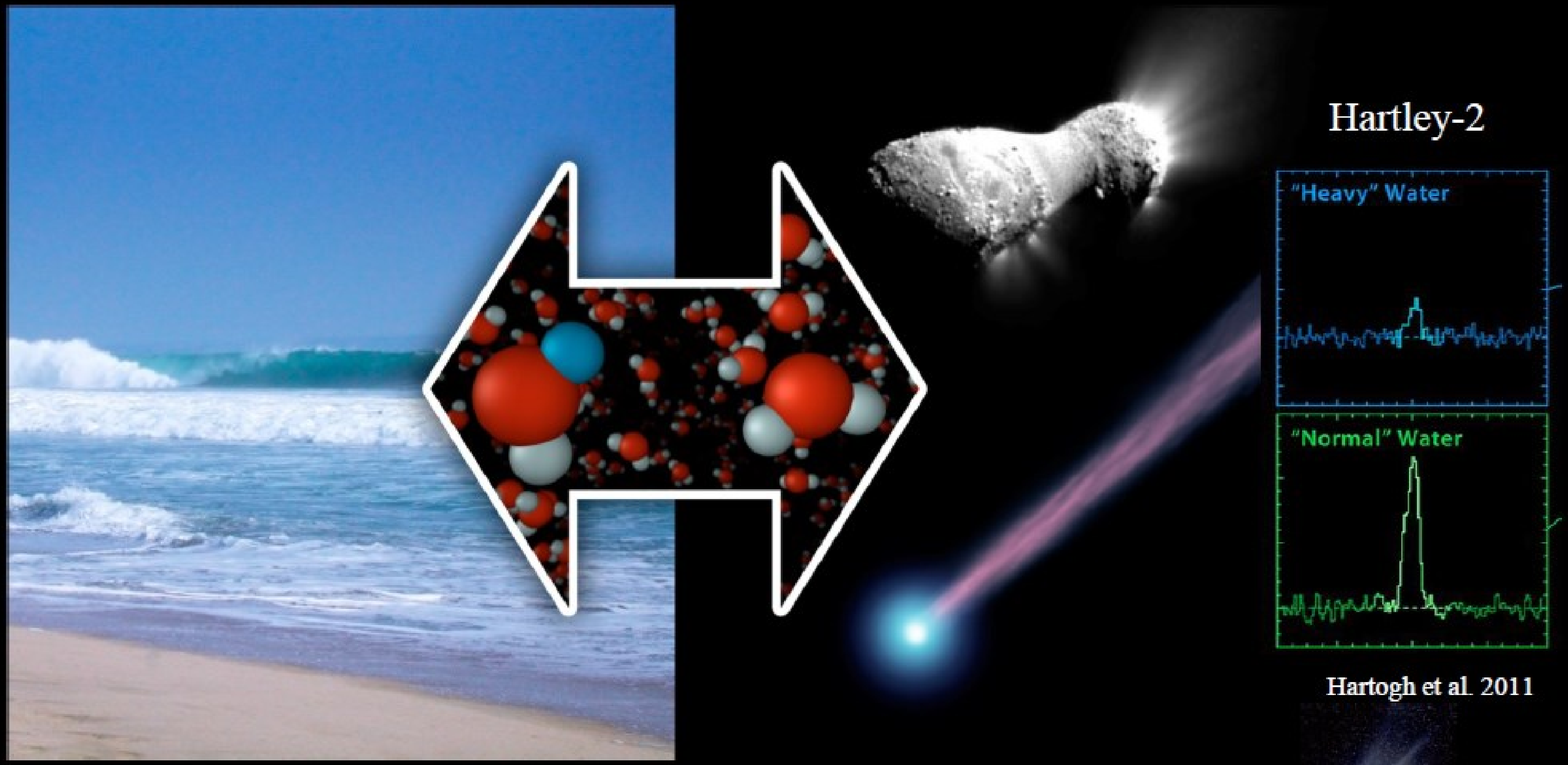


m/z 19: HDO vs $H_2{}^{17}O$ vs ^{18}OH



ROSINA:
Altwegg et al. 2014
Rubin et al. 2015

