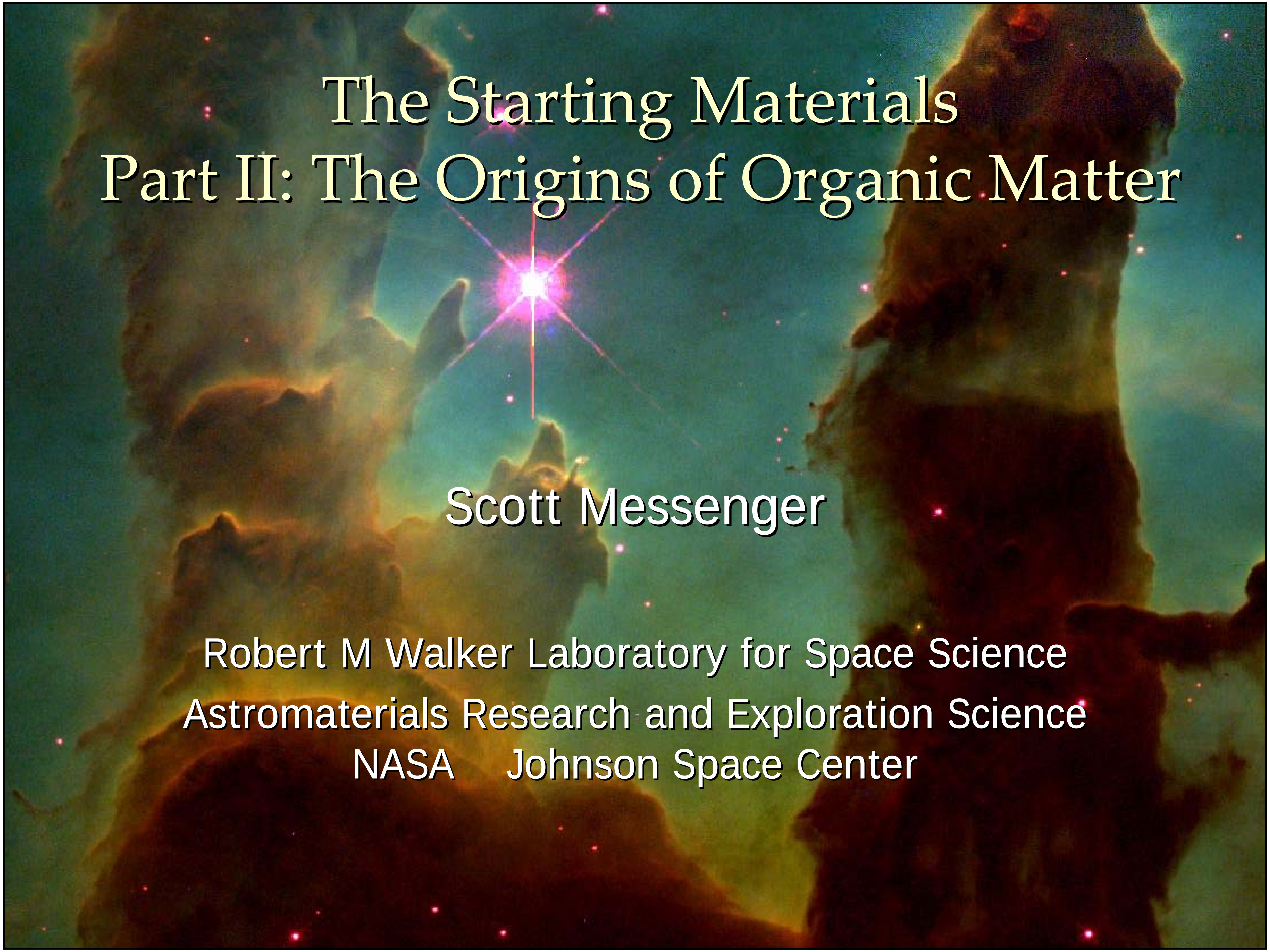

The Starting Materials
Part II: The Origins of Organic Matter

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Outline of This Lecture

- Introduction to organic molecules
- Molecular clouds to planetary disks
- Methods for studying interstellar organics
  - Radio spectroscopy
  - Infrared spectroscopy
- Interstellar chemistry
  - Ion-molecule reactions
  - Grain-surface chemistry
  - Radiation processing of ices
- Evidence for presolar organic matter
  - Meteorites
  - Interplanetary dust

What is Organic Matter?

INORGANIC

Calcium Carbonate: $CaCO_3$

Carbon black: pure C

Graphite: pure C

Diamond: pure C

ORGANIC

Crude oil: various hydrocarbons

Krispy Kreme donut

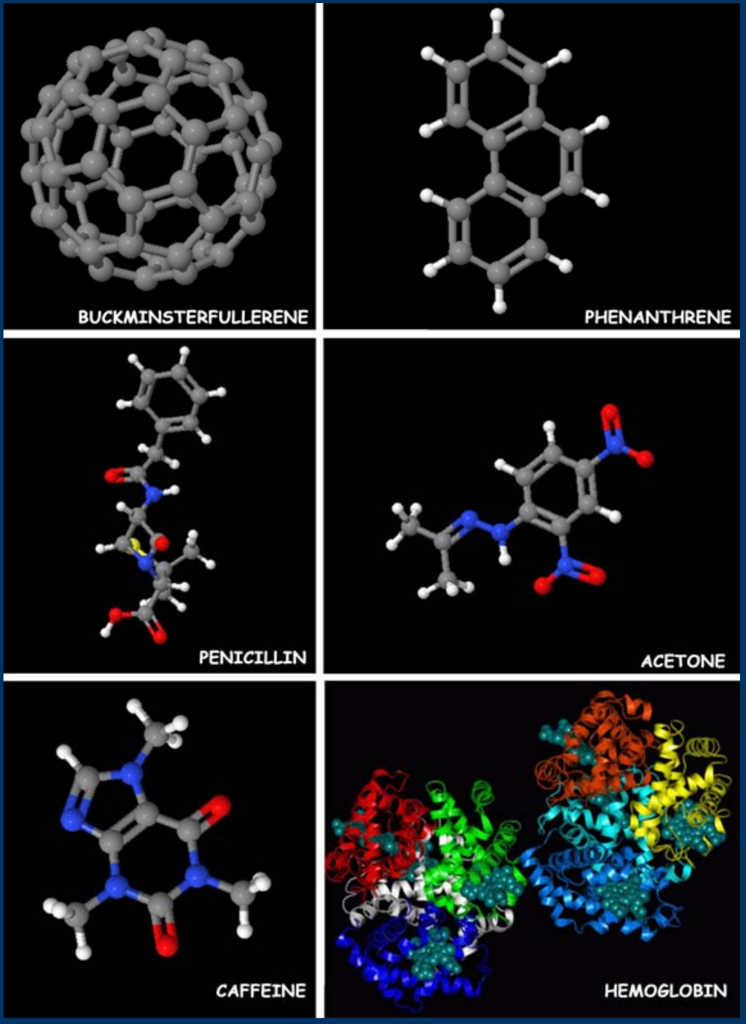
Acetone: CH_3COCH_3

Ichiro Suzuki

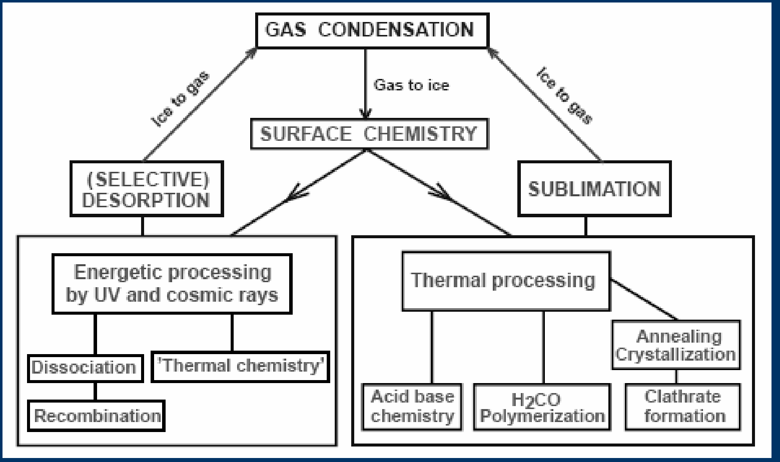
Organic molecules: Compound that contain both Carbon and Hydrogen

Organic molecules are <u>not necessarily</u> related to life

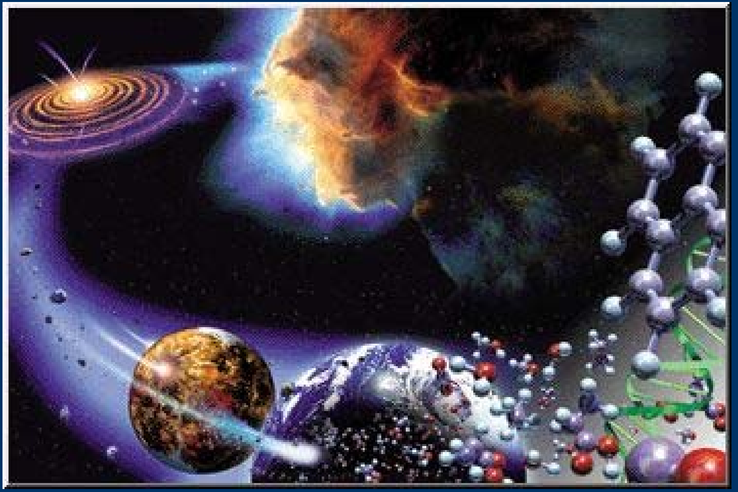
Astrophysical Importance of Organic Matter



Organic molecules have a wide variety of structures, reaching billions of atoms in human DNA



Formed/altered by numerous processes over an enormous range of physical conditions (Ehrenfreund)



Organic matter on Earth was originally delivered by meteorites and comets

Dark Interstellar Clouds

Masses: 10-500 solar masses

Sizes: 1-5 pc

Temperature: 10 K

Density: 10^4 cm^{-3}

Form a few low mass stars

This dark molecular cloud is relatively small (< 1 light year across) and isolated. This cloud is in its earliest stage of collapse, no active star formation yet.

ESO PR Photo 20a/99 (30 April 1999)

The "Black Cloud" B68
(VLT ANTU + FORS1)

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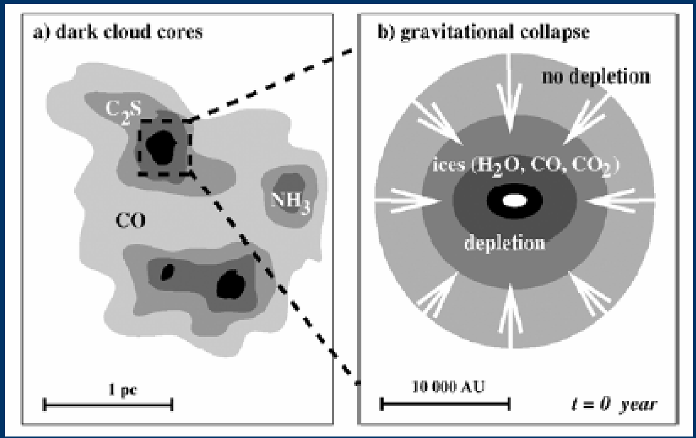
Cold, Dark Molecular Clouds in a Star-Forming Region

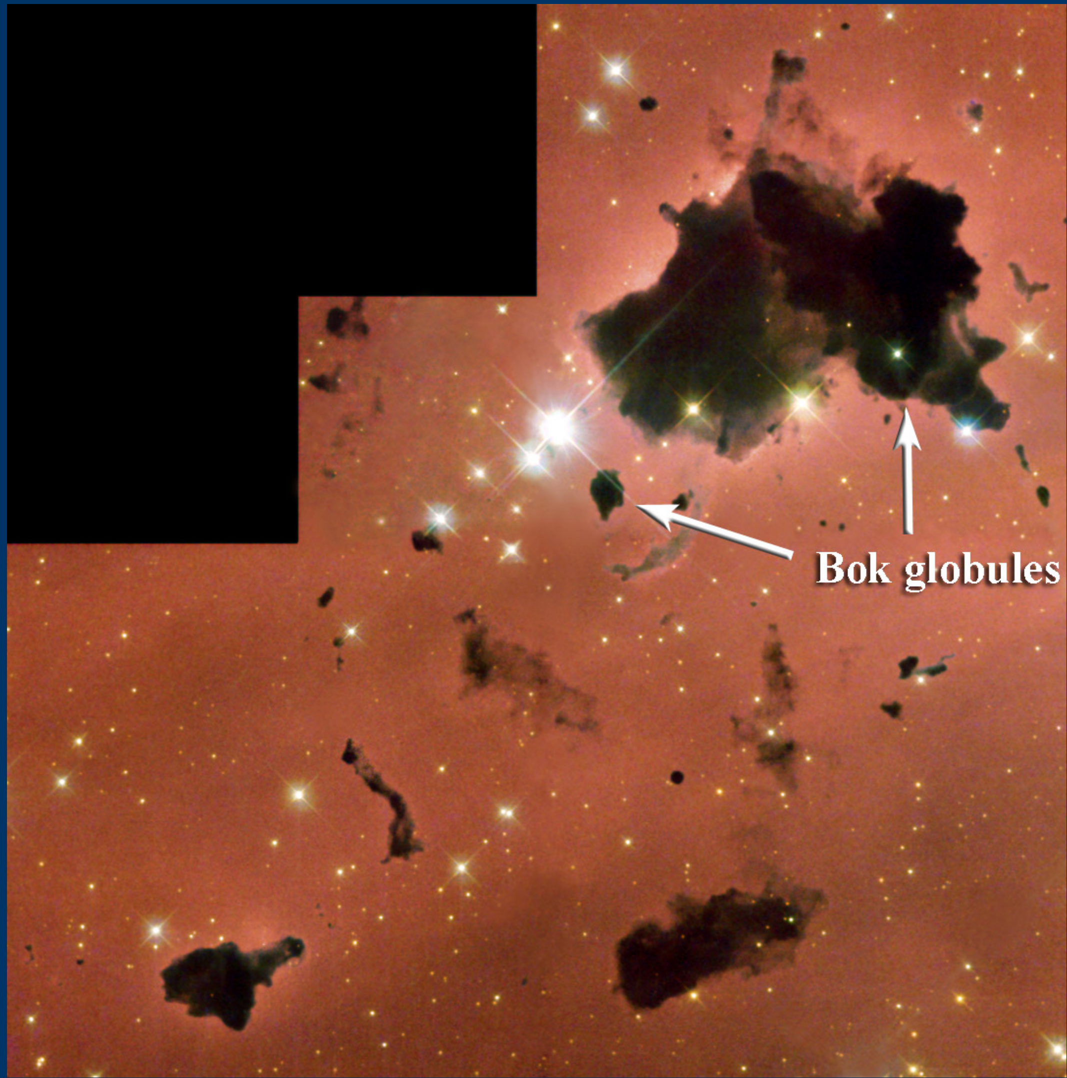


Ehrenfreund et al. 2002

- Stars form from cold, dense clouds
- Gravitational collapse is 'inside-out'
- Initially, the core is the coldest region volatiles are depleted onto grains: ice coatings
- Radiation from nearby hot young stars affects the outer regions of protosolar cores

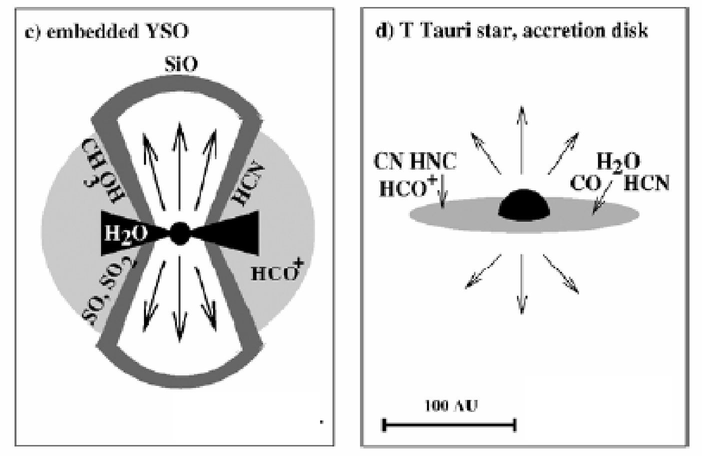
Dark cloud cores:
T ~ 10 - 100 K, $\rho < 10^4 - 10^6$ H cm^{-3}

