Organics in Meteorites:
Interstellar, solar and/or parent body.

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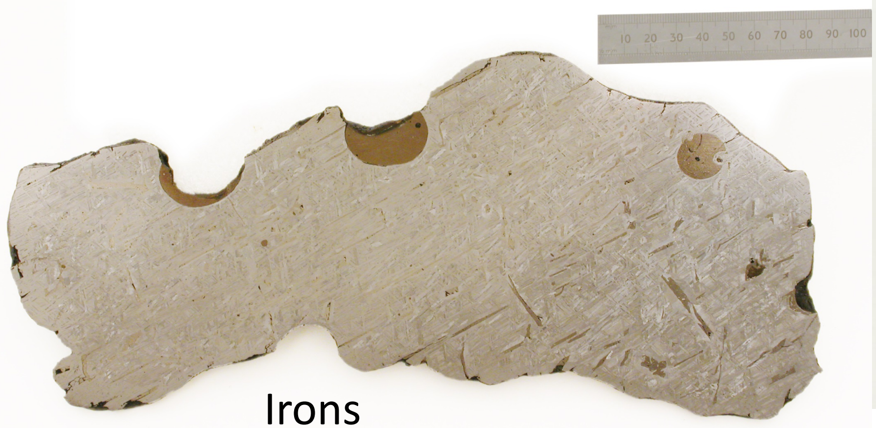
Meteorites: A quick introduction

(and influence of ^{26}Al, $t_{1/2} \approx 0.7$ Ma)

Achondrites



Irons

Chondrites

1 cm

4,567.3±0.2 million years old

~3.5-4 Ma

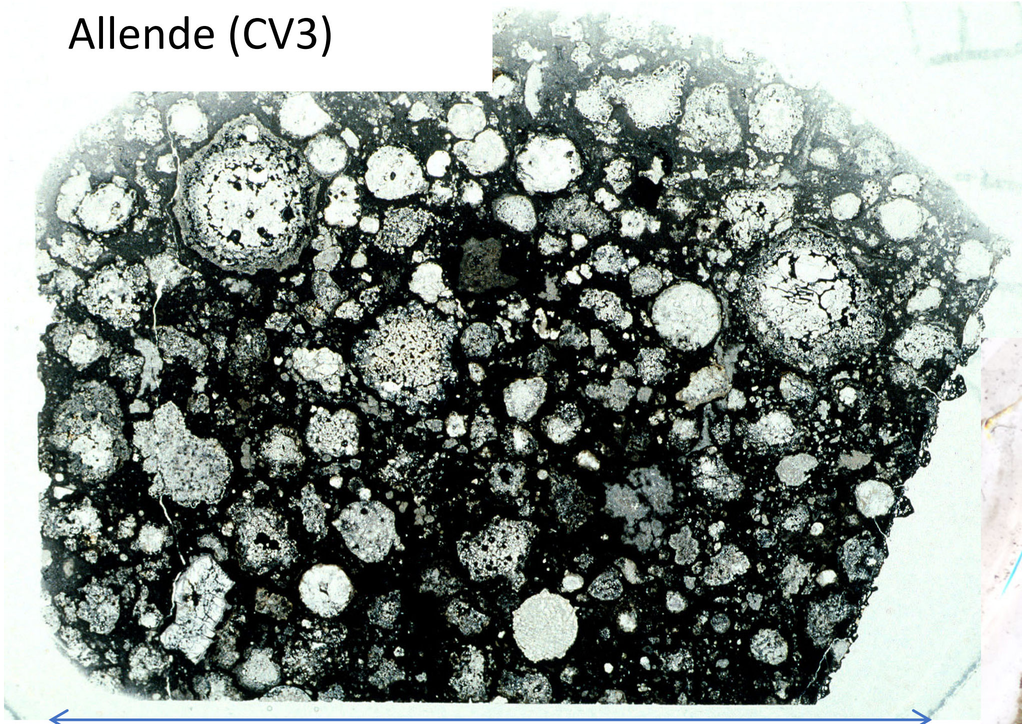
Melted and differentiated

Formed in <2 Ma

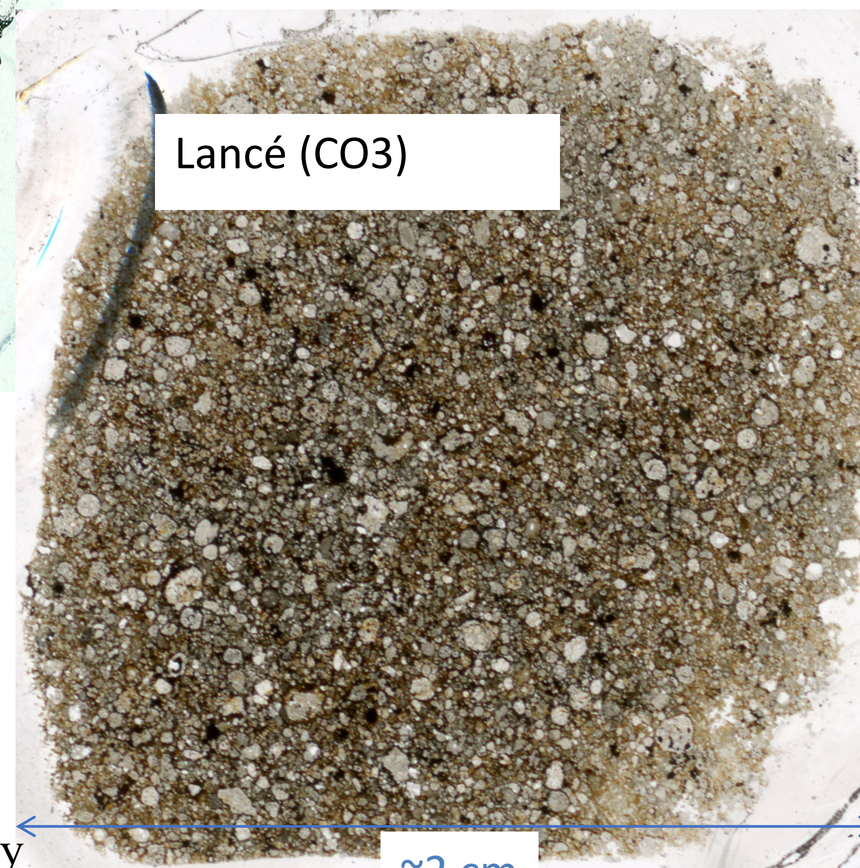
'Preserved'

Formed in ~2-4 Ma

Chondrites – ‘cosmic’ sediments



Three basic components:
Chondrules, CAIs, Matrix.