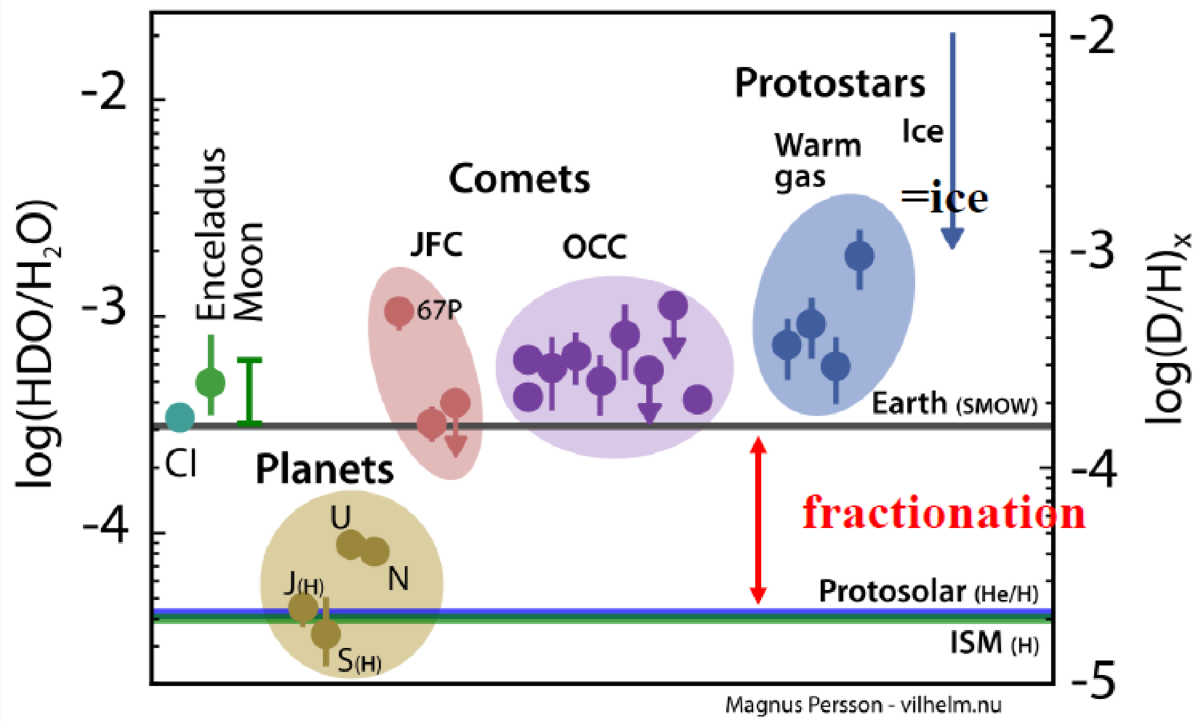
Did comets bring water to Earth?



HIFI: There is at least one family of comets with same abundance of heavy water:

$HDO/H_2O=1.5\ 10^{-4}$

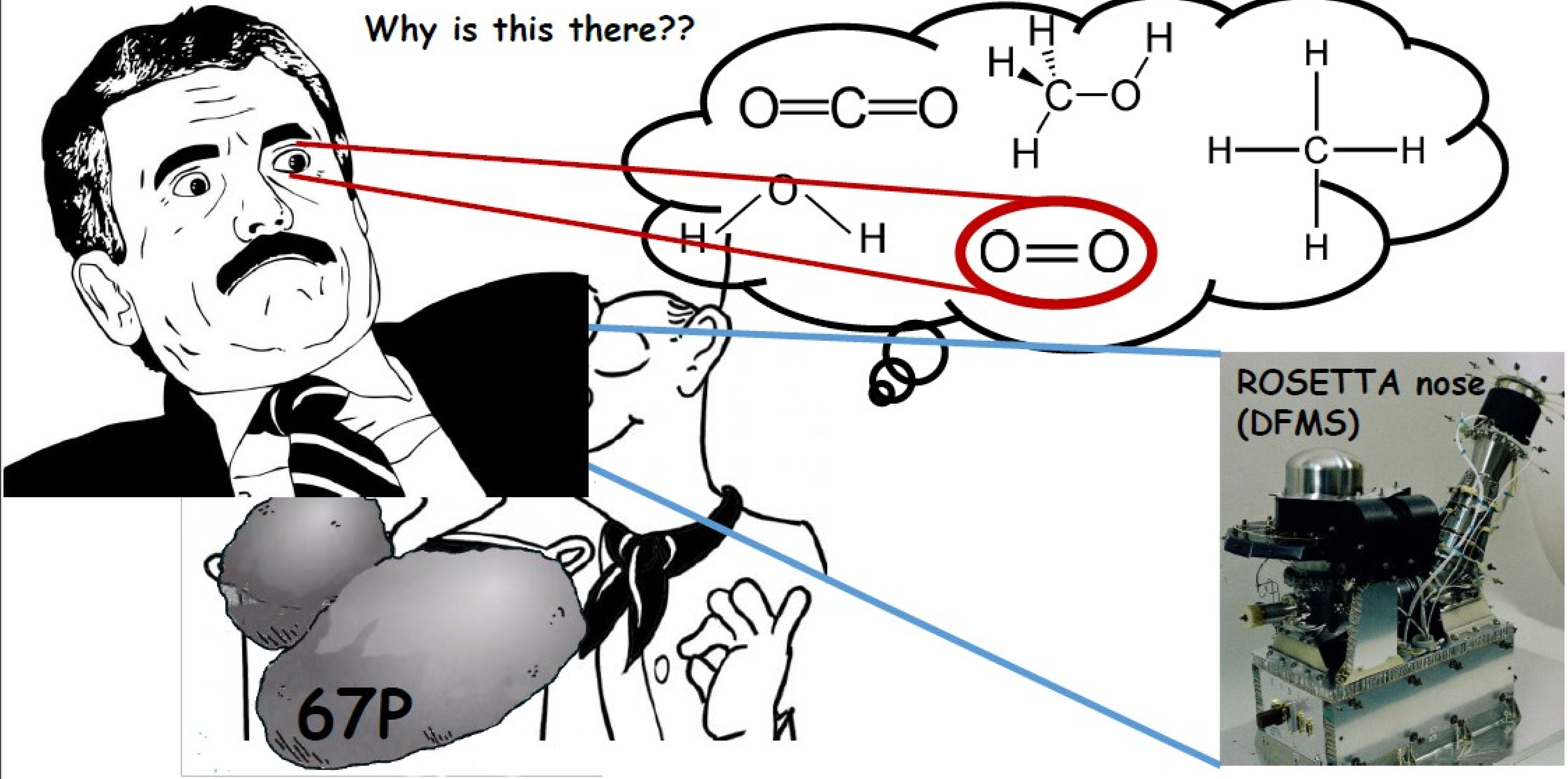
HDO/H_2O tracing history of Solar system?



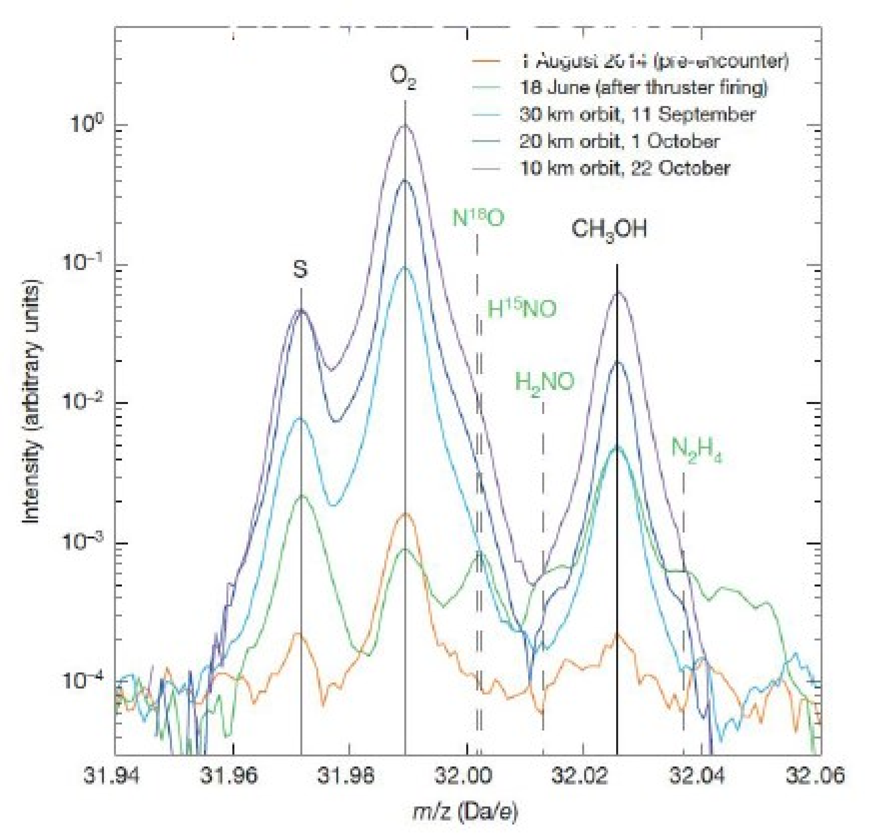
Persson et al. 2014
Bockelée-Morvan et al. 2014
Ceccarelli et al. 2014
Altwegg et al. 2014