Hot, radiation rich area near cloud cores:
T ~ 10,000 K, $\rho < 10^3$ H cm^{-3}



Protoplanetary Disks

Final stages of star formation

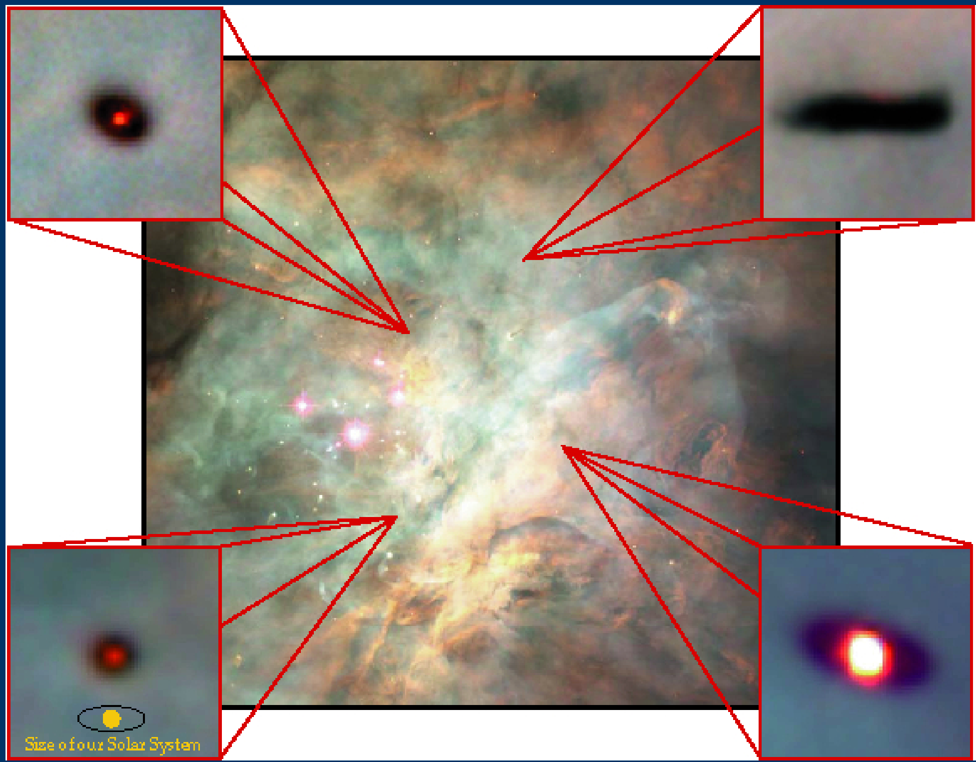


Ehrenfreund et al. 2002

Protoplanetary disk continually accretes matter

Accretion shock is a source of energy for the disk

Protoplanetary disks in Orion star forming region



HST WFPC2 McCaughrean & Dell (1995)

Environment Near a Young Star

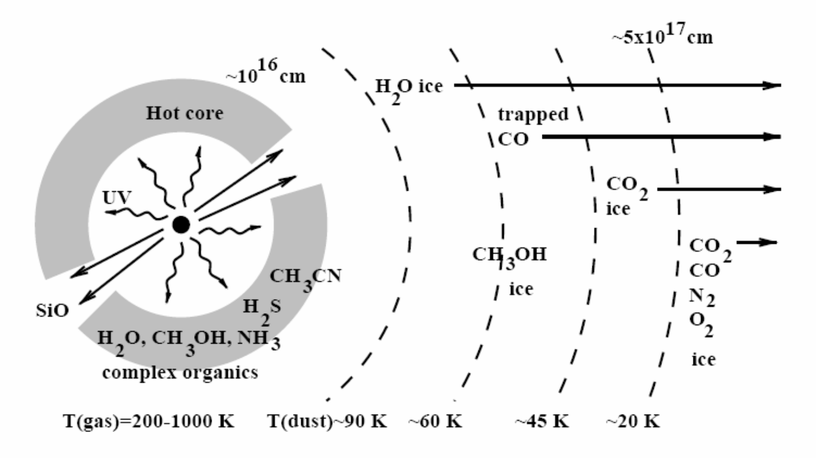


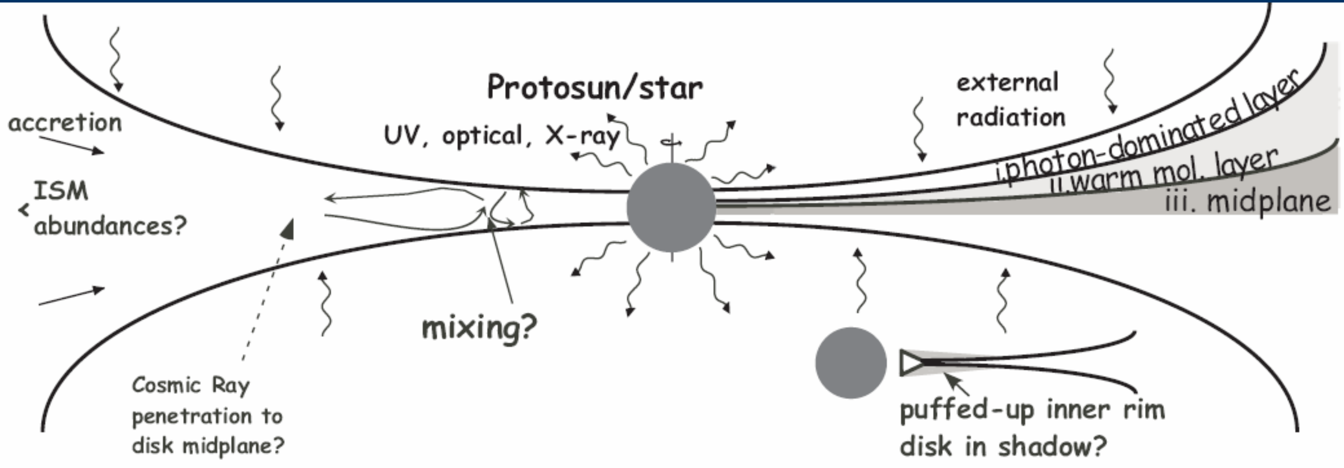
Figure 4 Schematic illustration of the chemical environment of massive YSOs. The variation in the chemical structure of the ice mantle in the envelope due to thermal desorption is shown (based on Tielens et al 1991, Williams 1993).

Van Dishoeck & Blake (1998) Ann Rev A&A

Chemical compositions vary with distance from the star, height above the midplane, and evolve with time

A protoplanetary disk is 3 dimensional!

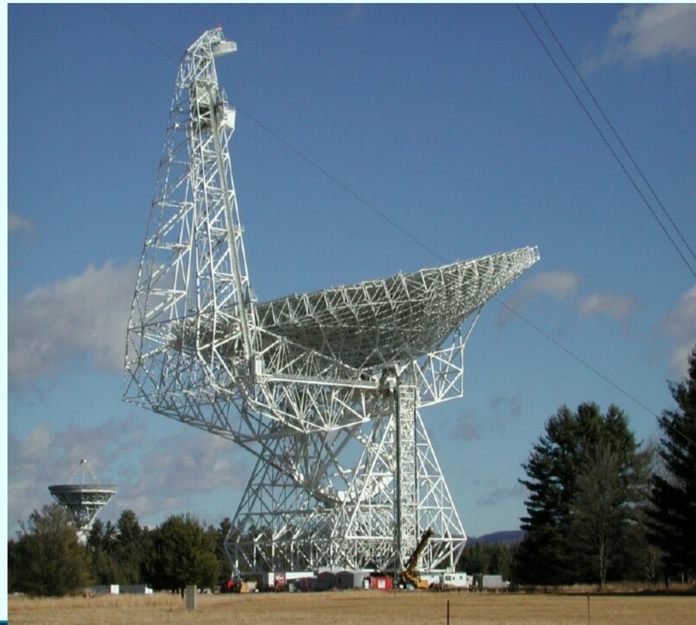
<u>Outer portion of the disk (> 100 AU)</u>
<u>Midplane</u>: Cold (<20K), volatiles accrete
<u>Warm molecular layer</u>: 10s of K, molecules occur in gas phase
<u>Photon dominated layer</u>: radiation-driven chemistry occurs



Bergin et al. Protostars and Planets V

Known Interstellar Molecules

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	>12 atoms
H_2	C_3*	c-C_3H	C_5*	C_5H	C_6H	CH_3C_3N	CH_3C_4H	CH_3C_5N (?)	HC_9N	C_6H_6* (?)	$HC_{11}N$
AlF	C_2H	l-C_3H	C_4H	l-H_2C_4	CH_2CHCN	$HCOOCH_3$	CH_3CH_2CN	$(CH_3)_2CO$			
AlCl	C_2O	C_3N	C_4Si	C_2H_4*	CH_3C_2H	CH_3COOH	$(CH_3)_2O$	$(CH_2OH)_2$ (?)			
C_2**	C_2S	C_3O	l-C_3H_2	CH_3CN	HC_5N	C_7H	CH_3CH_2OH	H_2NCH_2COOH,			
								Glycine?			
CH	CH_2	C_3S	c-C_3H_2	CH_3NC	CH_3CHO	H_2C_6	HC_7N	CH_3CH_2CHO			
CH^+	HCN	C_2H_2*	CH_2CN	CH_3OH	CH_3NH_2	CH_2OHCHO	C_8H				
CN	HCO	NH_3	CH_4*	CH_3SH	c-C_2H_4O	l-HC_6H* (?)					
CO	HCO^+	HCCN	HC_3N	HC_3NH^+	H_2CCHOH	CH_2CHCHO (?)					
CO^+	HCS^+	$HCNH^+$	HC_2NC	HC_2CHO							
CP	HOC^+	HNCO	HCOOH	NH_2CHO							
SiC	H_2O	HNCS	H_2CNH	C_5N							
HCl	$HOCO^+$	$HOCO^+$	H_2C_2O	l-HC_4H* (?)							
KCl	HNC	H_2CO	H_2NCN	l-HC_4N							
NH	HNO	H_2CN	HNC_3								
NO	MgCN	H_2CS	SiH_4*								
NS	MgNC	H_3O^+	H_2COH^+								
NaCl	N_2H^+	c-SiC_3									
OH	N_2O	CH_3*									
PN	NaCN										
SO	OCS										
SO^+	SO_2										
SiN	c-SiC_2										
SiO	CO_2*										
SiS	NH_2										
CS	H_3^+*										
HF	H_2D^+,										
	HD_2^+										
SH*	SiCN										
HD	AlNC										
FeO?	SiNC										
O_2?											



Green Bank radio telescope

Identifications by radio spectroscopy

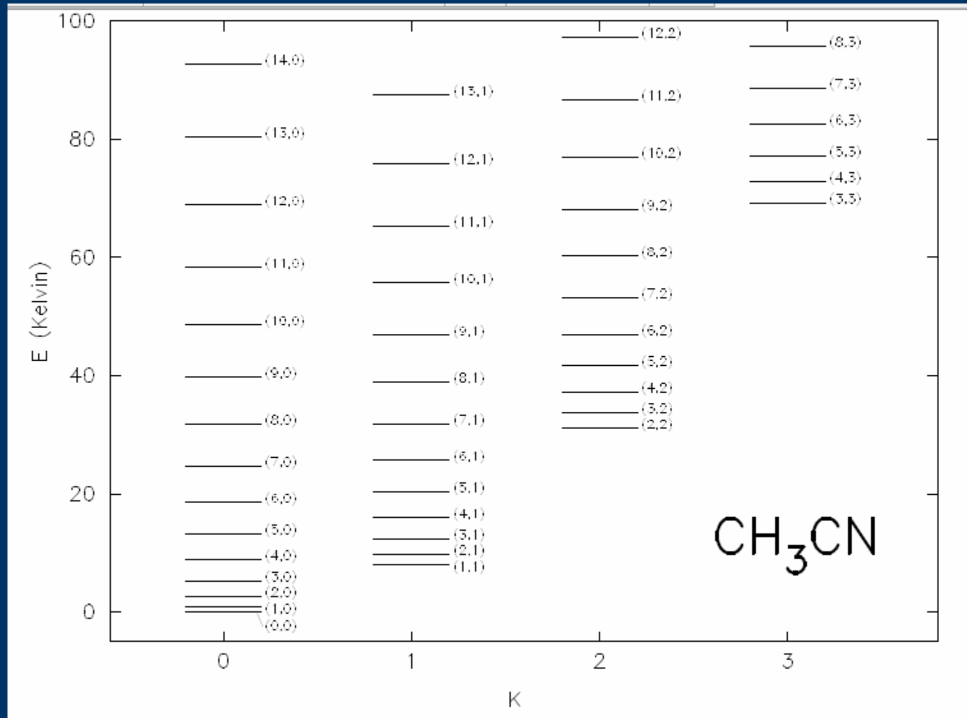
Müller et al. (2005) J. Mol. Struct. 742, 215

Rotational Spectroscopy

When a molecule's rotational state changes it releases a photon at radio or mm-wave frequencies.

Each molecule has a unique rotational spectroscopic 'fingerprint'

In some cases it is possible to identify 'isotopomers' of a molecule and determine its isotopic ratios



Rotational energy levels

<u>Probe of distant environments</u>

- Temperature
    - Suitable for cold molecular clouds
- Density
- Local velocity dispersion

<u>Limitations of rotational spectroscopy</u>

- Only possible for gas phase molecules
- Limited to relatively simple molecules

Infrared Spectroscopy

- IR spectra sensitive to functional groups, not entire molecules
- Best way to characterize dust, ice by spectroscopy
- Very limited ability to measure isotope ratios