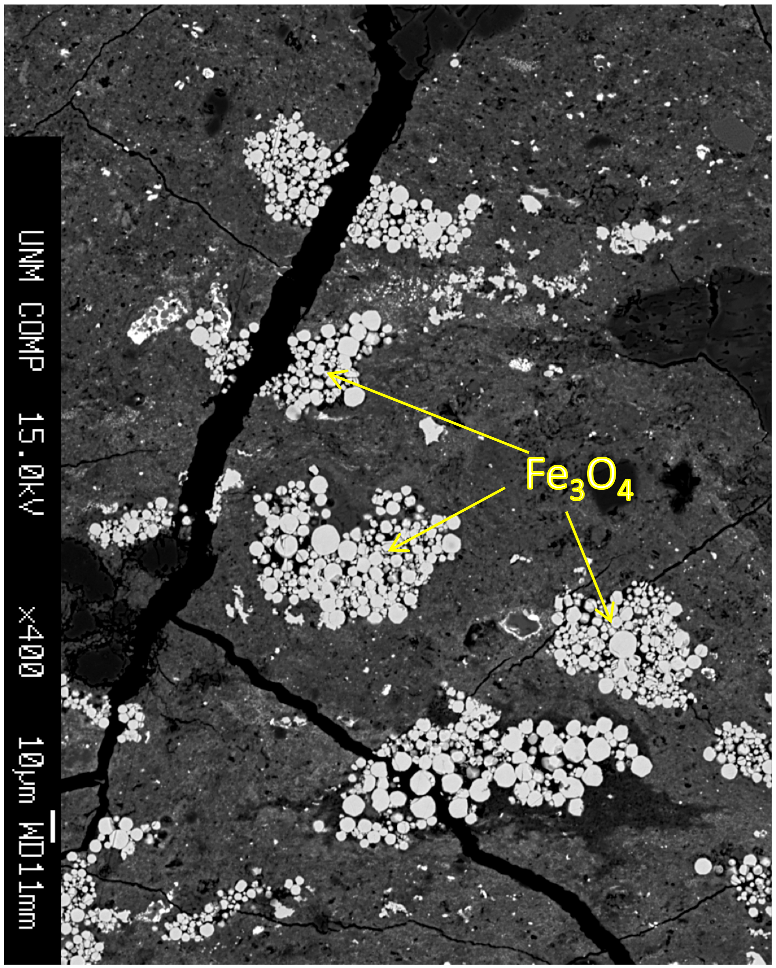
Distance from Sun?

Enstatite – EH, EL
Ordinary – H, L, LL (and R)

Carbonaceous – CO, CV, CK
CI, CM, CR

Photomicrographs Courtesy Adrian Brearley

Alteration≈Serpentization



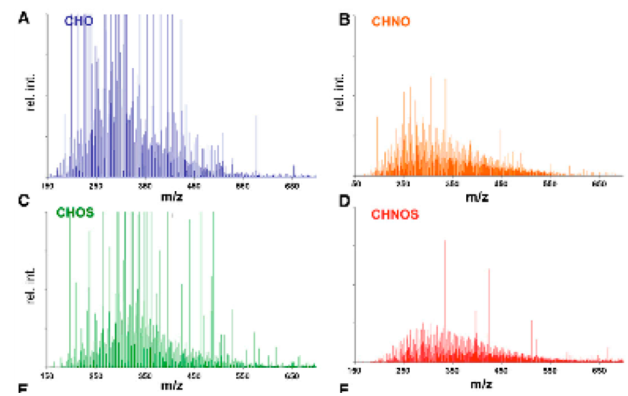
- Anhydrous silicates were converted to serpentines and clays.
- Fe-metal and FeS were oxidized generating H_2.
- Ubiquitous carbonates indicate CO_2 (or CO/CH_4) was present in the ices.
- Little evidence for FTT synthesis.

Meteorite Organics

Murchison (CM2) inventory

Insoluble Organic Matter (IOM)	Abundance
Macromolecular material ($C_{100}H_{70}N_3O_{12}S_2$)	70-99% total organic C
Soluble Organic Matter (SOM)	**Concentration (ppm)**
Carboxylic acids	>300
Polar hydrocarbons	<120
Sulfonic acids	67
Amino acids (92 named)	60
Dicarboxyimides	>50
Aliphatic hydrocarbons	>35
Dicarboxylic acids	>30
Polyols	30
Aromatic hydrocarbons	15-28
Hydroxy acids	15
Amines	13
Pyridine carboxylic acids	>7
N-heterocycles	7
Phosphonic acids	2
Purines and pyrimidines	1

Updated Table from *Meteorites and the Early Solar System II,* (2006) Pizzarello, S., Cooper, G. W., and Flynn, G. J., pp. 625-651, eds. D. S. Lauretta and H. Y. McSween



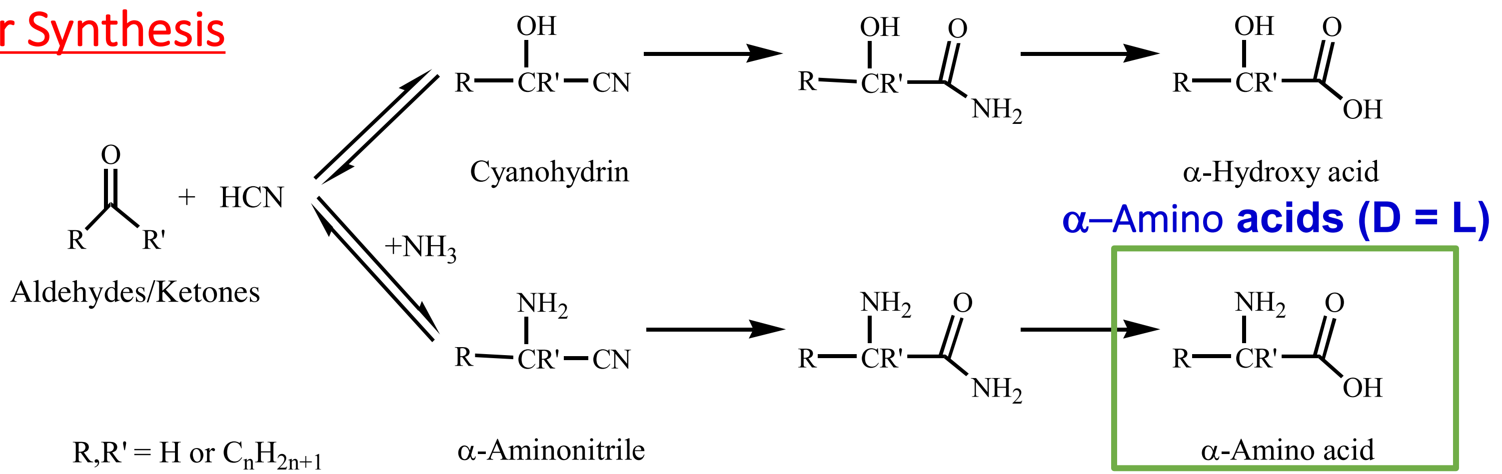
High resolution mass spectrometry analysis suggests millions of chemical structures