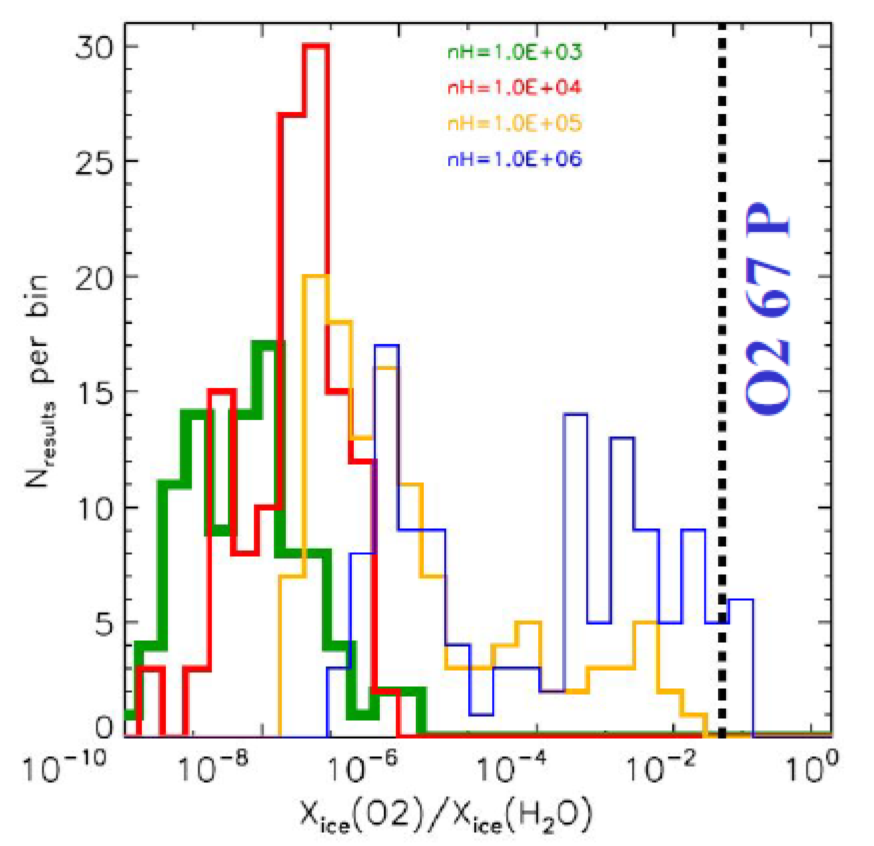
- Similarity of comets and interstellar ices could reflect inheritance of pre-stellar ices in large planetesimals that formed early
- Mixing in early solar system brought some of these water-rich bodies toward the terrestrial planet forming zone
- But comets do not have uniform D/H ratios whereas meteorites do.
- Current consensus: Comets probably contribute, but are not the sole originators of H_2O

ROSETTA has a very good nose (DFMS)



Abundant O_2 mystery





Taquet et al. 2016
Walsh et al. 2015

$O_2/H_2O = 3.7 \pm 1.5\%$, No O_3!

- Problem: O_2 readily transformed to H_2O in ice (remember video!)
- Only models with low H/O ratio (high density) and relatively warm conditions ($T \sim$ 20-30 K) can reproduce high observed O_2/H_2O ice ratio.

Organics on the surface

Table 1. The 16 molecules used to fit the COSAC mass spectrum.