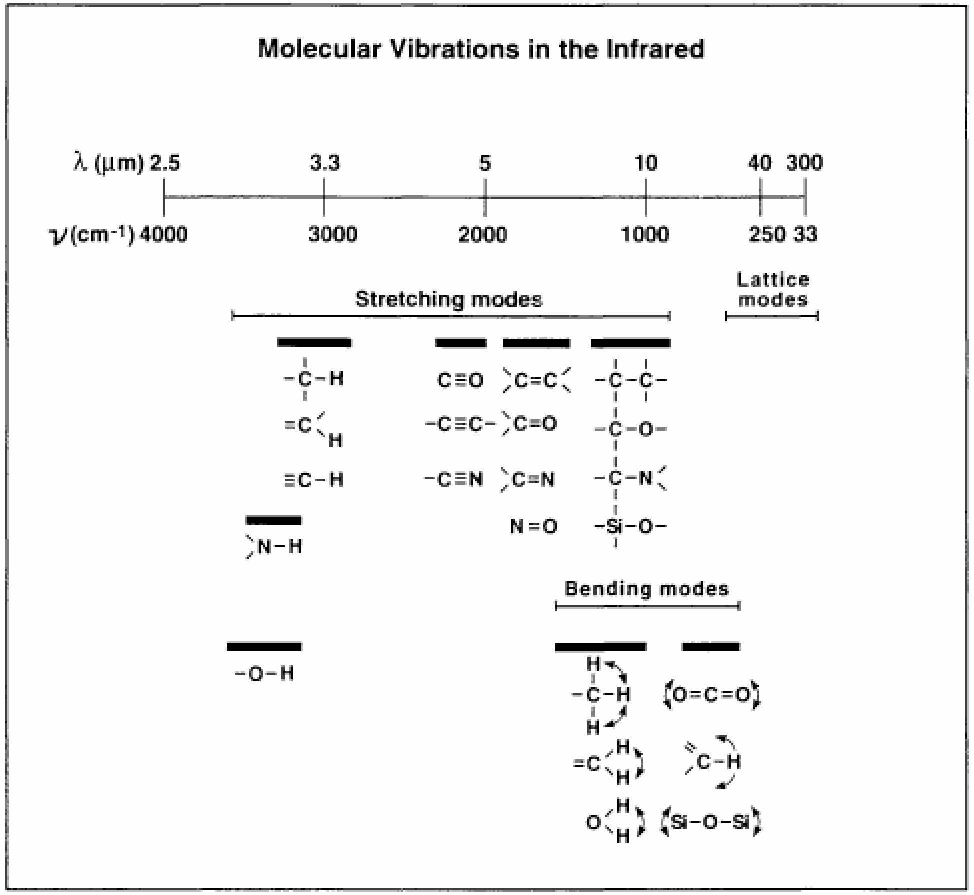
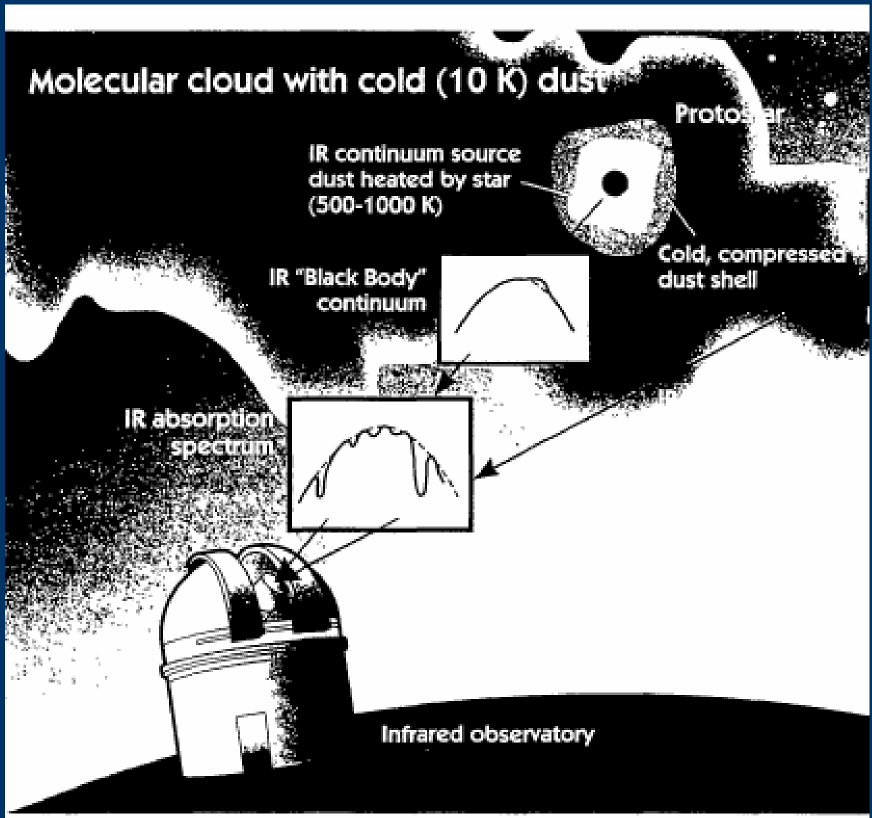
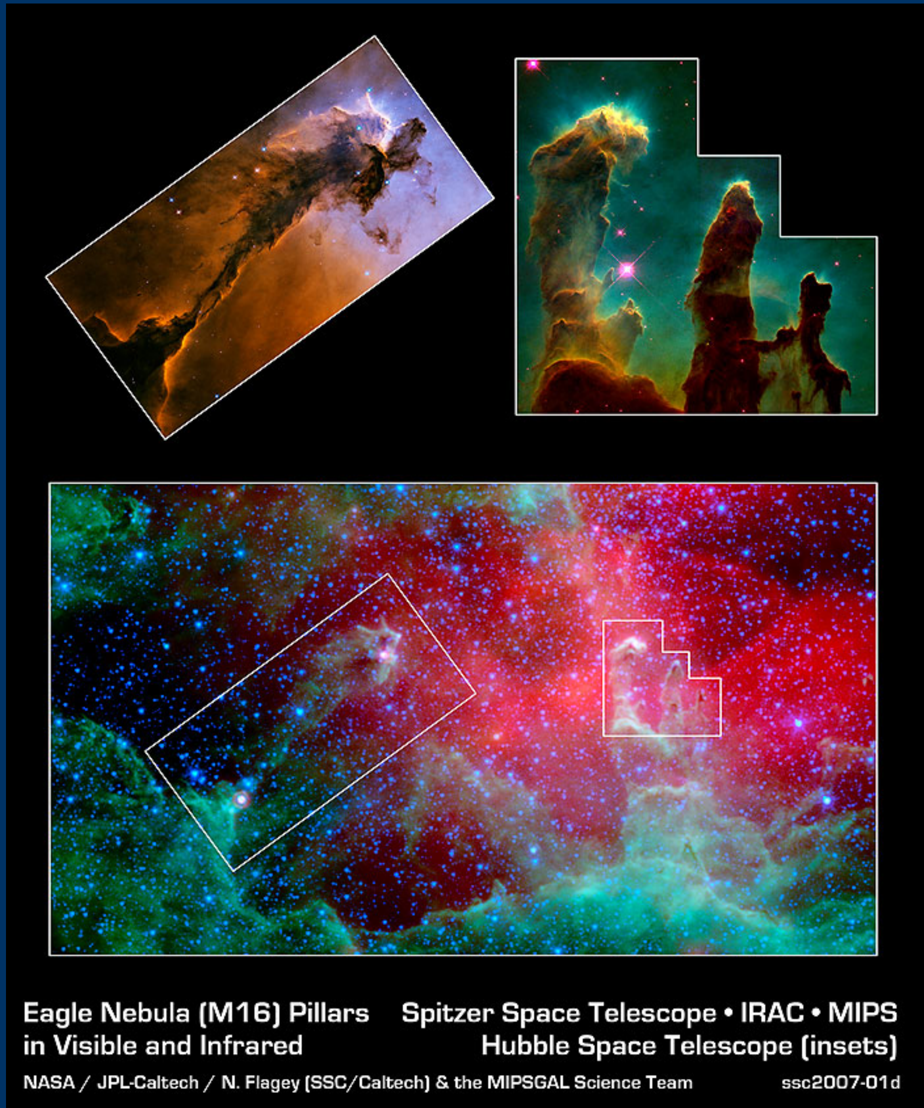


FIG. 1. A schematic drawing of the infrared spectral region between 4000 and 300 cm^{-1} (2.5–33 μm). The range over which the interatomic vibrations of a variety of common molecular bonds fall are signified by the horizontal bars. This portion of the infrared spans virtually all the fundamental vibrational modes of the different chemical bonds associated with the most common elements. (Figure adapted from Allamandola, 1984.)

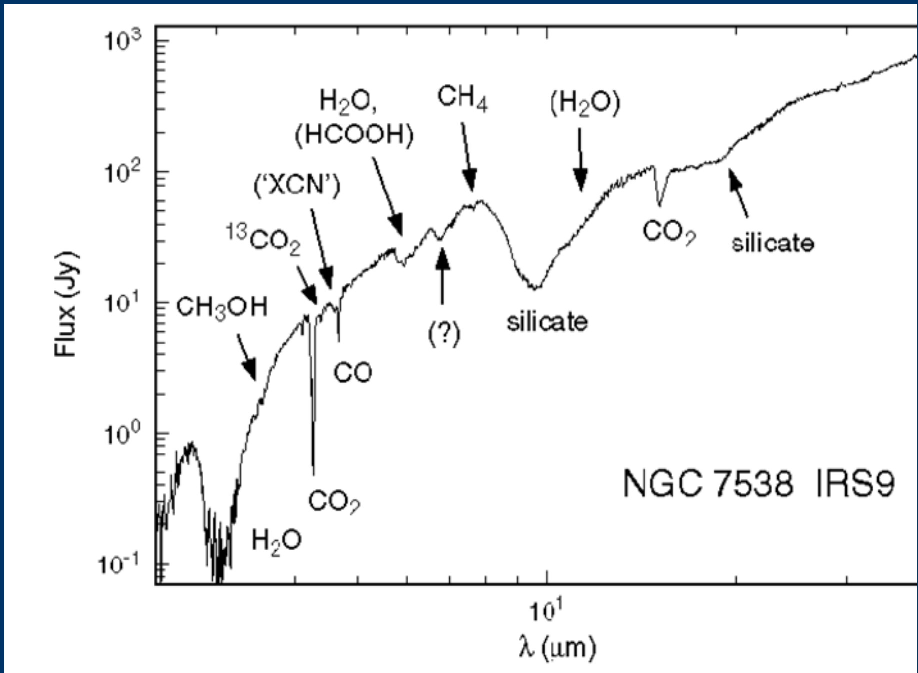
Seeing Through Dust in InfraRed



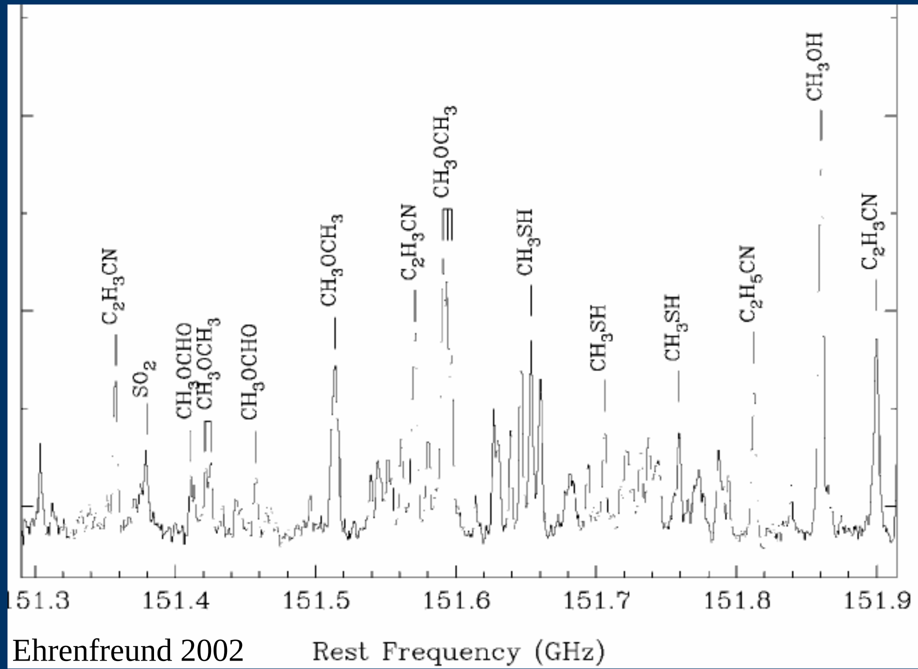
Basic sketch of infrared astronomy.
Sandford (1996) Meteoritics



Infrared and Radio Spectra

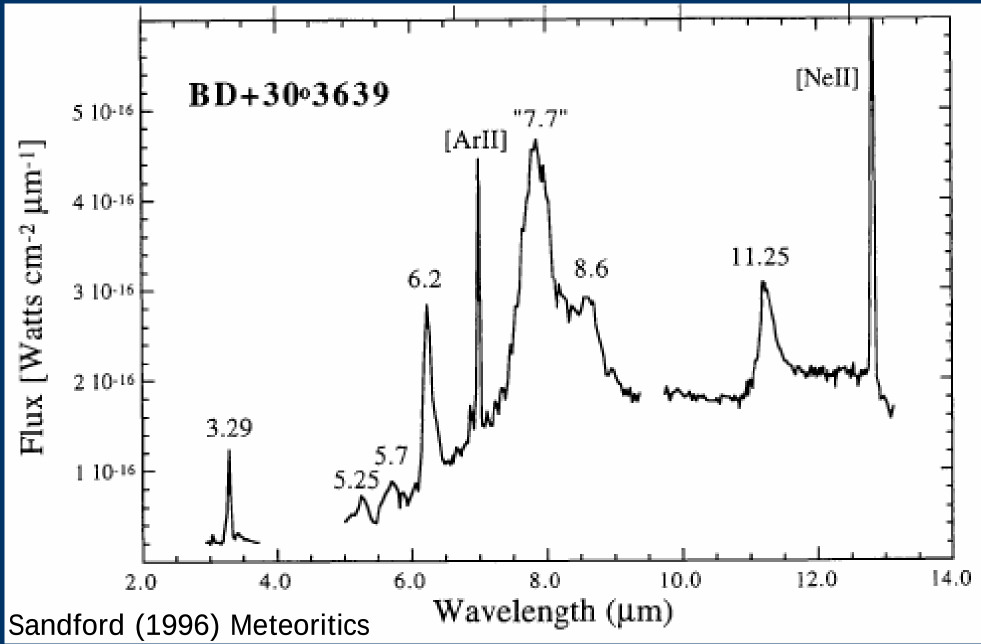


Infrared ISO SWS spectrum (Whittet et al. 1996)



Radio spectrum of a hot molecular cloud core. Note that many lines are still not identified!

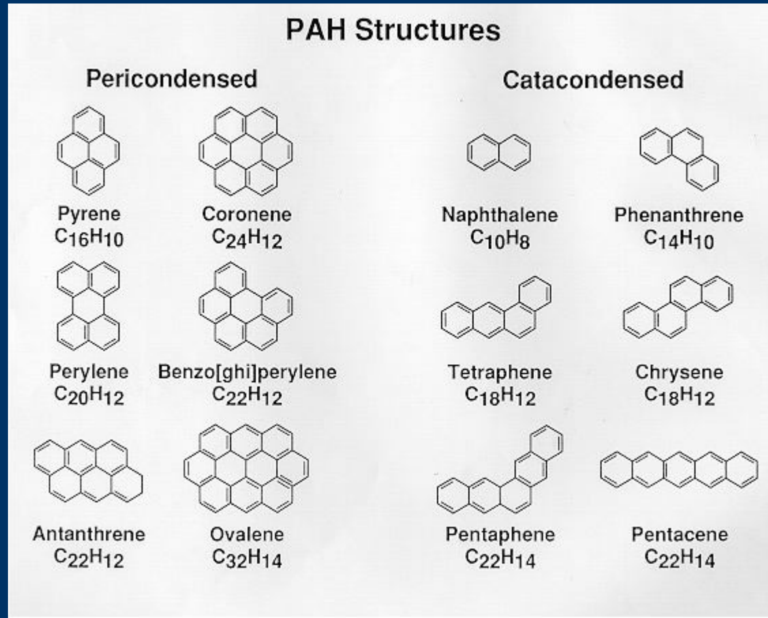
Polycyclic Aromatic Hydrocarbons (PAHs)



Sandford (1996) Meteoritics

IR spectrum of a planetary nebula showing emission features attributed to PAH molecules excited by UV radiation.