(Schmitt-Kopplin *et al.* 2010)

(Courtesy of Danny Glavin)

Alteration Drove Organic Chemistry

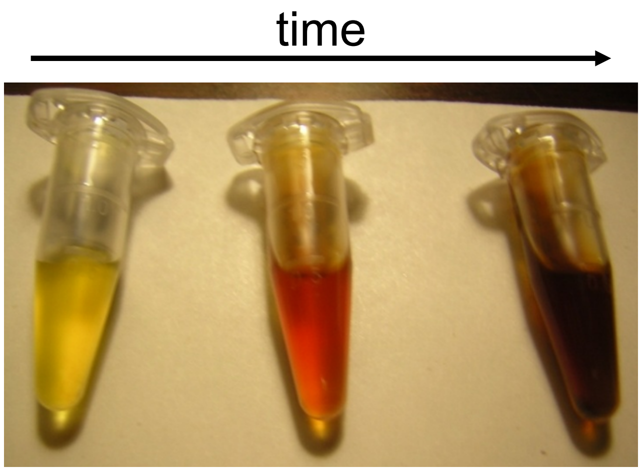
Strecker Synthesis



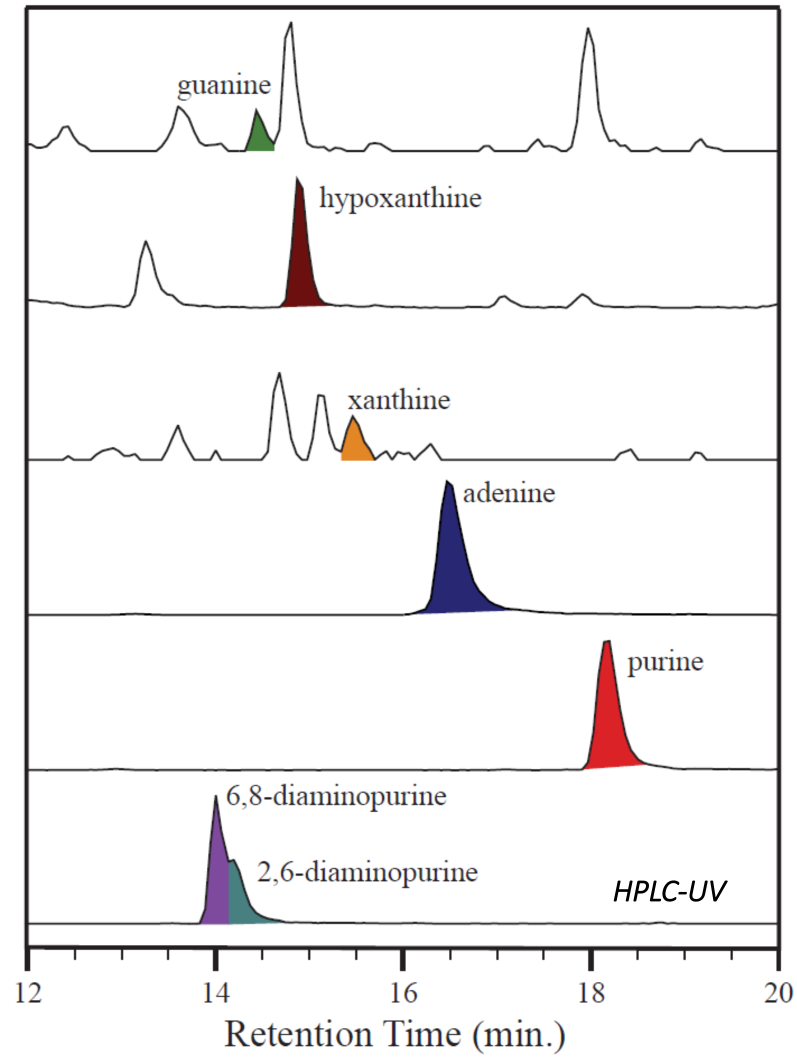
α-amino acids dominate in the least altered meteorites, but decrease dramatically with increasing alteration of hosts.

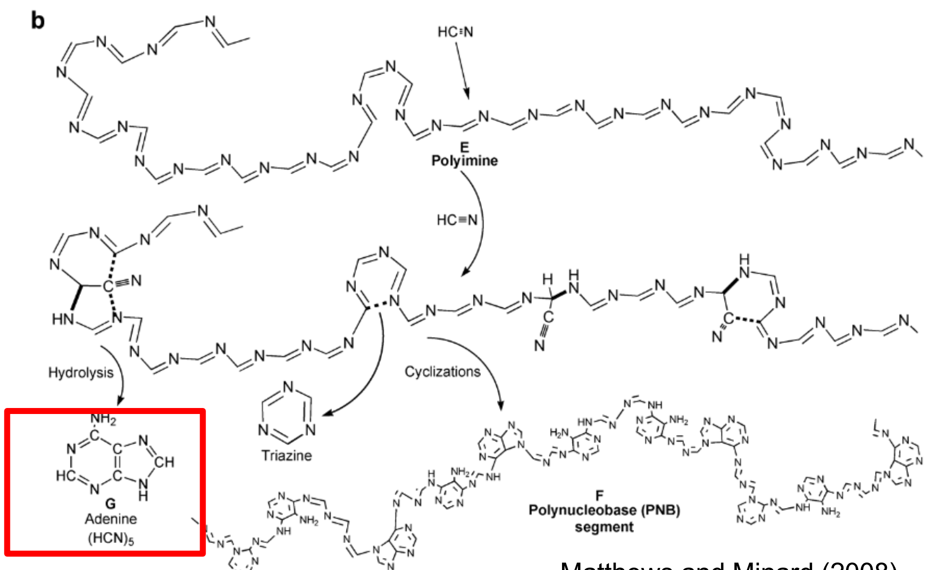
(Courtesy of Danny Glavin)

HCN Polymerization in Meteorites?