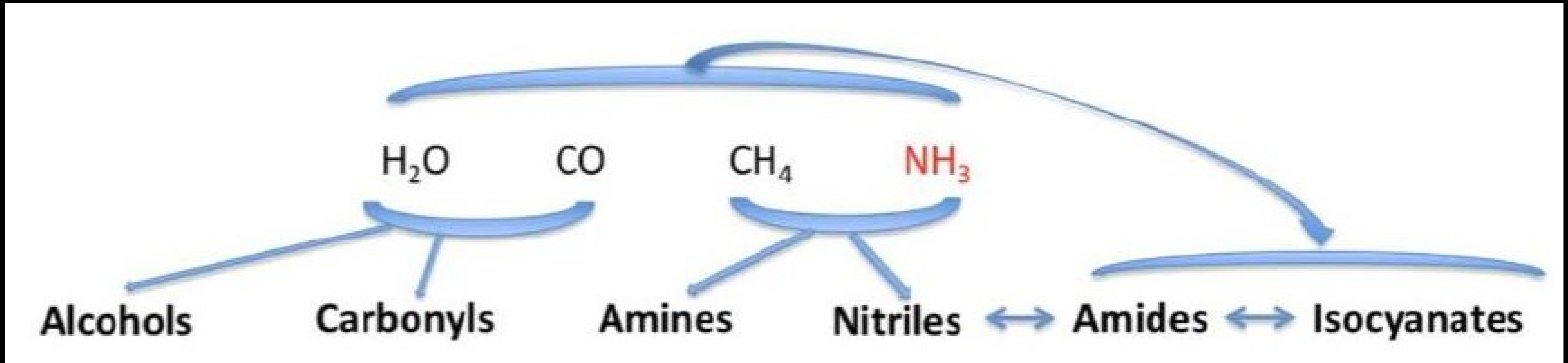
Name	Formula	Molar mass (u)	MS fraction	Relative to water
Water	H_2O	18	80.92	100
Methane	CH_4	16	0.70	0.5
Methanenitrile (hydrogen cyanide)	HCN	27	1.06	0.9
Carbon monoxide	CO	28	1.09	1.2
Methylamine	CH_3NH_2	31	1.19	0.6
Ethanenitrile (acetonitrile)	CH_3CN	41	0.55	0.3
Isocyanic acid	HNCO	43	0.47	0.3
Ethanal (acetaldehyde)	CH_3CHO	44	1.01	0.5
Methanamide (formamide)	$HCONH_2$	45	3.73	1.8
Ethylamine	$C_2H_5NH_2$	45	0.72	0.3
Isocyanomethane (methyl isocyanate)	CH_3NCO	57	3.13	1.3
Propanone (acetone)	CH_3COCH_3	58	1.02	0.3
Propanal (propionaldehyde)	C_2H_5CHO	58	0.44	0.1
Ethanamide (acetamide)	CH_3CONH_2	59	2.20	0.7
2-Hydroxyethanal (glycolaldehyde)	CH_2OHCHO	60	0.98	0.4
1,2-Ethanediol (ethylene glycol)	$CH_2(OH)CH_2(OH)$	62	0.79	0.2

COSAC instrument on Philae

"sniffing the ground truth"