3.29 µm: C-H stretch
5.25 µm: C-H bend
5.7 µm: C-H bend, C=C stretch
6.2 µm: C=C stretch
7.7 µm: C=C stretch
8.7 µm: C-H in-plane bend
11.25 µm: C-H out of plane bend



Aromatic (C-ring) molecules resist destruction by UV radiation

Energy emitted by fluoresence in several characteristic IR bands (at left)

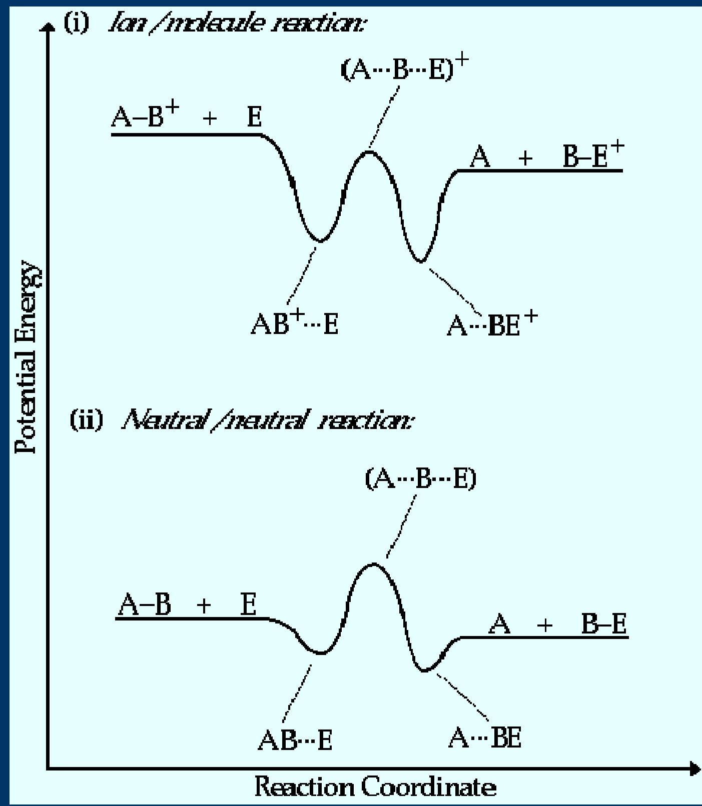
Observed in wide range of astrophysical environments, account for 1 - 10% of all C

Interstellar Chemistry

- Gas phase ion-molecule reactions
- Dust grain surface reactions
- Radiation-processing of ices

Ion-Molecule Chemistry

- Ion-molecule reactions have small or zero activation energy barriers for exothermic reactions
- Reaction rates of ion-molecule reactions may increase with decreasing temperature
- Ionization enables chemistry to occurs clouds with temperature as low as 10 K
- Ionization results from cosmic rays, that may penetrate deeply into dense clouds



Potential energy diagram Millar (2005)

Deuterium Fractionation

D bonds have lower zero point energy level compared to H bonds

i.e. D bonds are stronger than H bonds

In the reaction below, the difference in H and D binding energy is ΔE

$H_2^+ + D \longleftrightarrow HD + H^+ + \Delta E$

$\Delta E = kT$. When $T_{gas} < \Delta E$, strong isotopic fractionation can occur

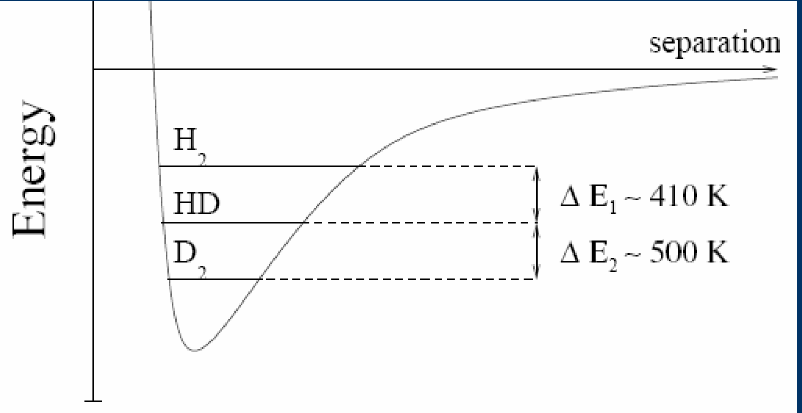


Figure 7. H_2, HD and D_2 potential energy diagram. ΔE_i is the difference between the zero point energies relative to the minimum of the molecular potential curve.

Phillips & Vastel (2002)

Exothermic exchange reactions

$H_3^+ + HD \longleftrightarrow H_2D^+ + H_2 + 230K$

$CH_3^+ + HD \longleftrightarrow CH_2D^+ + H_2 + 370K$

$C_2H_2^+ + HD \longleftrightarrow C_2HD^+ + H_2 + 550K$

D enrichment propagated into other molecules (X) by gas phase ion-molecule reactions

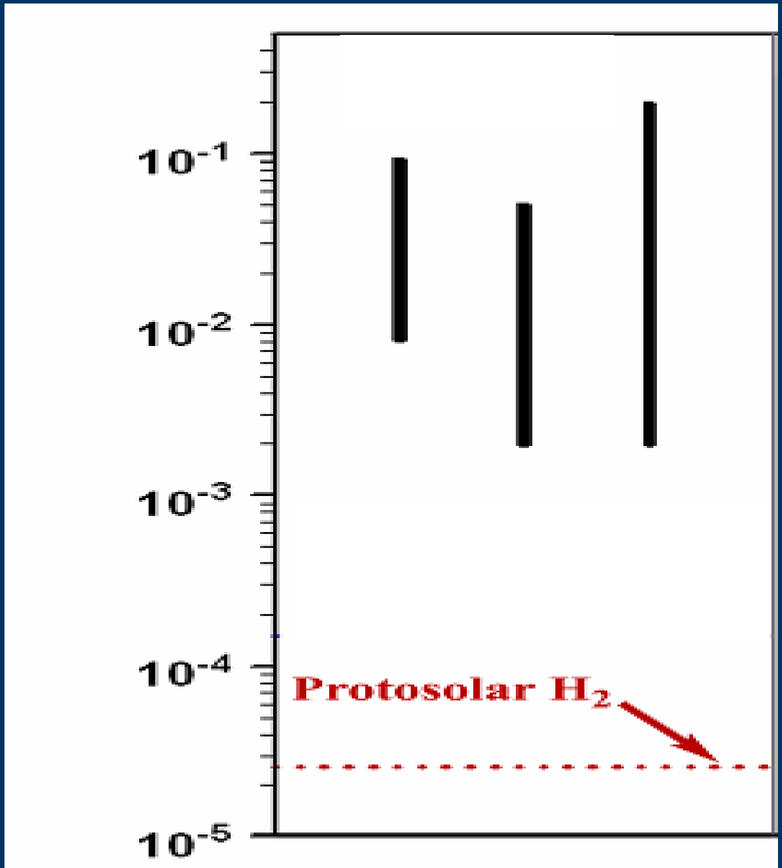
$H_2D^+ + X \longleftrightarrow XD^+ + H_2$

Molecules ‘deuterated’ on dust surfaces

Hydrogenation with D atoms from:
$H_2D^+ + e^- \longleftrightarrow H_2 + D$

Deuterium-Rich Interstellar Molecules

D/H ratios of interstellar molecules



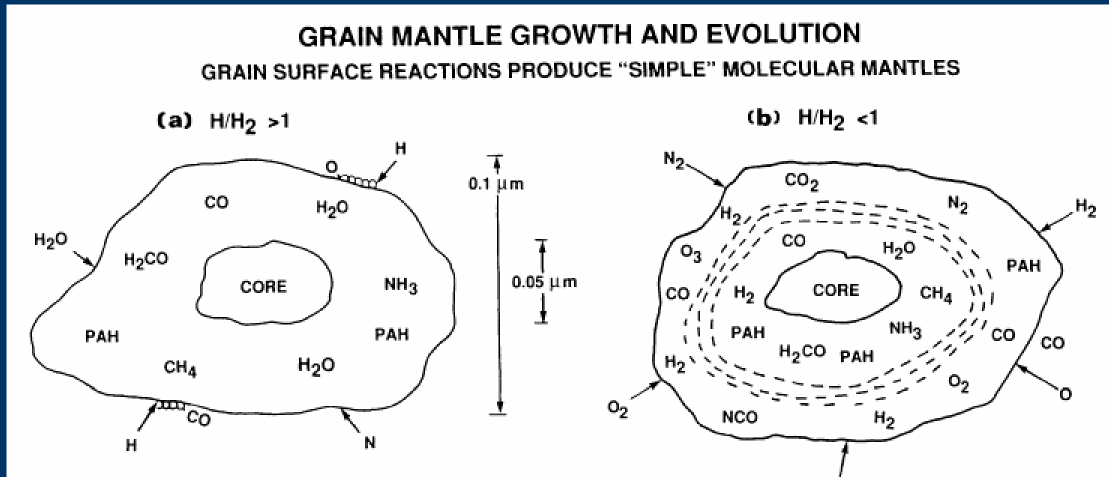
D/H ratios if molecules in cold clouds enriched in D/H relative to H_2

D/H fractionation reaches 10,000!

For comparison, the total range of D/H on Earth varies by ~20 %

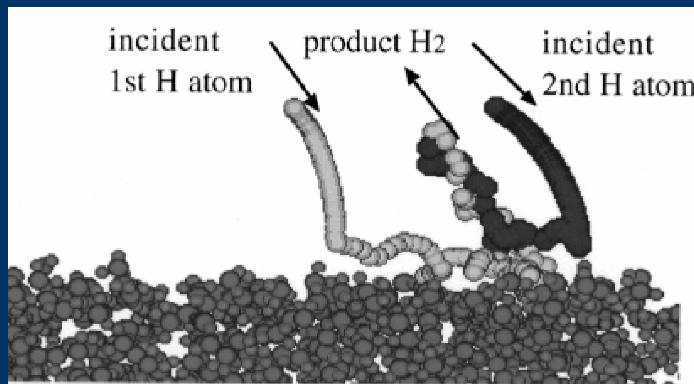
Grain Surface Chemistry

Model of a sub-micrometer dust grain



Sandford (1996) Meteoritics

- Grain surface chemistry necessary to form H_2
- Most effective way to deuterate molecules
- Chemical composition of ice determined by H/H_2
- More difficult to model than gas-phase chemistry

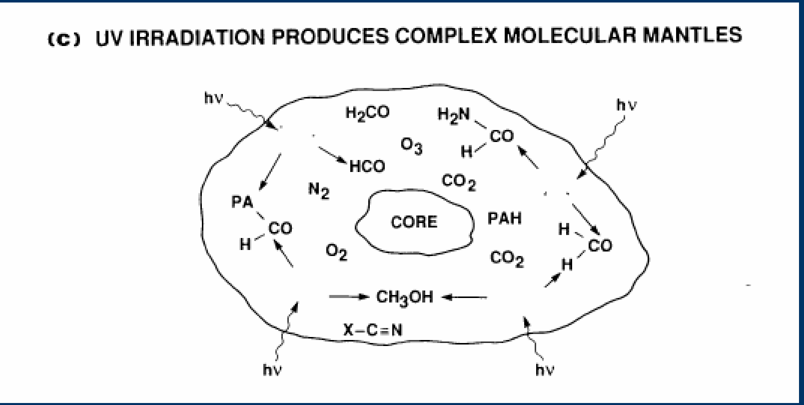


Takahashi (1999) EPSL

Simulation of H_2 formation on H_2O ice grain

Radiation Processing of Ice Mantles

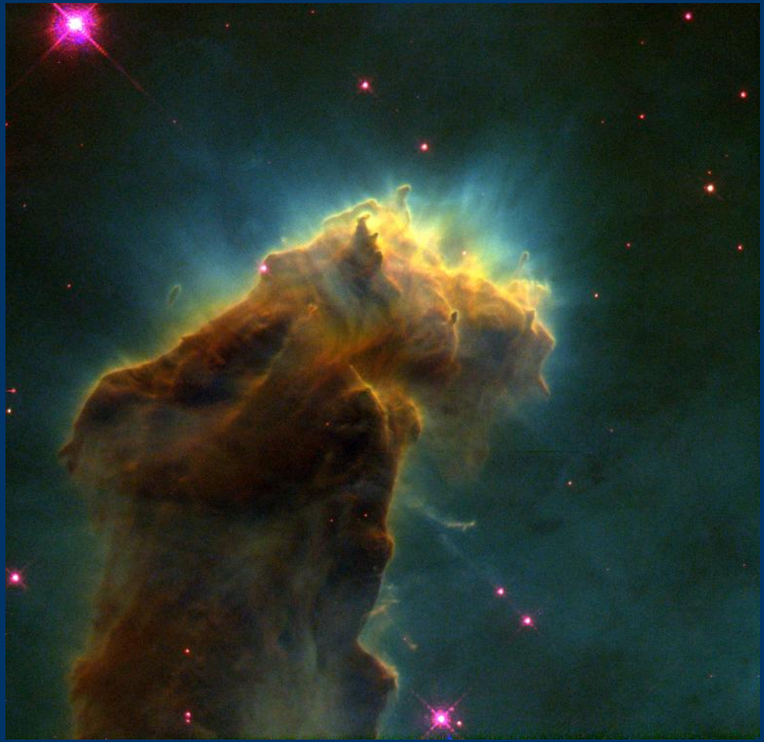
Model of a sub-micrometer dust grain



Sandford (1996) Meteoritics

Ices composed of simple molecules such as H_2O, CO, HCO, etc. are altered into complex organics by UV irradiation

Surface of dense cloud irradiated by nearby hot young stars

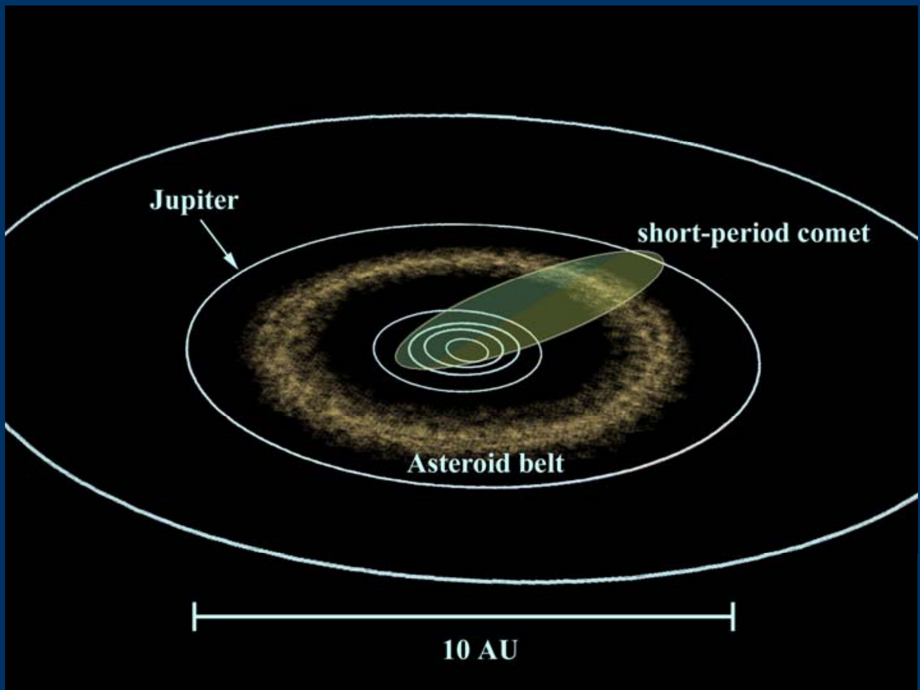


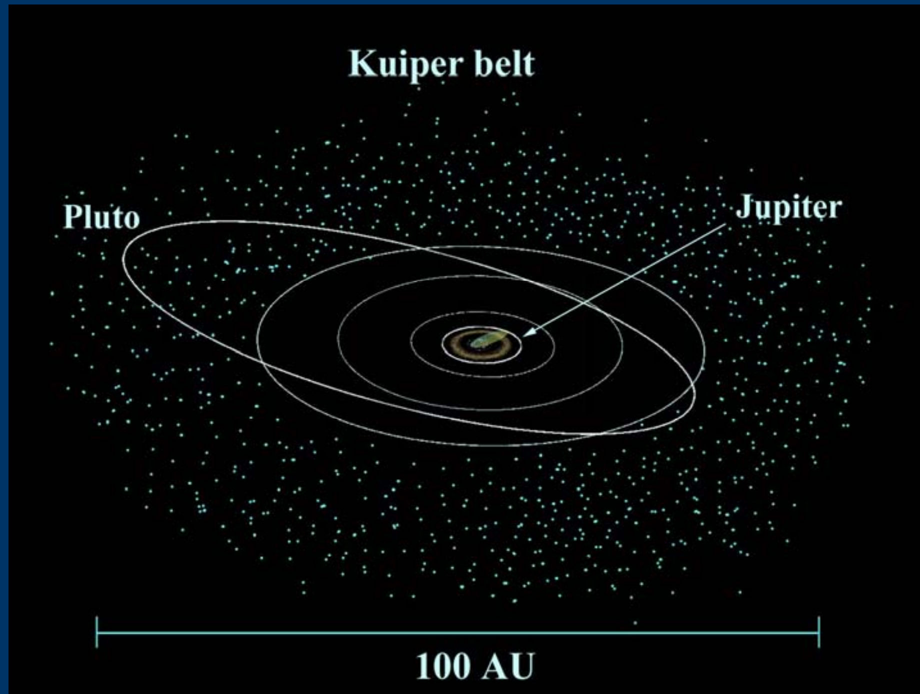
Dense cloud eroding by UV light from nearby hot stars (photoevaporation), uncovering small globules of denser gas within the cloud.