Lab reactions with HCN, NH_3, and H_2O produce the ***same suite*** of purines found in meteorites (Callahan *et al.* 2011).

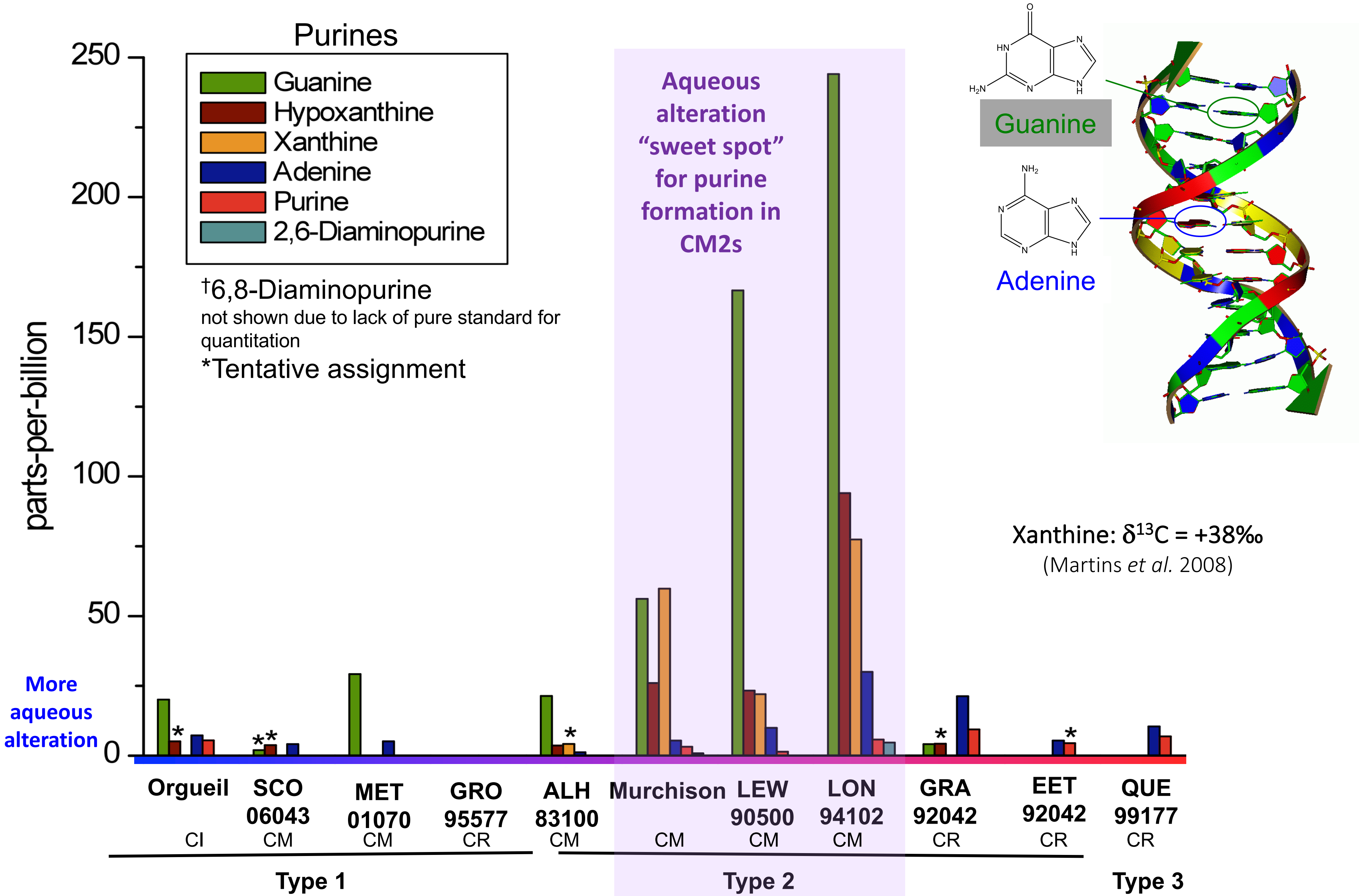




Matthews and Minard (2008)

(Courtesy of Danny Glavin)

Extraterrestrial Purines in Carbonaceous Meteorites

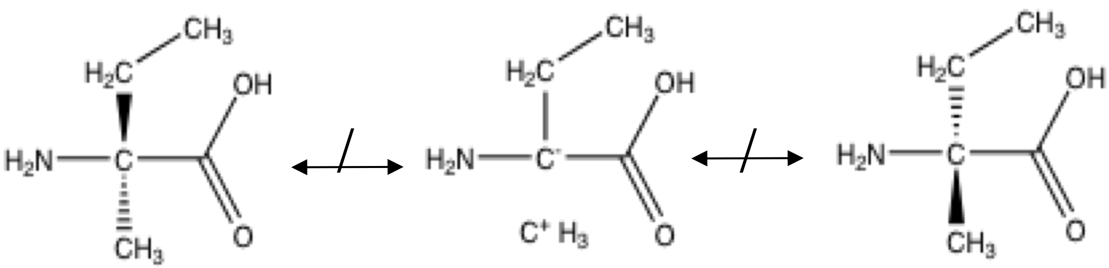


(Courtesy of Danny Glavin)

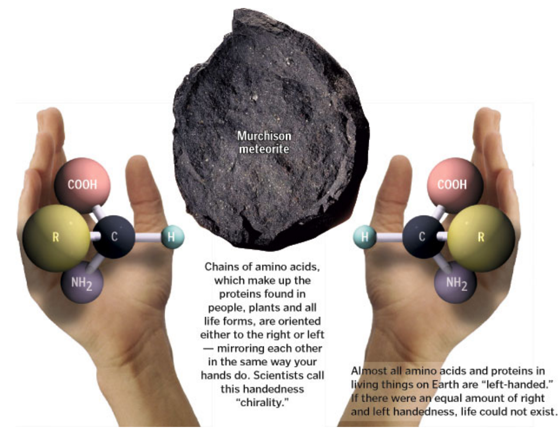
Callahan *et al.* (2011) *PNAS* **4108**: 13995-13998

Isovaline Asymmetry

- **Isovaline is a chiral α-amino acid that is rare in biology, 'abundant' in many carbonaceous meteorites, <u>and resistant to racemization.</u>**



L-isovaline   **Very slow**   D-isovaline



- **L-isovaline (and other α-dialkyl amino acids) excesses are observed in a wide range of carbonaceous meteorites.** (Cronin and Pizzarello, 1997; Pizzarello and Cronin, 2000; Glavin and Dworkin, 2009; Elsila *et al.* 2016)

- **Origin of asymmetry remains unclear.**

(Courtesy of Danny Glavin)

What about Protein L-Amino Acid Excesses?