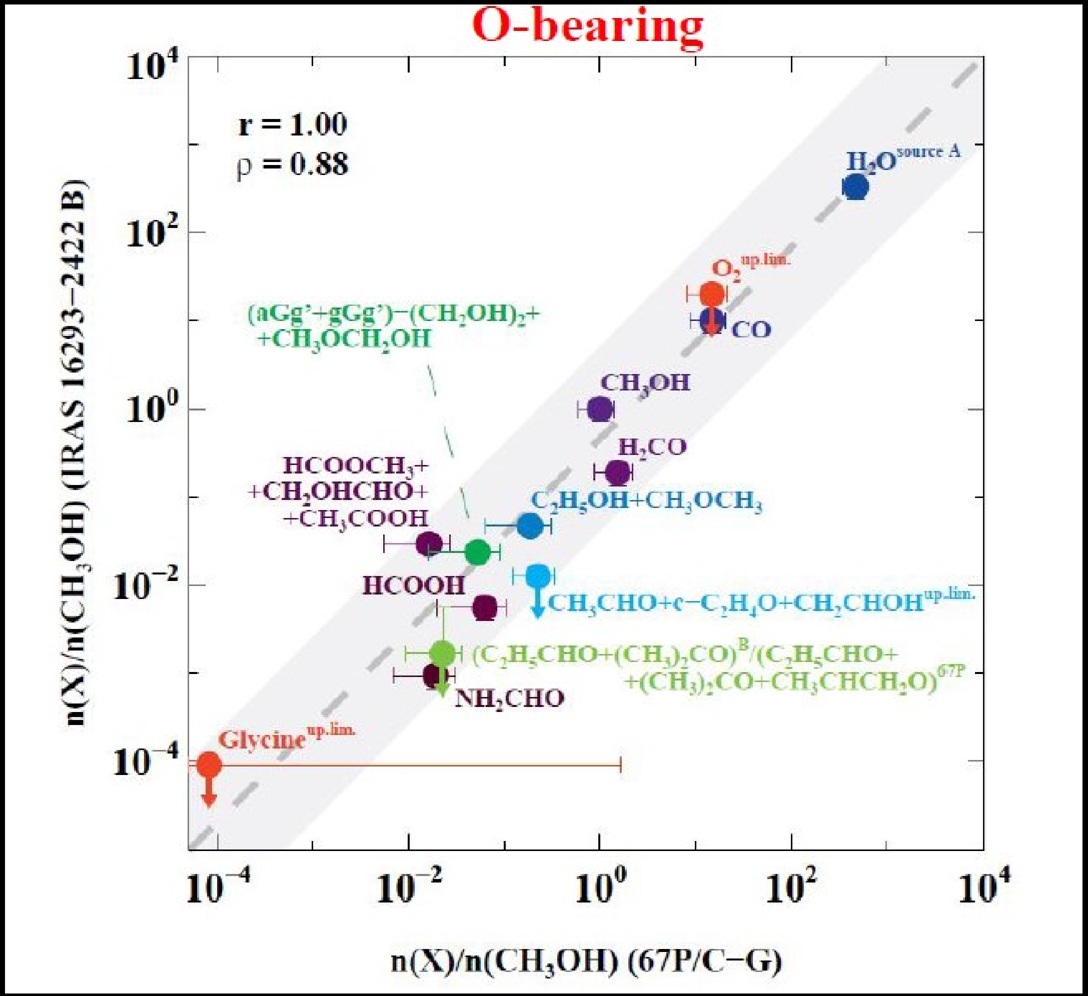
Goesmann et al. 2015

Note: COSAC has $m/\Delta m \sim 1$: cannot distinguish species with same mass




ROSINA Zoo
Methane
Ethane
Propane
Butane
Pentane
Hexane
Heptane
Glycine
(Aminoacid
S2
S3
S4
Methanethiole (CH3SH)
Ethanethiol (C2H5SH)
Thioformaldehyde (CH2S)
Ammonia
Methylamine
Ethylamine
Formic acid
Acetic acid
Acetaldehyde
Ethylenglycol
Propylenglycol
Butanamide
Argon
Krypton
Xenon
Acetylene
HCN
Acetonitril
Formaldehyde
HF
HCl
HBr
P
CH3Cl
Benzene
Toluene
Xylene
Benzoic acid
Naphthalene
N≡N
Nitrogen
Oxygen
Hydrogenperoxyd
Carbon monoxide
Carbon dioxide
Methanol
Ethanol
Propanol
Butanol
Pentanol
Cyanogen
Hydrogensulfide
Carbonylsulfide
Sulfur monoxide
Sulfur dioxide
Carbon disulfide
Na, K, Si, Mg
Detected in IRAS16293
Upper limit
Drozdovskaya et al. 2019
Altwegg et al. 2019, ARAA

Comparison of young disk and comet



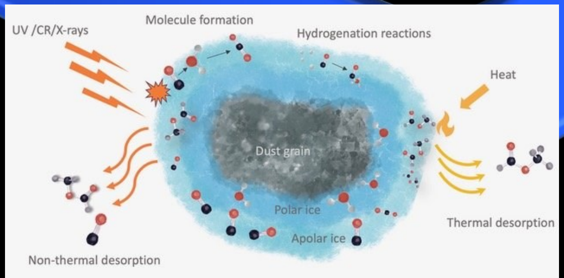
- Overall similarity points to at least some preservation
- Comet somewhat richer in COMs than young disk
- (also holds for N- and S-bearing species)

Drozdovskaya et al. 2019

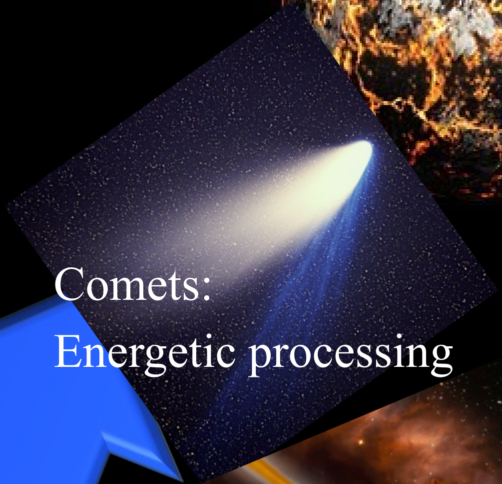
Building the Solar system's organic inventory