Summary of Interstellar Chemistry

- ❑ Organic molecules observed around evolved stars, cold molecular clouds, and protostellar envelopes
- ❑ Organic molecules formed/altered by
    - ❑ Gas phase reactions
    - ❑ Grain surface reactions
    - ❑ Radiation processing of ices
- ❑ Interstellar molecules are highly enriched in D from low temperature chemical fractionation
- ❑ Chemistry of protostellar clouds/disks varies with time and distance from the star

Primitive Solar System objects: Asteroids and Comets





Asteroids: 2.2 – 3.3 AU. Compositions vary with distance from the Sun. Water and organic-rich asteroids prevalent in outer belt

Short-period comets originate from the Kuiper belt (35 – 50 AU). Nebular temperatures estimated to have been 30 – 100 K.

Primitive and Processed Components

Origins of asteroid/comet components

- Inner Solar System - CAIs and chondrules?
- Asteroid belt
- Kuiper Belt
- Cold molecular clouds
- Interstellar medium
- Red giant stars and supernovae

How did delicate presolar materials become intermixed with processed materials in asteroids and comets?

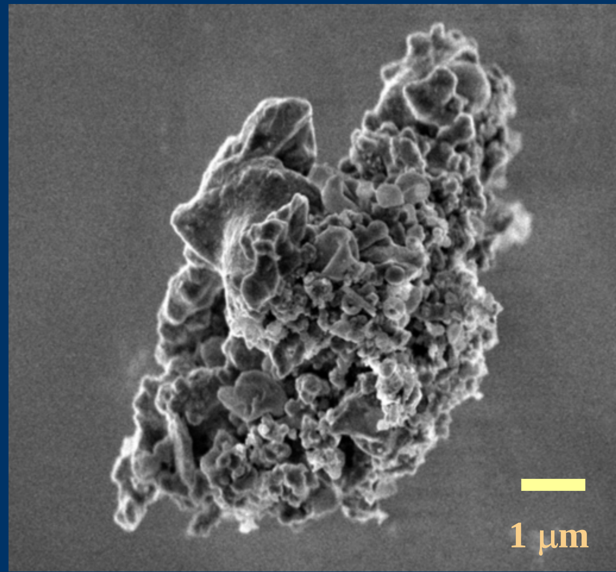
How can we identify the original (least altered) organic materials?

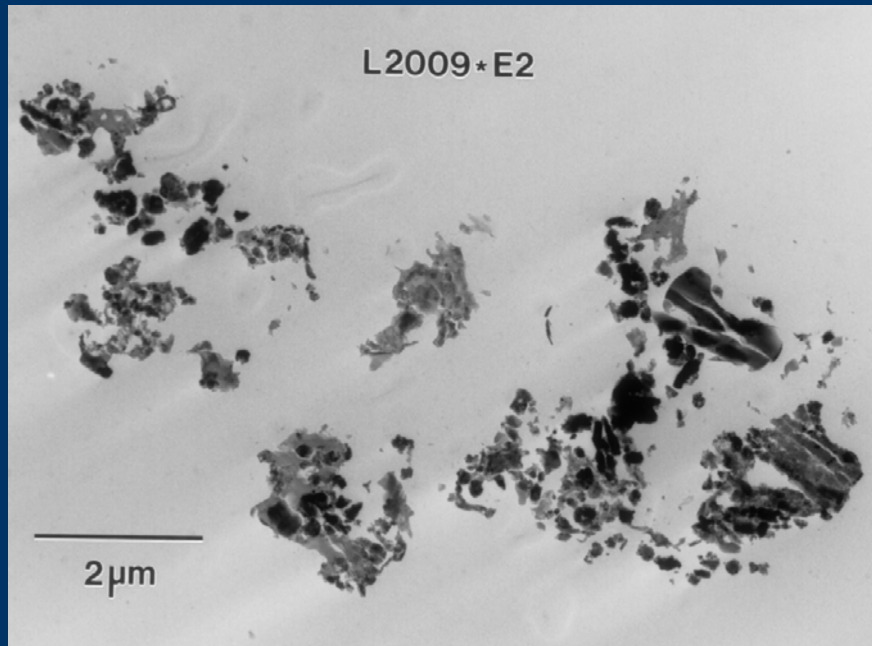
- Presolar materials <10% (?)

Characteristics of Anhydrous 'cometary' IDPs

- Porous, fragile, fine grained
- Not hydrothermally altered
- Unequilibrated mineralogy
- C- and N-rich (~3XCI)
- Volatile trace element-rich
- Abundant stardust
- molecular cloud material

These materials are the least altered remnants of the primordial solar system



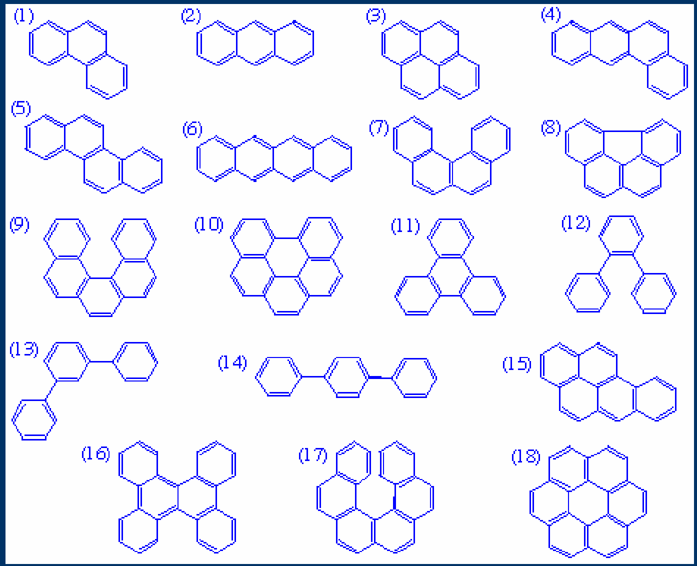


Searches for presolar organic matter

- H and N Isotopic signatures
  - Interstellar materials are isotopically distinct
- Bulk chemical analyses
  - Detailed molecular characterization
  - Difficult to distinguish components
- Microscopic studies
  - Reveal highly heterogeneous compositions
  - Limited chemical analysis tools at sub-nanogram scale
- Look in the least altered materials
  - Carbonaceous chondrite meteorites
  - ‘Cometary’ Interplanetary dust particles (IDPs)
  - Stardust mission samples: direct samples of comet Wild 2

Meteoritic Organic Matter

- Major component: Acid insoluble, kerogen-like material. Low mass aromatic molecules linked with aliphatic chains. Analysis requires extraction by HF/HCl acid treatment or equivalent (demineralize the meteorite)
- Minor (1 - 30 %) soluble organic compounds
- >500 individual compounds identified
- Complete structural diversity, supporting abiogenic origin



Polycyclic aromatic hydrocarbons

Murchison Meteorite
Aromatic Hydrocarbons

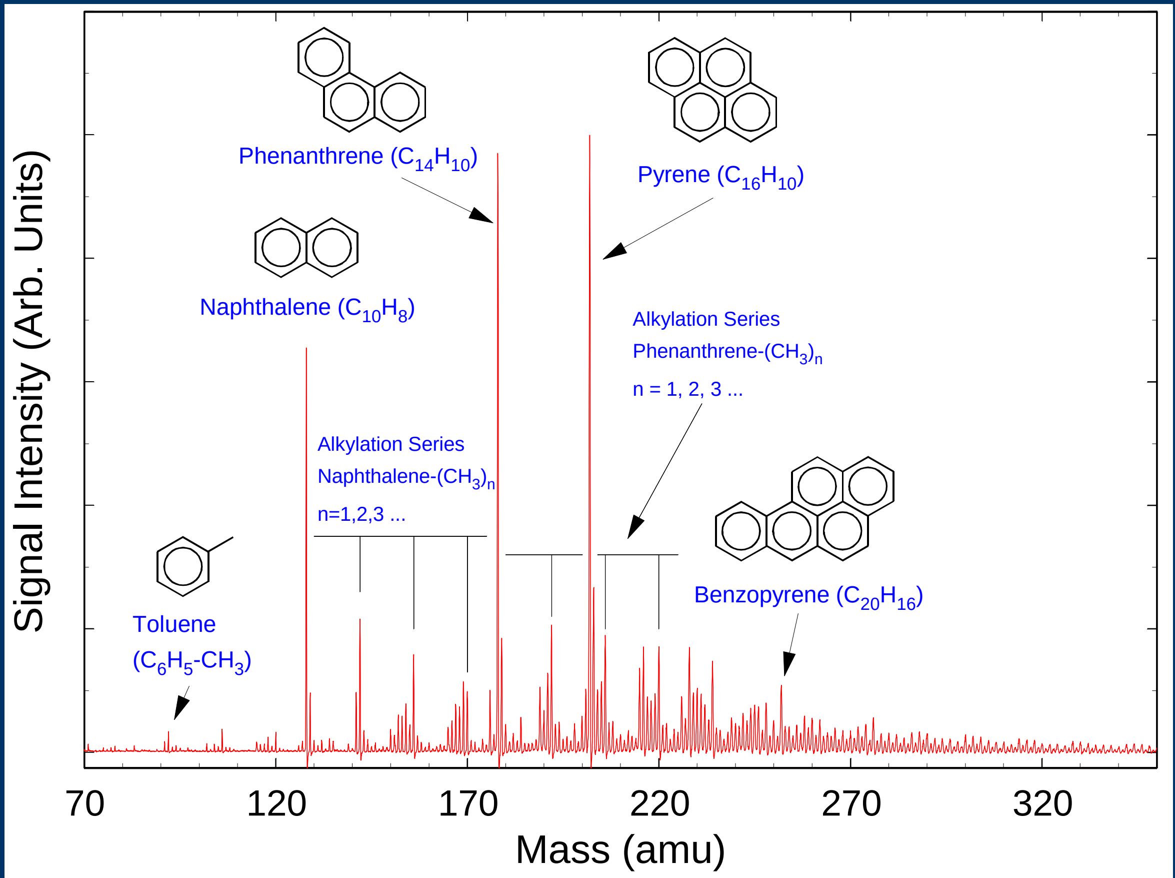
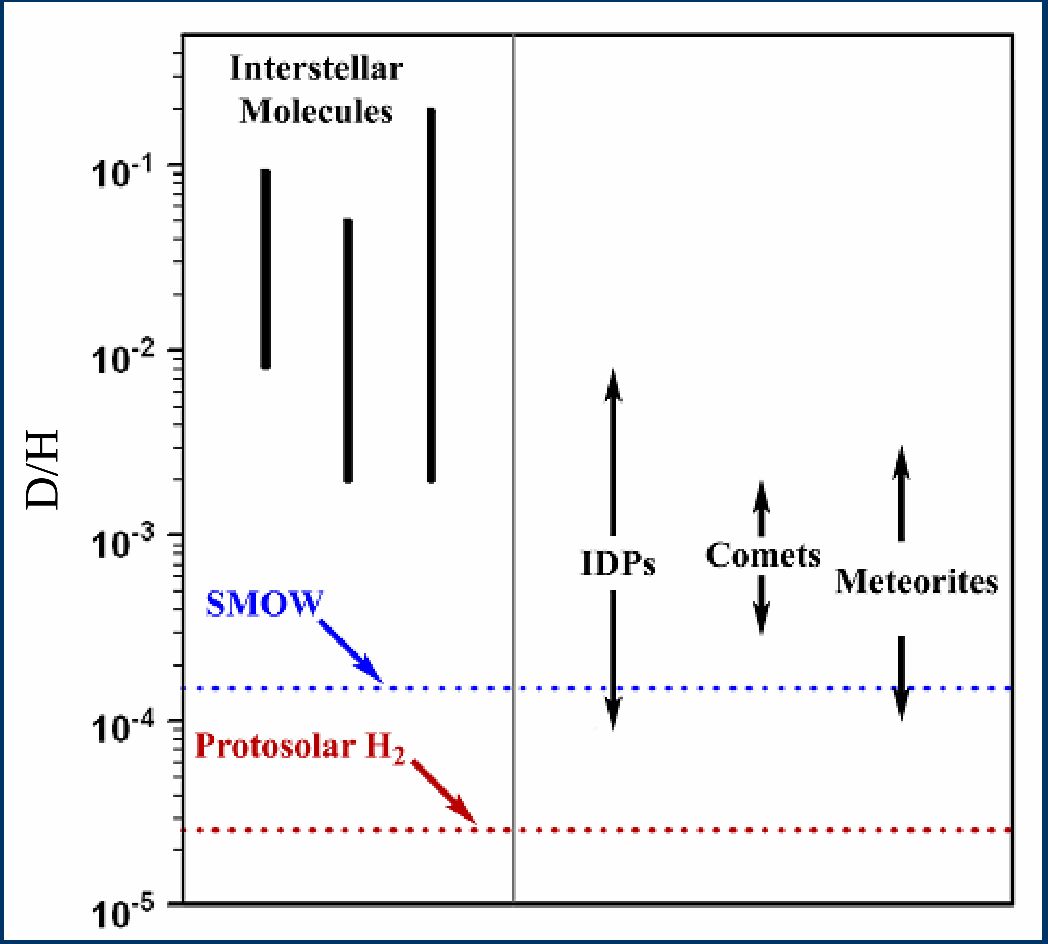


Figure courtesy of S. Clemett

Aromatic hydrocarbons in meteorites are low-mass and highly substituted – primarily alkylation series

Mass spectra such as this vary significantly with meteorite class (parent body alteration)

D-Enrichments in Primitive Solar System Materials: Link to Cold Molecular Clouds?



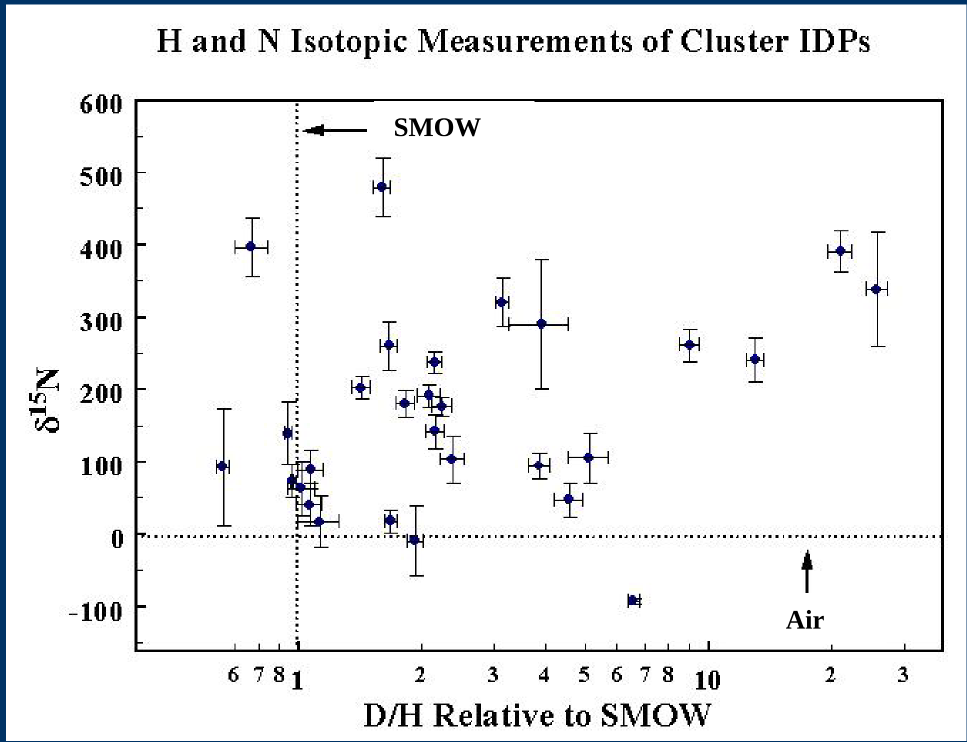
Interstellar molecules are highly enriched in D/H

Meteorites, IDPs, and comets are D-rich, preserving some presolar organic compounds

D/H ratios highly variable in IDPs, meteorites

D/H fractionation may have also occurred in the outer (>50 AU) Solar System where conditions were similar to cold clouds.
Aikawa & Herbst (1999) ApJ

^{15}N enrichment: interstellar origin?