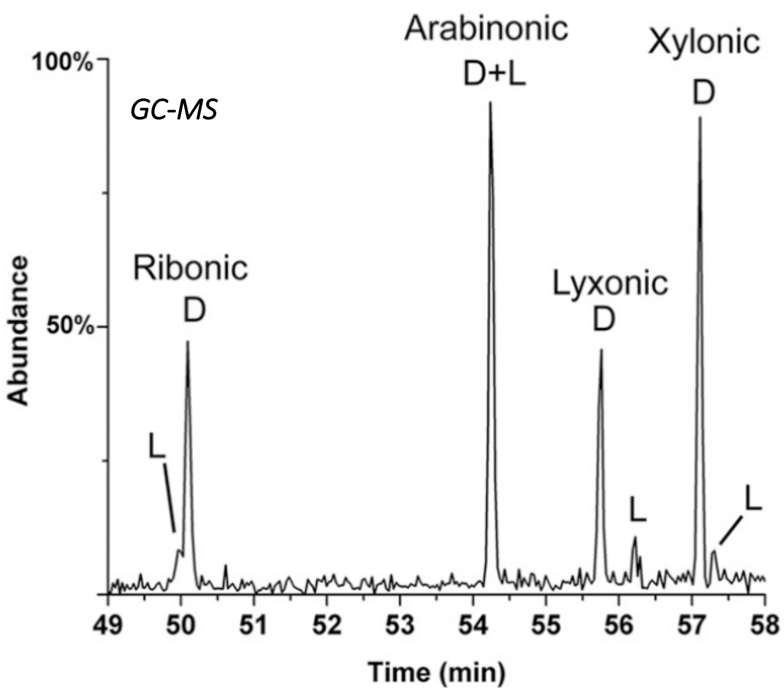
- L-enantiomeric excesses of up to ~60% have been seen.
  - Glavin *et al.* 2012 (L-aspartic acid in C_{ung} Tagish Lake)
  - Pizzarello *et al.* 2012 (L-isoleucine in CR2 MET 00426)
- **Even greater caution** must be taken in analyzing protein amino acids due to potential for biologic contamination!
- Complete analysis of potential interfering compounds and stable isotopic analysis is required

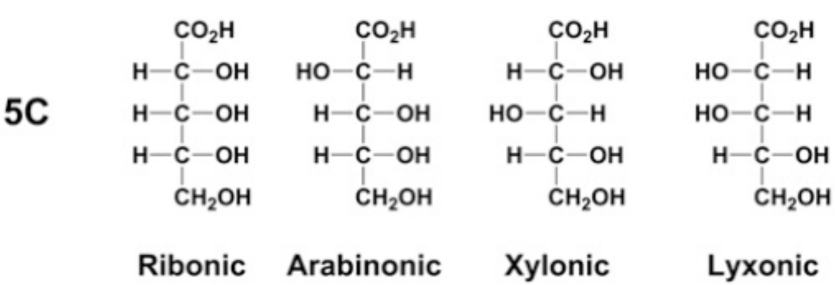
CR
Type 2

C_{ung}

Polyols and D-Sugar Acid Enantiomeric Excesses

Murchison





(rare in biology)

(Courtesy of Danny Glavin)

Several 5C sugar acids detected in Murchison with D-excesses ranging from ~50 to 100% (enantiopure)

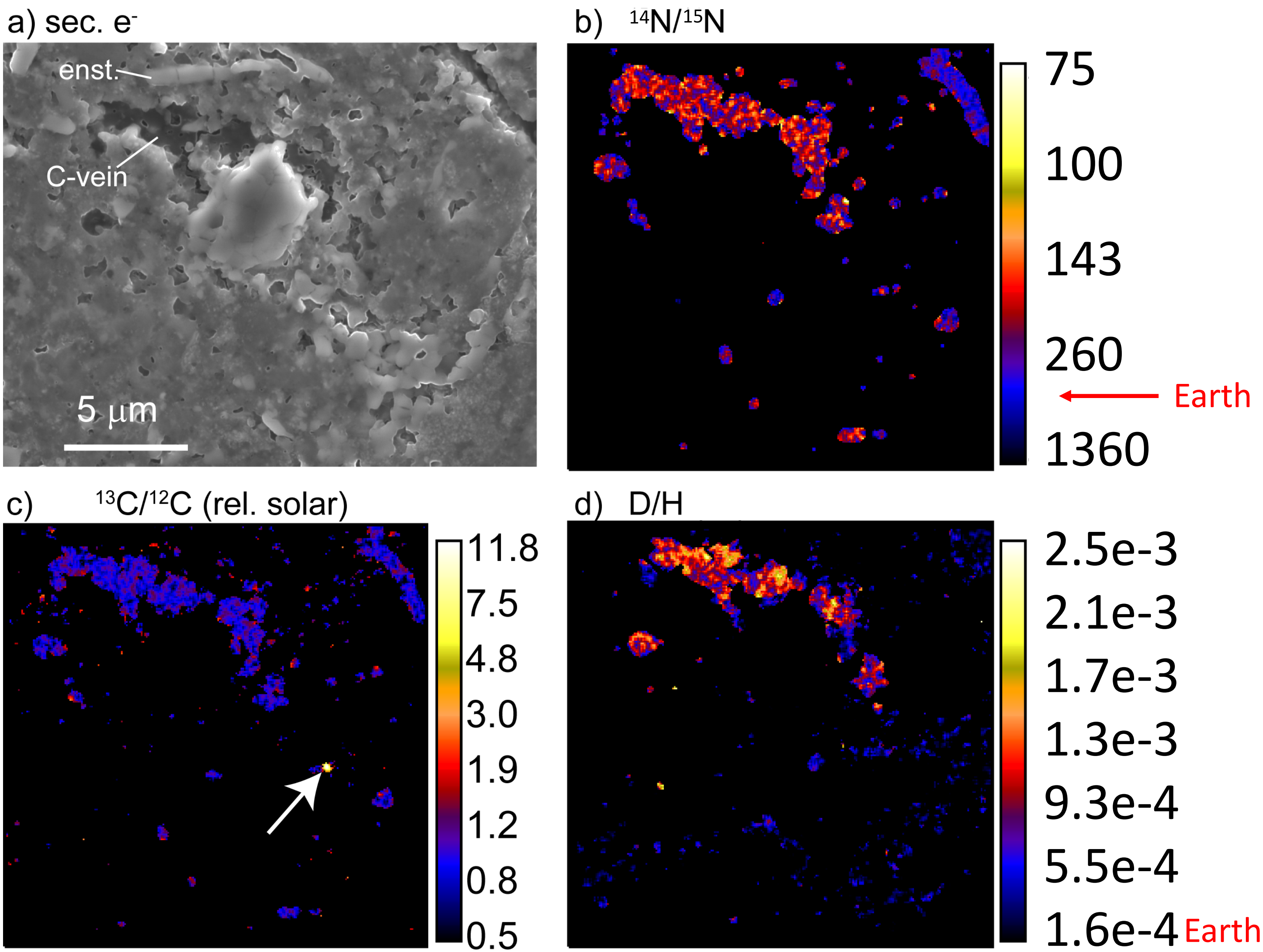
No D-enrichment observed for any of the chiral sugar alcohols detected.