CO reservoir

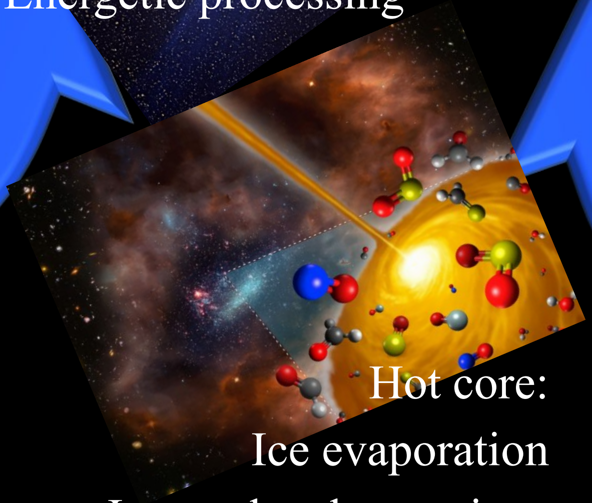
Gas:
ion-molecule reactions
Cosmic-ray photolysis



Ices:
Hydrogenation, photolysis, thermal polymerization, ice-ion-molecule, ice segregation



Comets:
Energetic processing

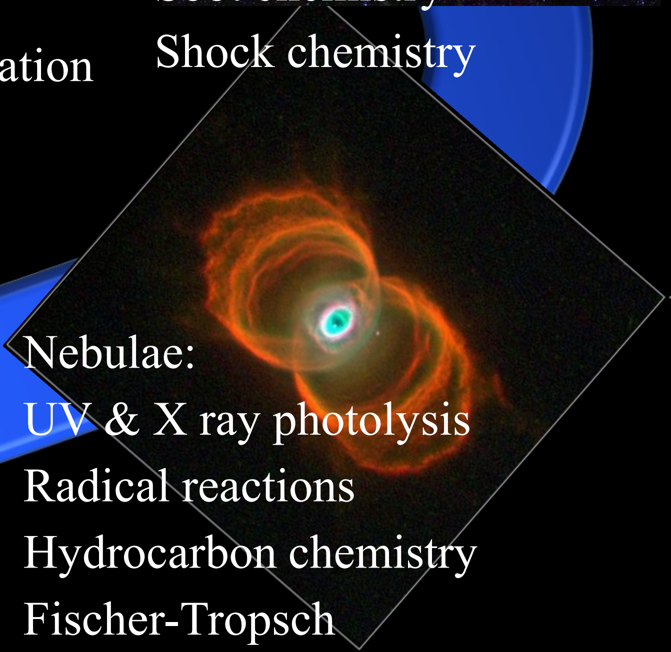


Hot core:
Ice evaporation
Ion-molecule reactions

Asteroids:
Aqueous alteration

PAH reservoir

Stars:
Soot chemistry
Shock chemistry



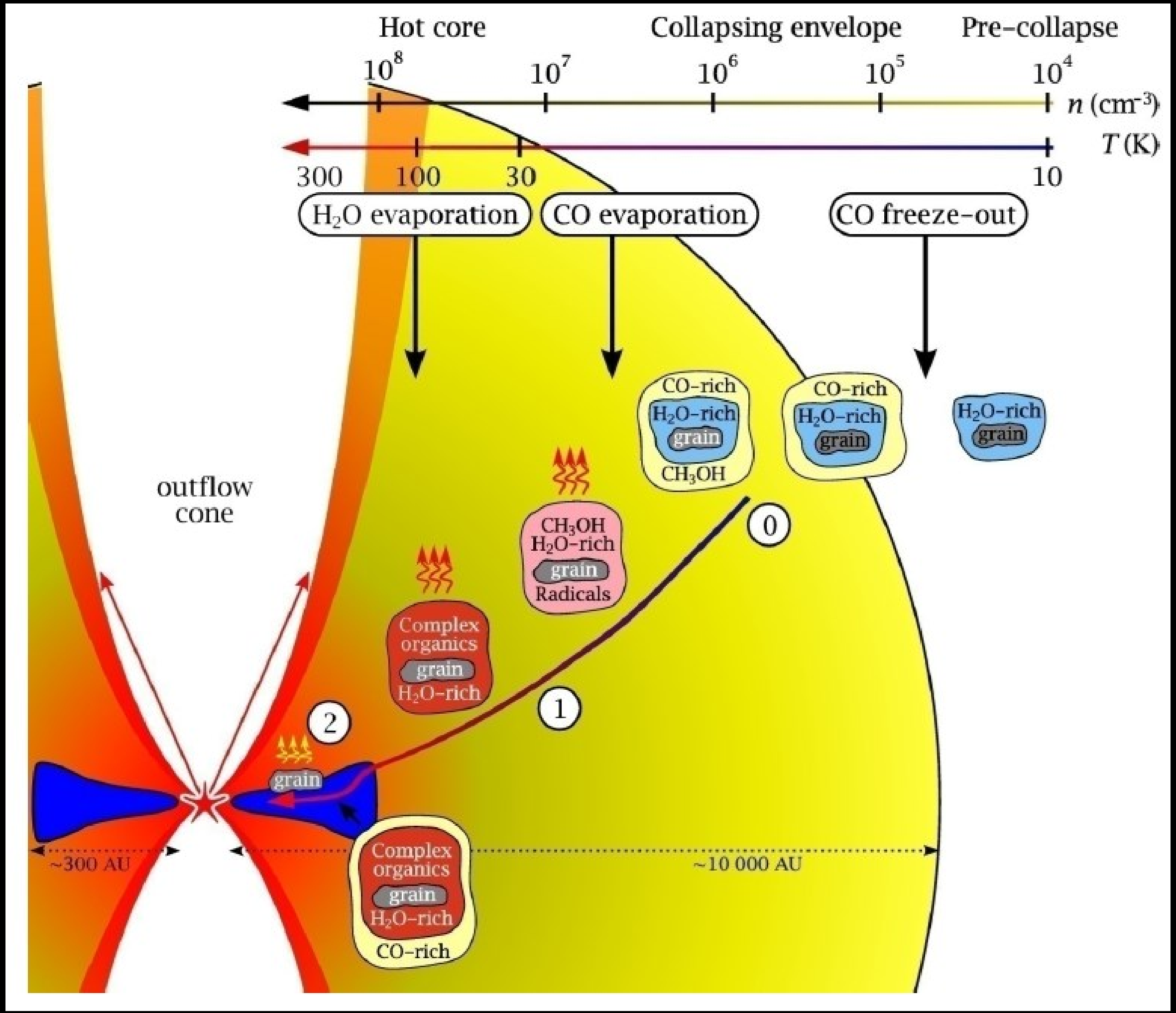
Nebulae:
UV & X ray photolysis
Radical reactions
Hydrocarbon chemistry
Fischer-Tropsch
Shocks, intermittent accretion, diffusion