- N isotopic fractionation requires extremely low T (10 – 20 K)
- Not possible to determine precise $^{15}N/^{14}N$ ratios in cold interstellar clouds
- Recent models approach necessary level of N isotopic fractionation (Charnley & Rogers ApJ 569, L133)
- But new observations of still higher $^{15}N/^{14}N$ ratios challenge interstellar chemistry models

Evolution of Interstellar Molecules

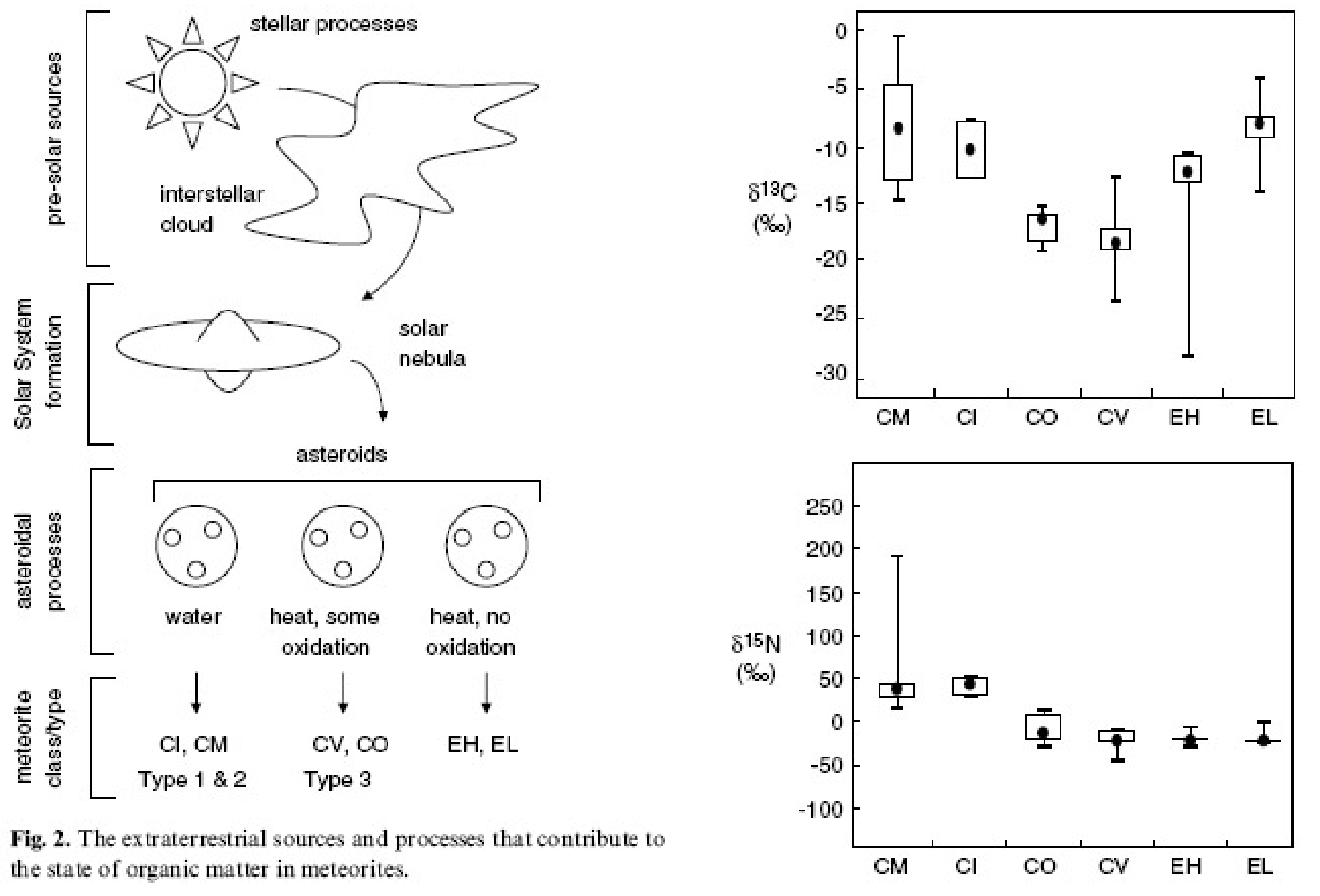


Fig. 2. The extraterrestrial sources and processes that contribute to the state of organic matter in meteorites.

Chemical compositions and isotopic signatures vary across meteorite classes, reflecting effects of parent body processing

Isotopic variability of soluble organics from meteorites

50 carboxylic acids

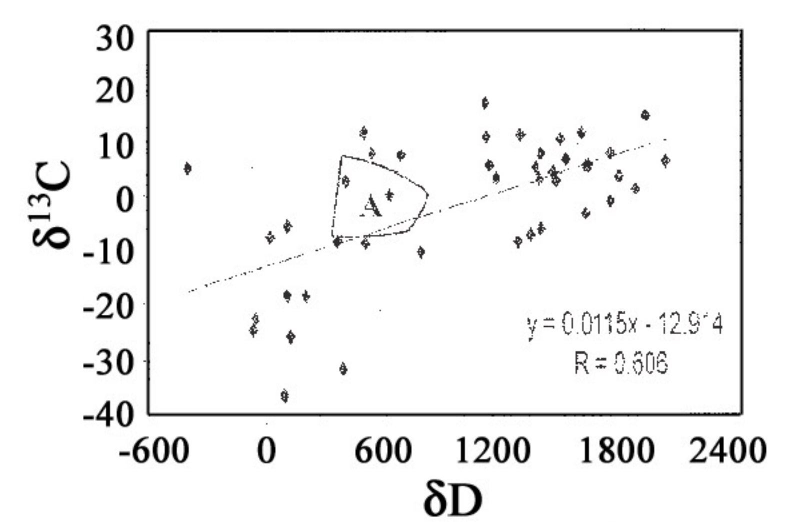


Fig. 5. The $\delta^{13}C$ vs. δD plot for 50 acids in Murchison meteorite, whereas A denotes a $\delta^{13}C$ vs. δD plot for Murchison monocarboxylic, dicarboxylic, and hydroxy acids reported by Cronin and Chang (1993).

Huang et al. 2005

Amino acids

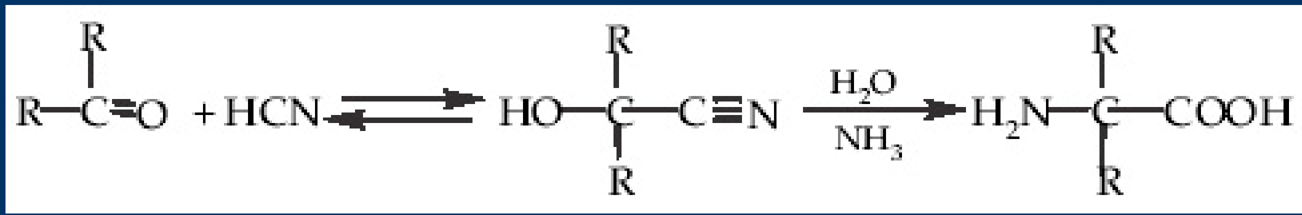
Table 1. δD (‰, VSMOW) of Murchison and Murray 2-amino alkanoic acids.

Amino acid (a.)	Murchison δD (n)[a]	Murray δD (n)[a]
Glycine	—	399 ± 17 (3)
D-Alanine	429 ± [b]127 (3)	614 ± 61 (3)
L-Alanine	360 ± 140 (3)	510 ± 53 (3)
D-2-Aminobutyric a.	1338 ± 2 (2)	1633 ± 32 (3)
L-2-Aminobutyric a.	1225 ± 135 (3)	—
D-Norvaline[c]	—	1505 ± 9 (2)
2-Aminoisobutyric a.	3058 ± 186 (3)	3097 ± 86 (4)
DL-Isovaline[d]	3419 ± 118 (2)	3181 ± 108 (4)
L-Isovaline[c]	—	3283 ± 46 (3)
D-Valine[c]	—	2432 ± 11 (2)
L-Valine	—	2266 ± 101 (3)
DL-2-Methylnorvaline	2686 (1)	3021 ± 45 (4)
D-2, 3-Dimethylbutyric a.	3318 (1)	3604 ± 13 (2)
D-Allo isoleucine	—	2251 ± 45 (3)
L-Allo isoleucine	—	2465 ± 31 (3)
L-Isoleucine	—	1819 ± 27 (3)

Pizzarello & Huang 2005

- Variable D/H observed among dozens of compounds extracted from meteorites
- D enrichment commonly ascribed to interstellar heritage

Meteoritic α-Amino Acids: Byproducts of Aqueous Alteration?

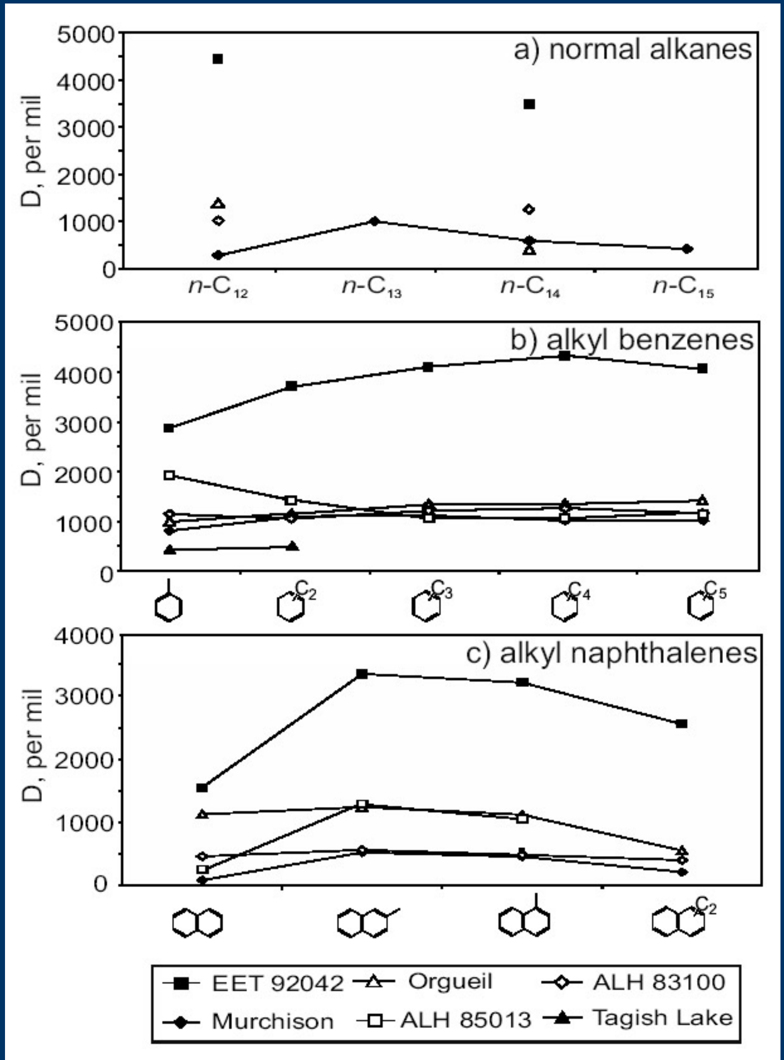


Production of α-amino acids through 'strecker synthesis.'
Pizzarello et al. (2006), Peltzer & Bada (1978)

α-amino acids in meteorites are thought to have formed from reactions between aldehydes, ketones, NH_3 and HCN during aqueous alteration

The D-enrichments in these molecules are thus not primary, but a remnant signature from interstellar precursors

D-rich pyrolysis products

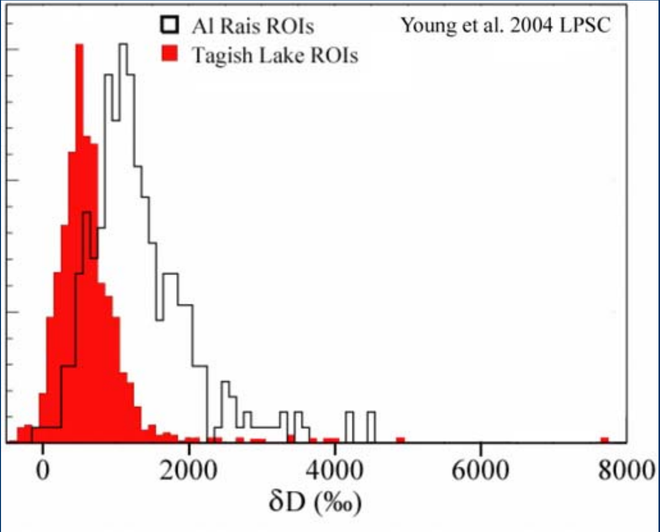


Wang et al. (2005) GCA 69, 3711

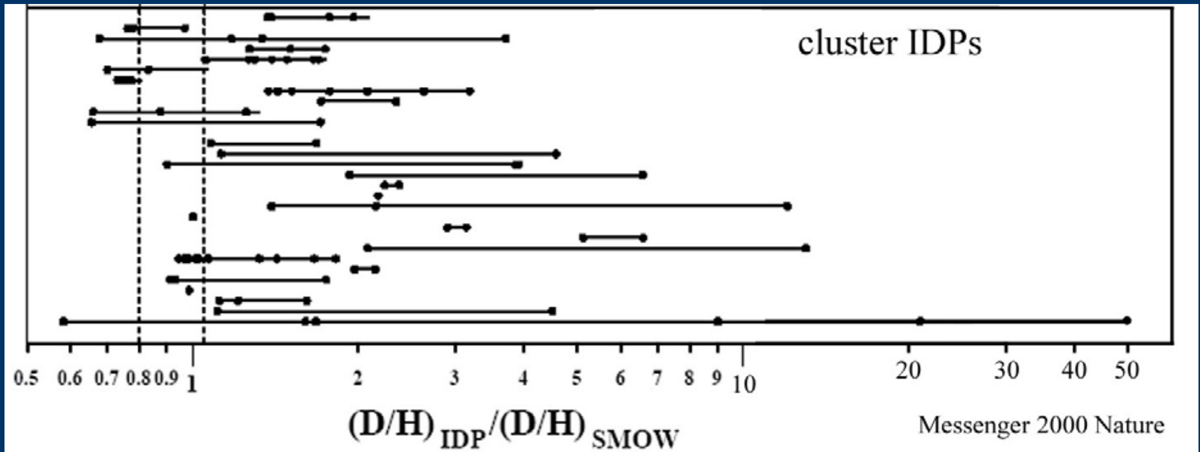
Experiments to disentangle the components of insoluble organic matter reveal minor, highly D-enriched subcomponents

Isotopic variations suggest the subcomponents of the insoluble organic matter had differing formation/alteration histories

H Isotopic *Spatial* Variations in Meteorites and IDPs

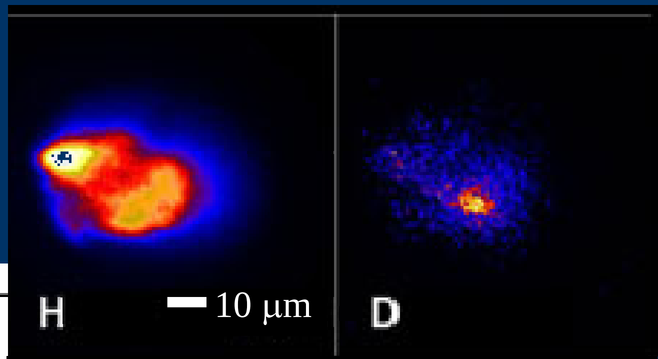


- Primitive meteorites and IDPs exhibit μm-scale heterogeneity in their D/H ratios
- Average δD of cluster IDPs (≳ +1,300 ‰) is similar to CR chondrites (1,000 – 1,300 ‰)
- Very high D/H ratios (> 5 x SMOW) are more common in cluster IDPs than in meteorites so far.