Meteorite 3C to 6C sugar acid distribution distinct from soil and microbial activity.

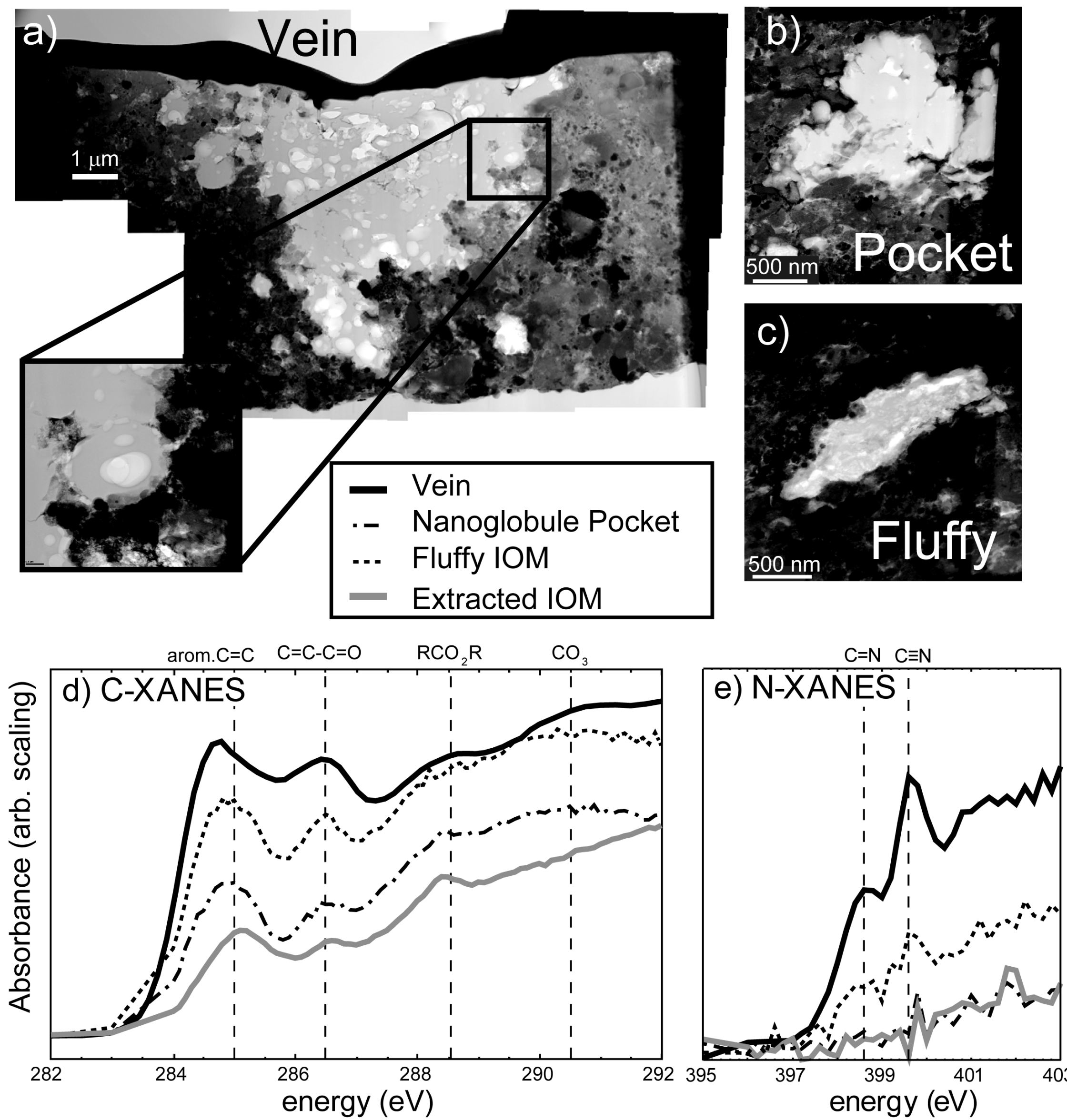
No obvious correlations between D-sugar acid and L-amino acid excesses in the few meteorites that have been studied.

Cooper and Rios (2016) *PNAS* **113**: E3322-E3331

The macromolecular material (IOM)