Right-hand branch not discussed in these lectures => Astrochemistry 2!

7.10 Summary

- Systematic trends in ices and gas-phase data allow chemical scenario during low- and high-mass star formation to be developed
    - 'Quantitative astrochemistry has come of age'
- Chemistry in pre-stellar cores and cold envelopes driven by freeze-out
    - Directly observed through ices
    - Explains lack of O_2, extreme deuteration, N_2H^+…
- Chemistry in inner warm envelope driven by sublimation of ices followed by a 'hot core' chemistry
    - Most complex organics produced as zeroth or first generation on surfaces?

Summary: molecules from cloud to disks



Herbst & van Dishoeck 2009

Visser et al. 2009, 2011

- 0th generation: cold ices: CH_3OH + ?
- 1st generation: warm ices: more complex organics
- 2nd generation: high-T gas-phase chemistry

Summary (continued)

- Different IR and sub-mm features can be used as diagnostics of the earliest stages of star formation
  - Cold pre/proto-stellar cores: N_2H^+, H_2D^+, ices
  - Warm inner envelopes: CH_3OH
  - Hot cores: Complex organics
  - Shocks: SiO, SO, SO_2

Summary (continued)

- Chemistry in disks being studied
  - Inner disk: high *T* chemistry at high densities
  - Outer disk: layered chemical structure
- Comets provide clue to composition of material from which our solar system is made
  - Large similarity between cometary and interstellar ices
- Laboratory data and theoretical studies of basic molecular processes remain essential for further progress.

Future is bright with ALMA and JWST in full swing and ELT, Ariel, Habitable Worlds coming soon!

The ALMA (r)evolution

- New molecules
  - More complex (prebiotic) species
    - Weeding out known molecules
  - Known molecules outside Sgr B2 / Orion
- Spatial distribution
  - Resolve relevant physical-chemical scales
- New processes and excitation
  - Probe hotter gas, state-selective chemistry
- Extragalactic chemistry
  - High-z galaxies like Orion 40 years ago

The JWST (r)evolution

- CO_2 in exoplanet atmospheres
- Photochemistry in exoplanet atmospheres (SO_2)
- Detection of the methyl (CH_3^+) cation in a star-forming region
- Complete inventory of ice chemistry (CH_3OH, OCS, numerous minor species)
- Rich carbon chemistry around young stars (C_2H_2, HCN, CO_2...) and hydrocarbons from dust processing close to host in carbon-rich protoplanetary disk (C_4H_2, benzene...)
- PAH features in T Tauri stars

JWST & ALMA are astrochemistry machines!

Thank you for coming to lectures!