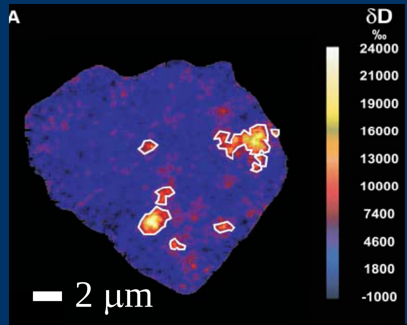


Microscopic ‘nuggets’ having large isotopic anomalies in IDPs and meteorites may be intact samples of the organic starting materials

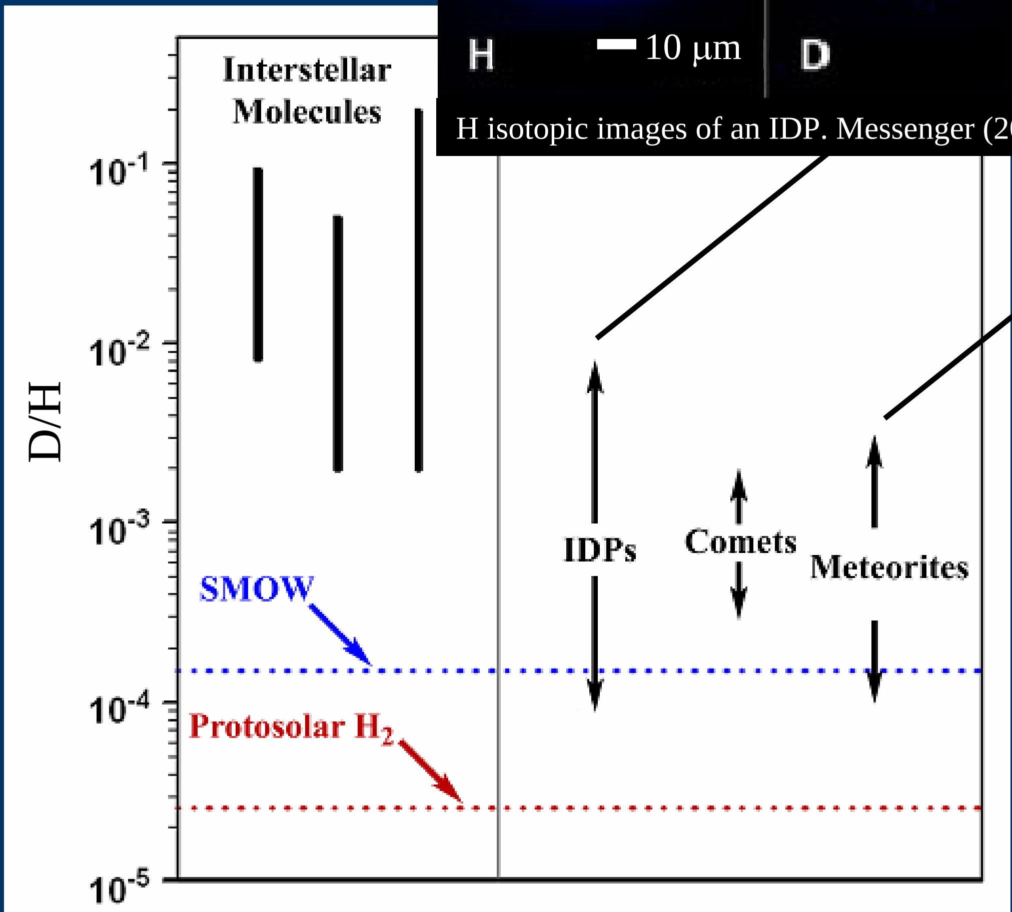
Preserved molecular cloud material?



H isotopic images of an IDP. Messenger (2000)



D/H ratio image of a meteorite
Busemann et al. (2006)

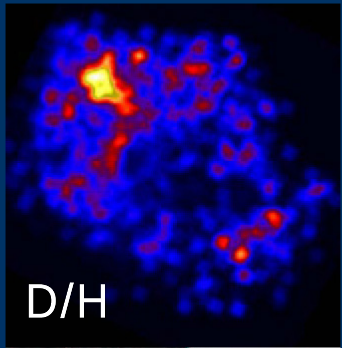


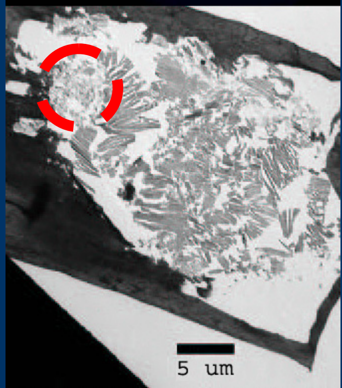
Meteorites, IDPs, and comets have D-rich organic components, possibly preserved molecular cloud material

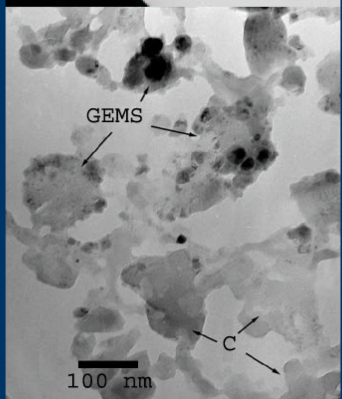
Rare, microscopic regions of IDPs and meteorites have D/H ratios that reach those of interstellar molecules

D- and ^{15}N-rich hotspots far exceed values observed in organic extracts

Analysis of D-hotspot by TEM and FTIR







Sample Description

- 30 µm IDP pressed into Au foil
- <1 µm enstatite, forsterite, anorthite, amorphous silicates, Fe sulfides, abundant organic material

Organic characteristics (FTIR):

D hotspot has abundant aliphatic hydrocarbons compared with meteorites

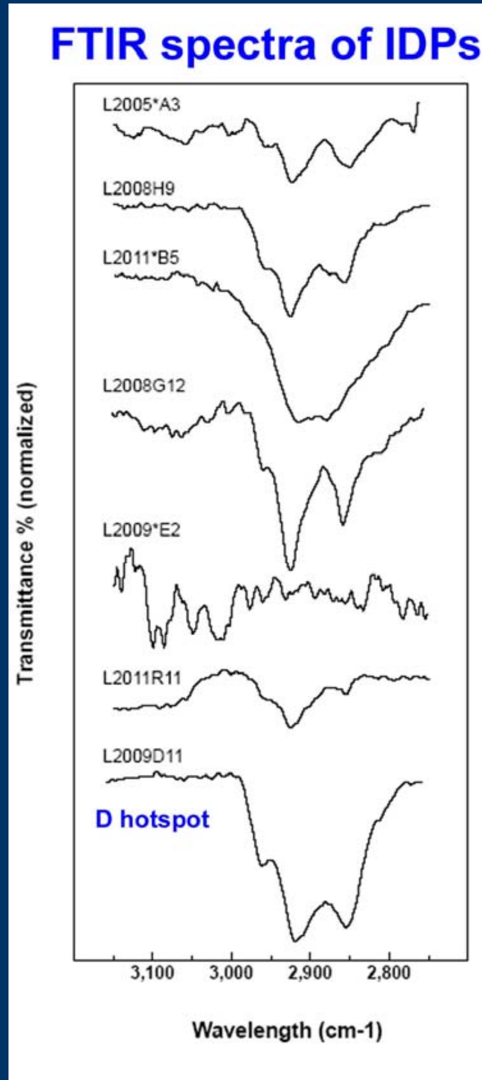
Isotopic Measurements

D/H ratio is 50 x terrestrial values – *the highest value found in the Solar System*

1 silicate stardust grain (300 nm) found!

The D-hotspot contains many crystalline silicates that formed in the Solar System

Conclusion: This is not an interstellar rock ☹
Big question: What was the original form of the organic matter?



Keller et al. 2004 GCA

Tagish Lake Meteorite Recovery

<u>Carbonaceous chondrite fall</u>

- Unique classification as CI2 – intermediate between CI and CM [1]
- Orbit traced to outer asteroid belt [1]
- Reflectance spectra similar to outer belt asteroids [2]
- Abundant presolar SiC and nanodiamonds [3]
- High abundance of organic C [3]
- Minimal terrestrial contamination: ideal sample to study indigenous organics

1: Brown et al. (200) Science 290, 320
2: Hiroi et al. (2001) Science 293, 2234
3: Grady et al. (2002) Met Planet Sci 37, 713

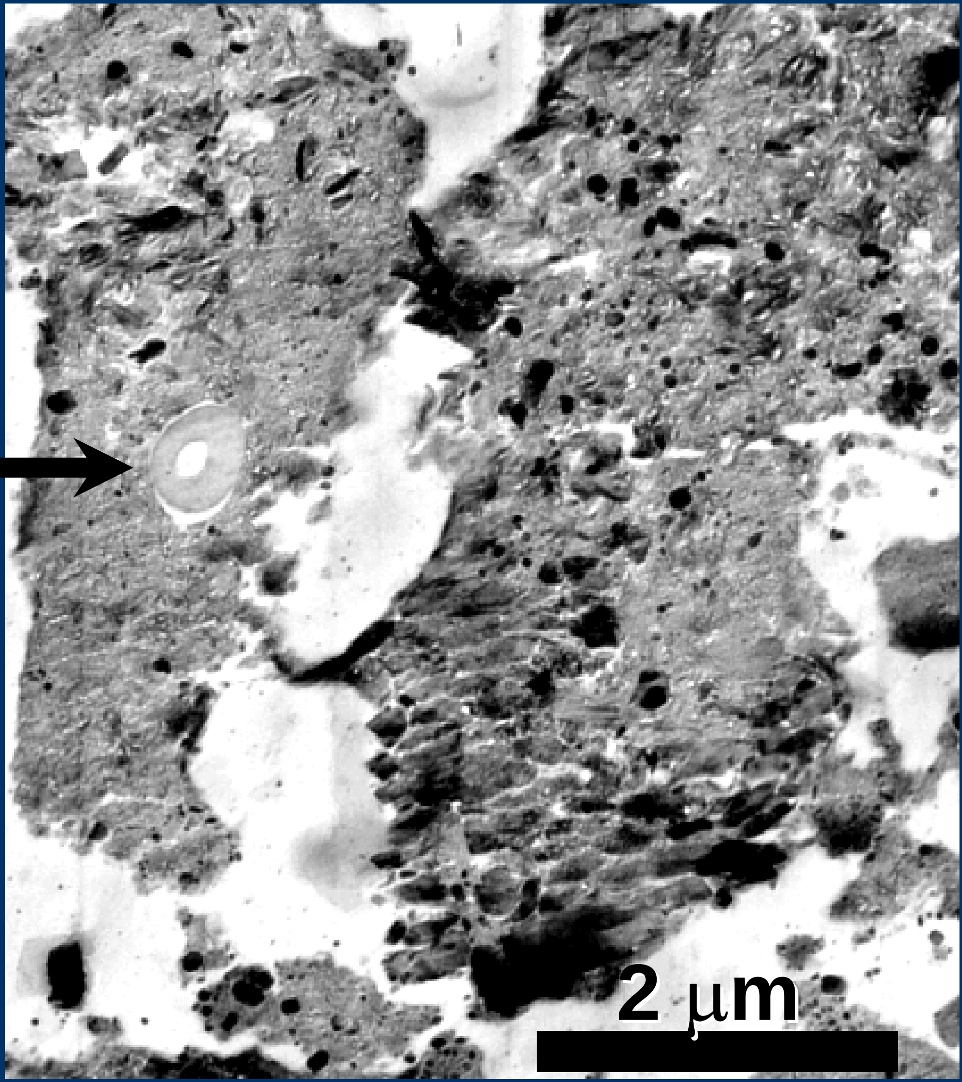
Sub-μm Organic Globules in Tagish Lake

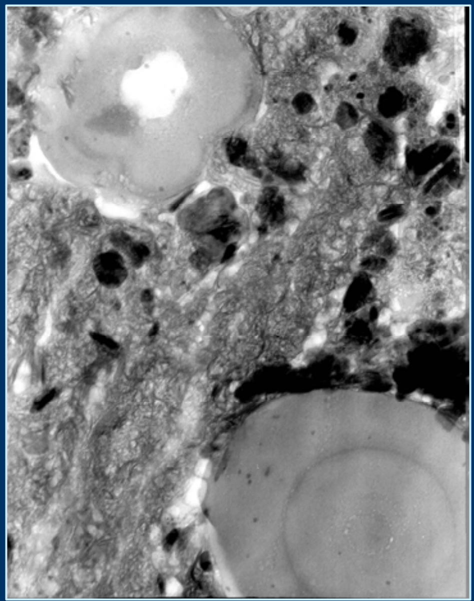
Numerous (>100) sub-mm hollow globules observed in situ. Approximately 1 per 100 μm^2

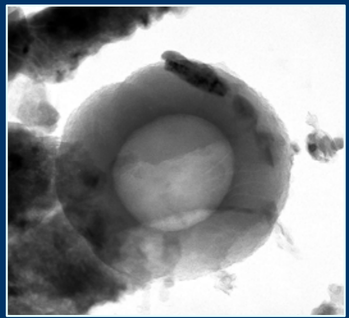
Size range: 100 – 1000 nm

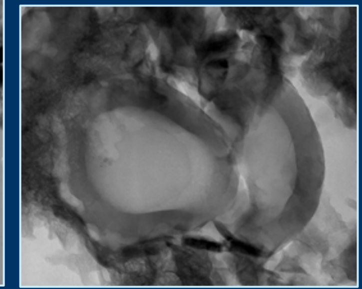
Structure: Rounded, hollow, concentric shells observed