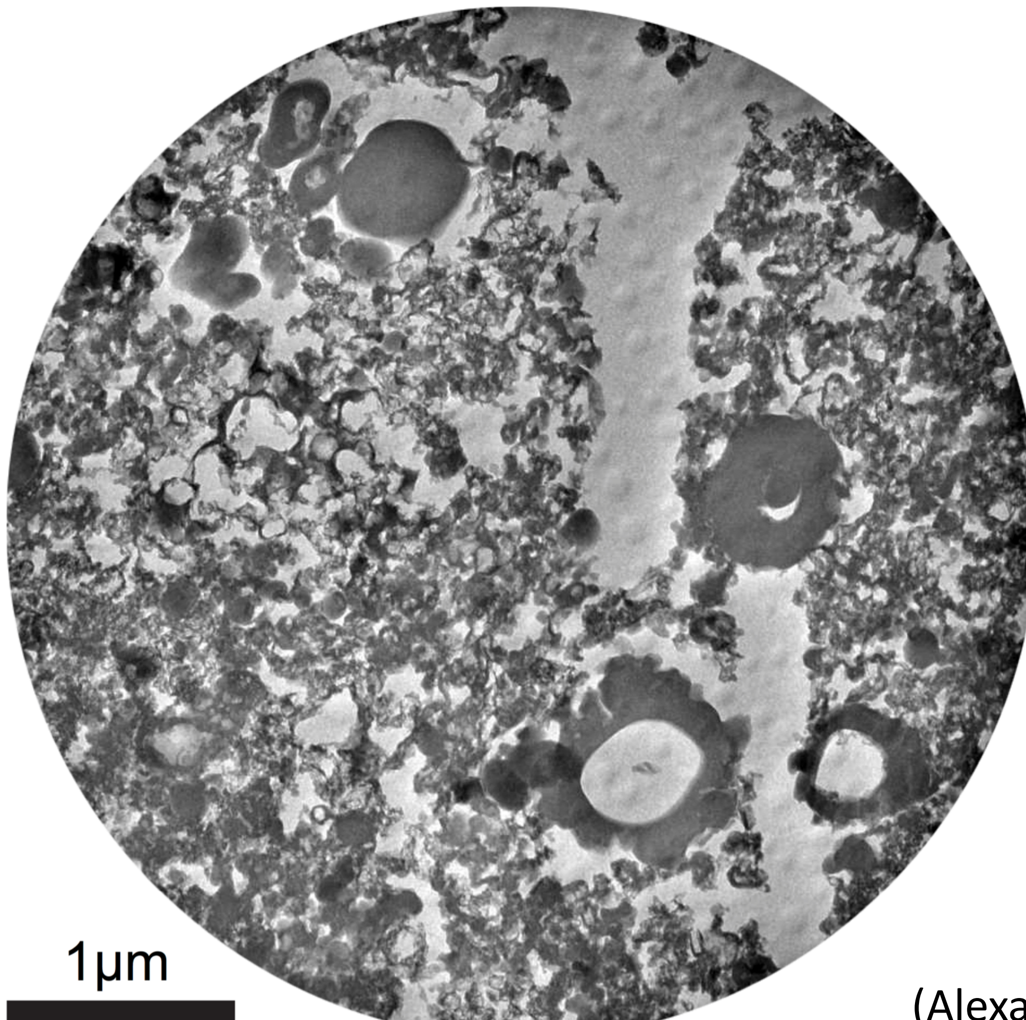


(Alexander et al. 2017)



(Alexander et al. 2017)

Purified IOM
(aggregates of nm-μm grains)



(Alexander et al. 2017)

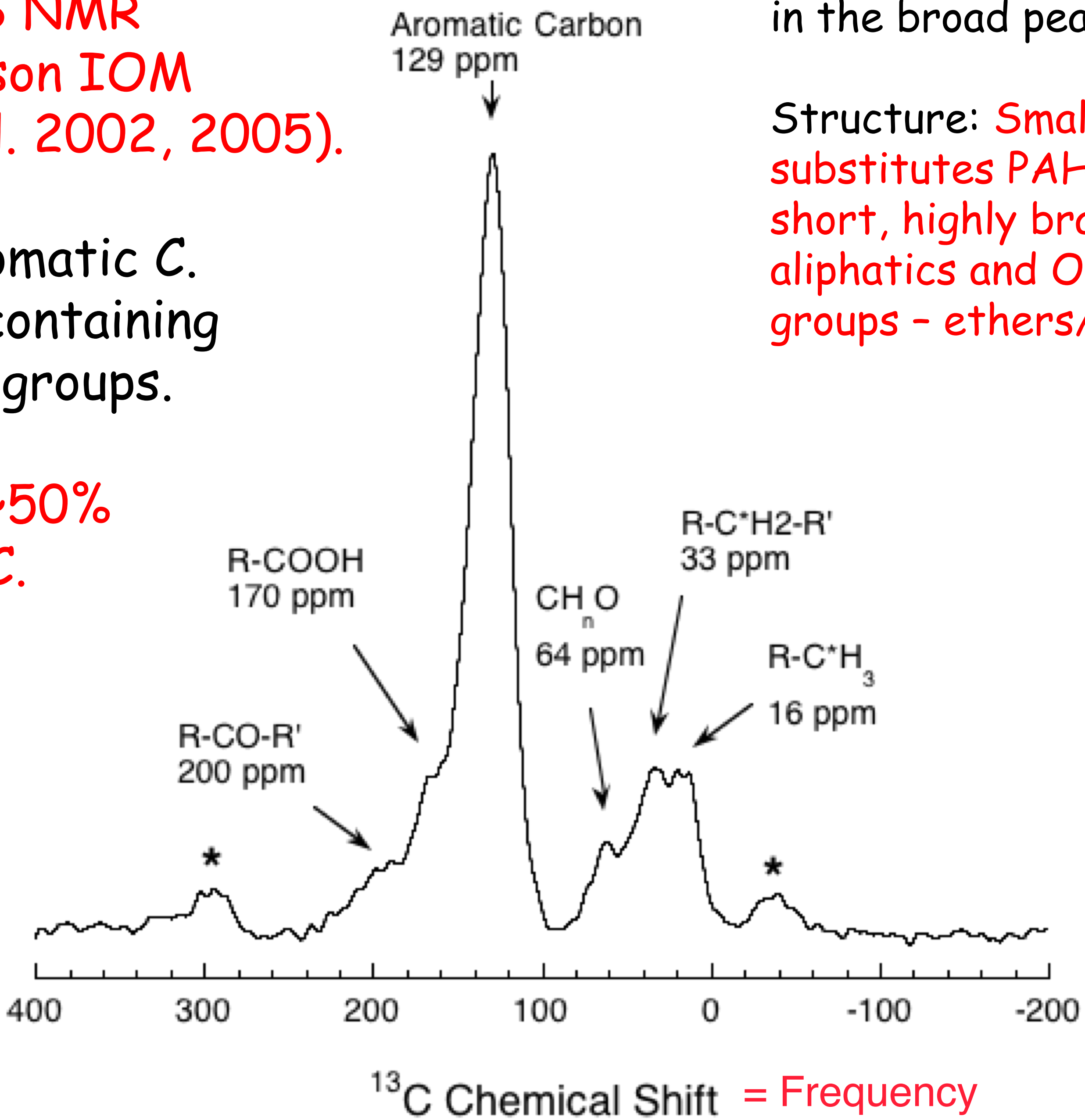
^{13}C CPMAS NMR of Murchison IOM (Cody et al. 2002, 2005).

~ 60 % aromatic C. Rich in O containing functional groups.

CRs have ~50% Aromatic C.