Composition: amorphous C
trace H, N, O, S

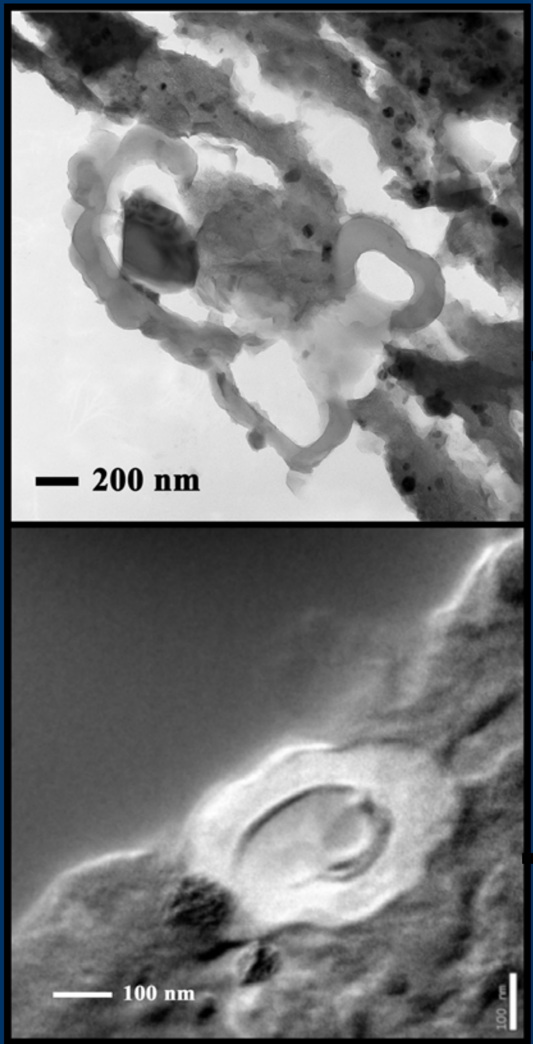


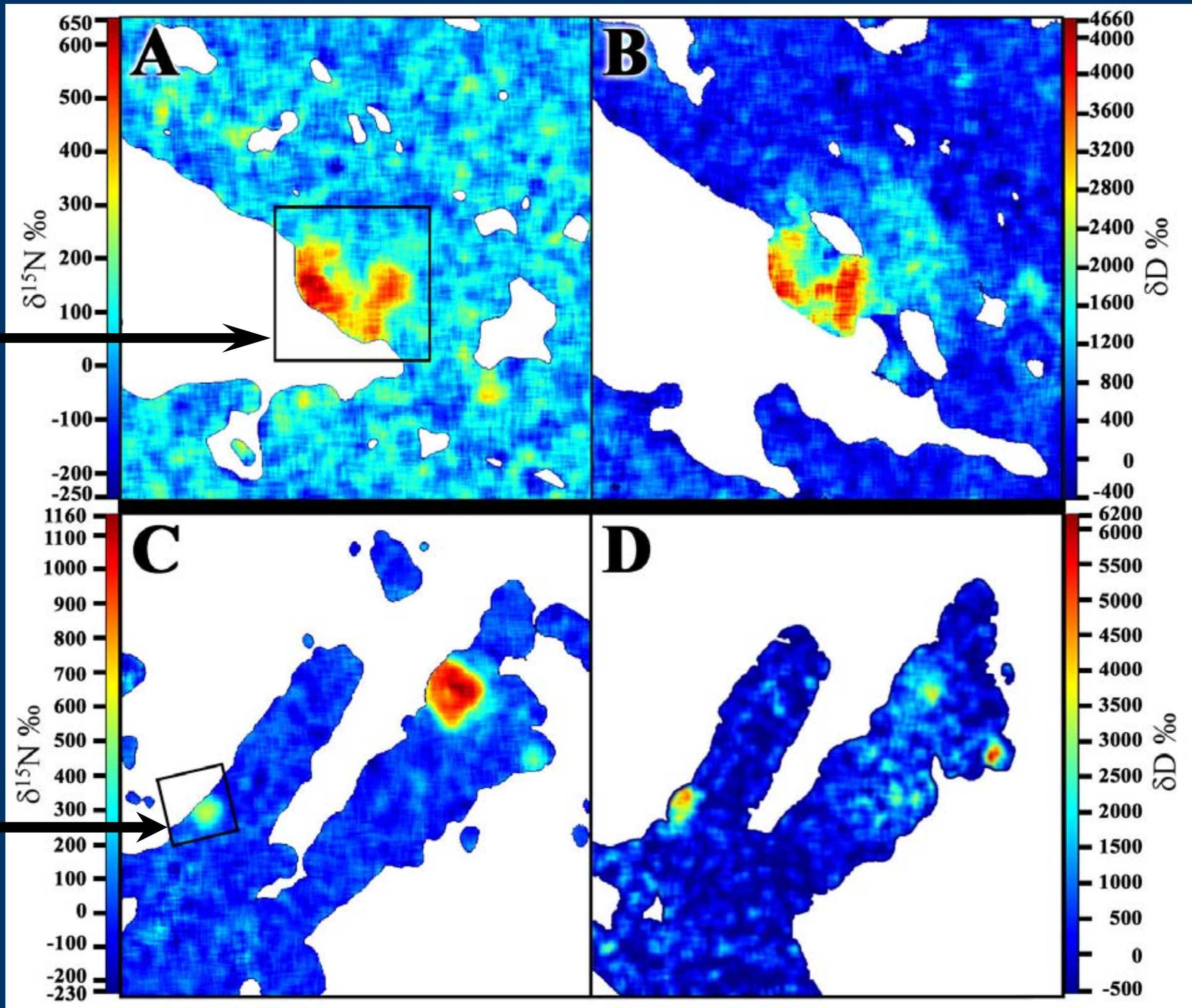






H and N Isotopic Anomalies in Organic Globules



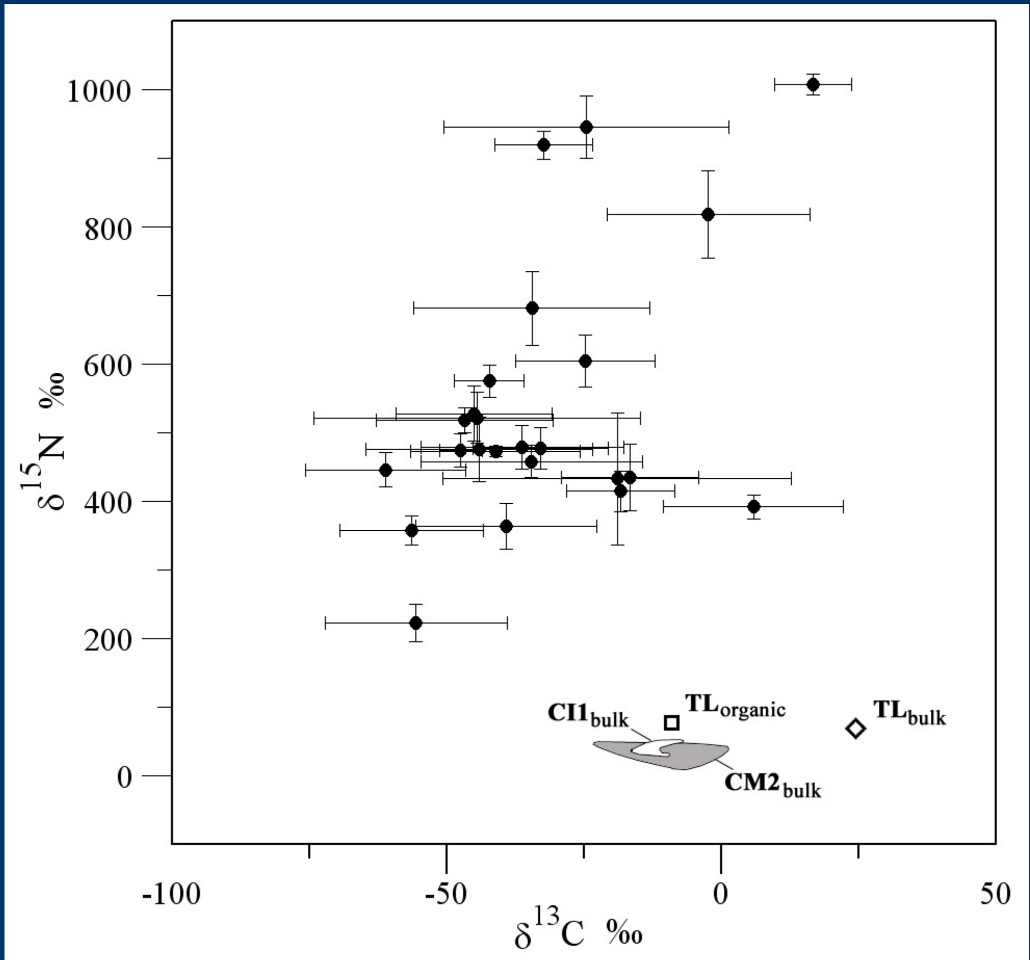


Top: Brightfield TEM image
Bottom: Energy filtered C image

D/H ratios of the globules are 2.5 – 9 x terrestrial

Nakamura-Messenger et al. (2006) Science

C and N Isotopic Compositions of Tagish Lake Organic Globules



Comparison of C, N isotopic compositions of TL organic globules with bulk meteorite samples

$\delta^{15}N$ of TL organic globules ranges from 200 to 1000 ‰

Organic globules account for most of the high ^{15}N rich material in Tagish Lake

Narrow range of $\delta^{13}C$ of the organic globules rules out their possible origin from evolved stars

Isotopic Constraints on the Organic Globule Formation Environments

D enrichments due to low T chemical fractionation
Fractionation increases exponentially as T drops

D/H enrichment of ~10 x terrestrial may have been possible in the Kuiper Belt. (T<50 K, ionization)

Smaller mass difference in N isotopes reduces difference in bond strength: Fractionation is smaller and occurs at lower T

$^{15}N/^{14}N$ enrichment of ~2 x terrestrial may only have been possible at T ~10 K

<u>Primary H fractionation reaction</u>

$H_3^+ + HD \longleftrightarrow H_2D^+ + H_2 - 178K$

Accretion of D onto grain surfaces dominates deuteration into solids

<u>Primary N fractionation reaction</u>

$^{15}N + {}^{14}N_2H^+ \longleftrightarrow {}^{14}N + {}^{15}N^{14}NH^+ + 30K$

This reaction can be retained in solids when nearly all volatiles have condensed

Charnley & Rogers ApJ 569, L133

Origins of Organic Globules

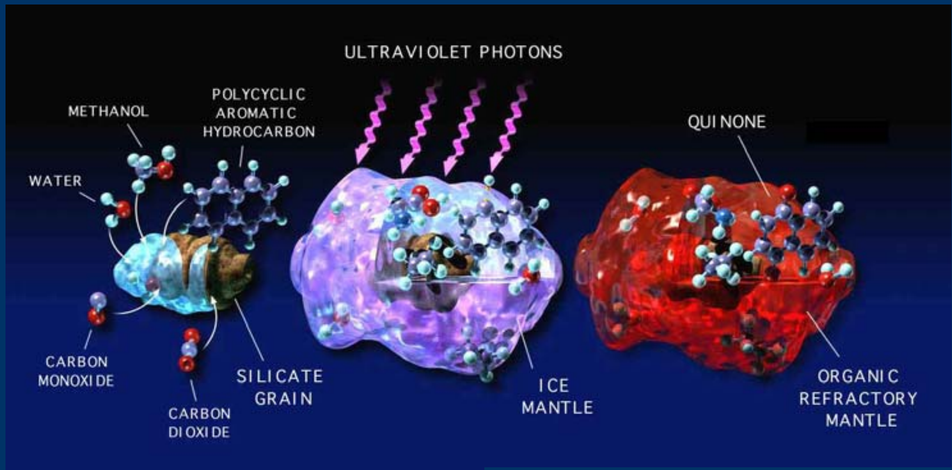
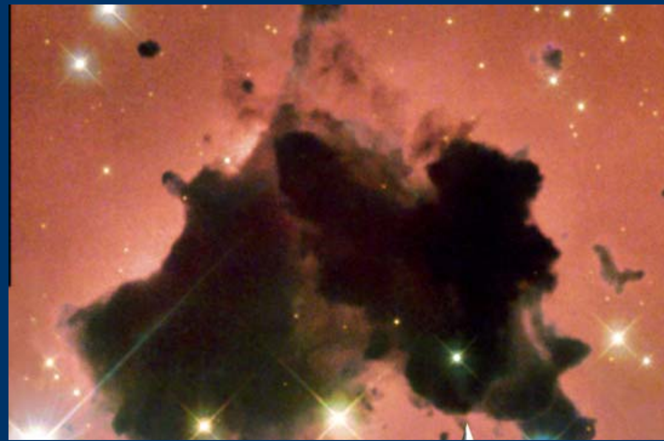
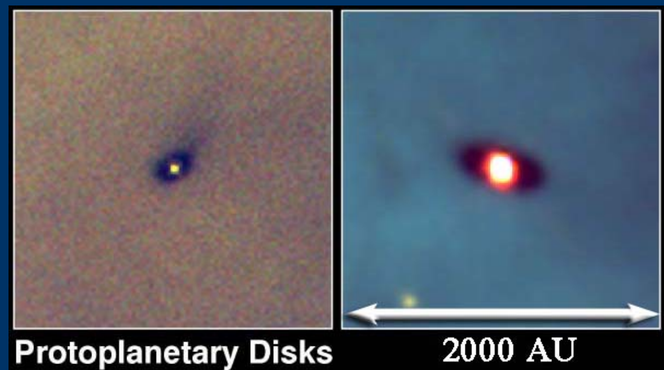


Figure courtesy of S. Sandford



Cold, irradiated molecular cloud



Dust grains in cold molecular clouds accrete all condensable species.

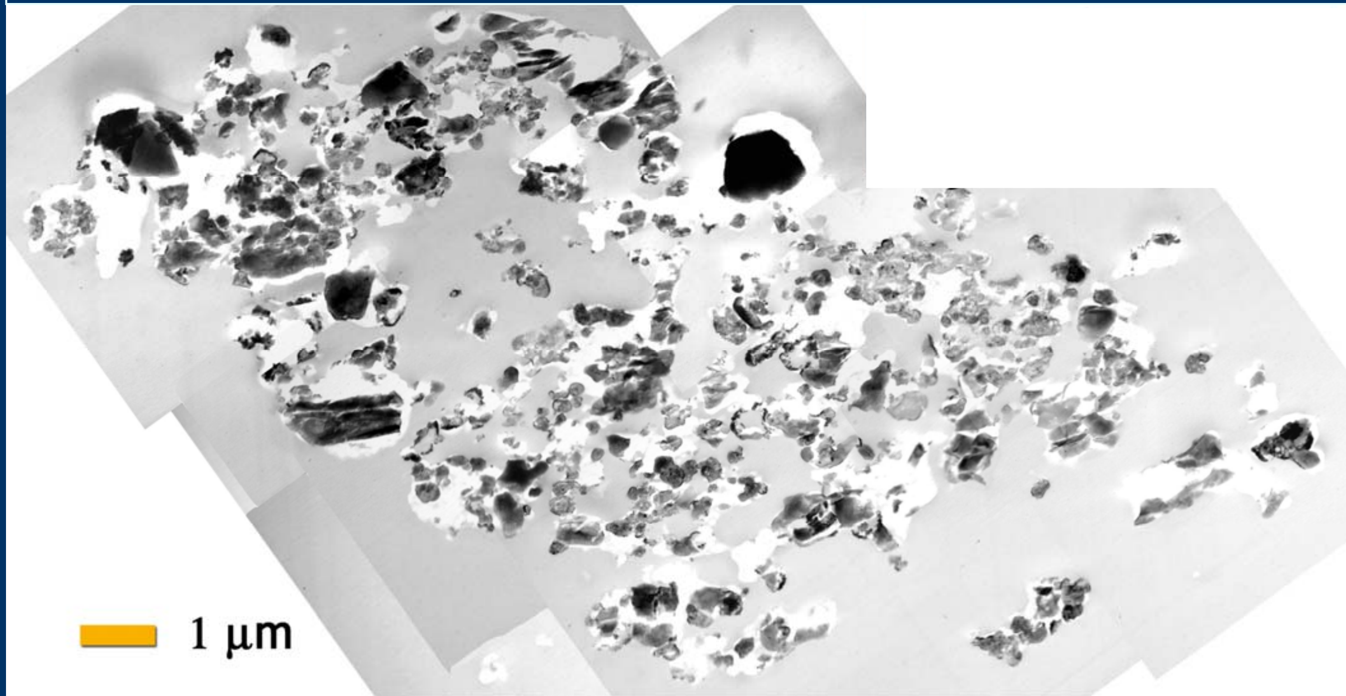
UV converts icy coatings into refractory organics

The organic globules may have condensed on H_2O ice grains that later sublimed, leaving them hollow

The organic globules originated in a cold molecular cloud or at the outermost regions (>100 AU) of the protosolar disk

Summary: The Starting Materials

- The Solar System was constructed from sub-μm mineral grains, solid organic matter, and mixed organic ices
- Source materials included: evolved stars, interstellar clouds, various stages of evolving protosolar core and protoplanetary disk
- Primitive solar system materials are complex mixtures of presolar and solar system materials at μm-scales
- The search continues for the least processed remnants of the starting materials. New comet samples and improving technology lead the way.



Cometary dust particle: typical view of the Solar System starting materials