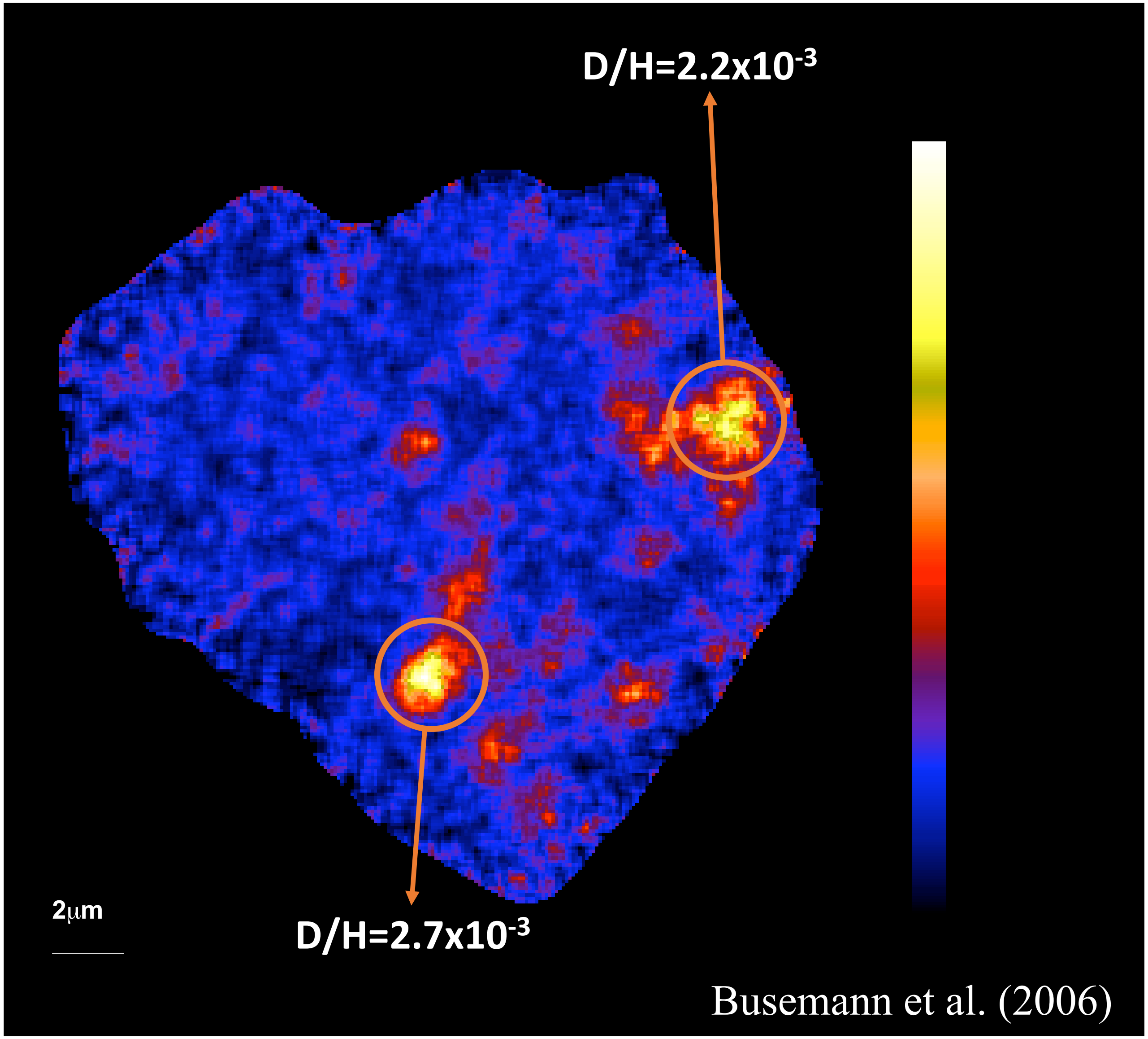
Complex structure evident in the broad peaks.

Structure: Small, highly substitutes PAHs, bridged by short, highly branched aliphatics and O functional groups – ethers/furans.



= Frequency

Insoluble Organic Material (IOM)



The most primitive IOM in bulk

$D/H \approx 6 \times 10^{-4}$
$^{14}N/^{15}N \approx 190$,

but contains isotopic hotspots with

D/H up to $\sim 6 \times 10^{-3}$
$^{14}N/^{15}N$ up to ~70.

C isotope variations are rare.

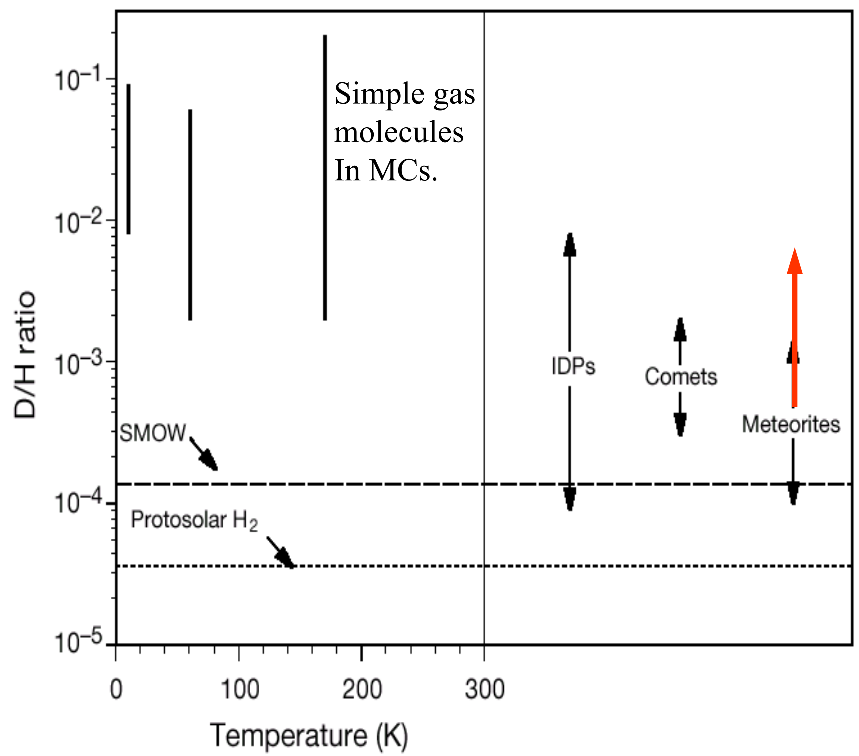
	Earth	Solar
D/H	1.6×10^{-4}	2×10^{-5}
$^{14}N/^{15}N$	270	440

Interstellar Organics?

- Large enrichments in D and ^{15}N point to formation in molecular clouds (MCs) or perhaps the outer Solar System.

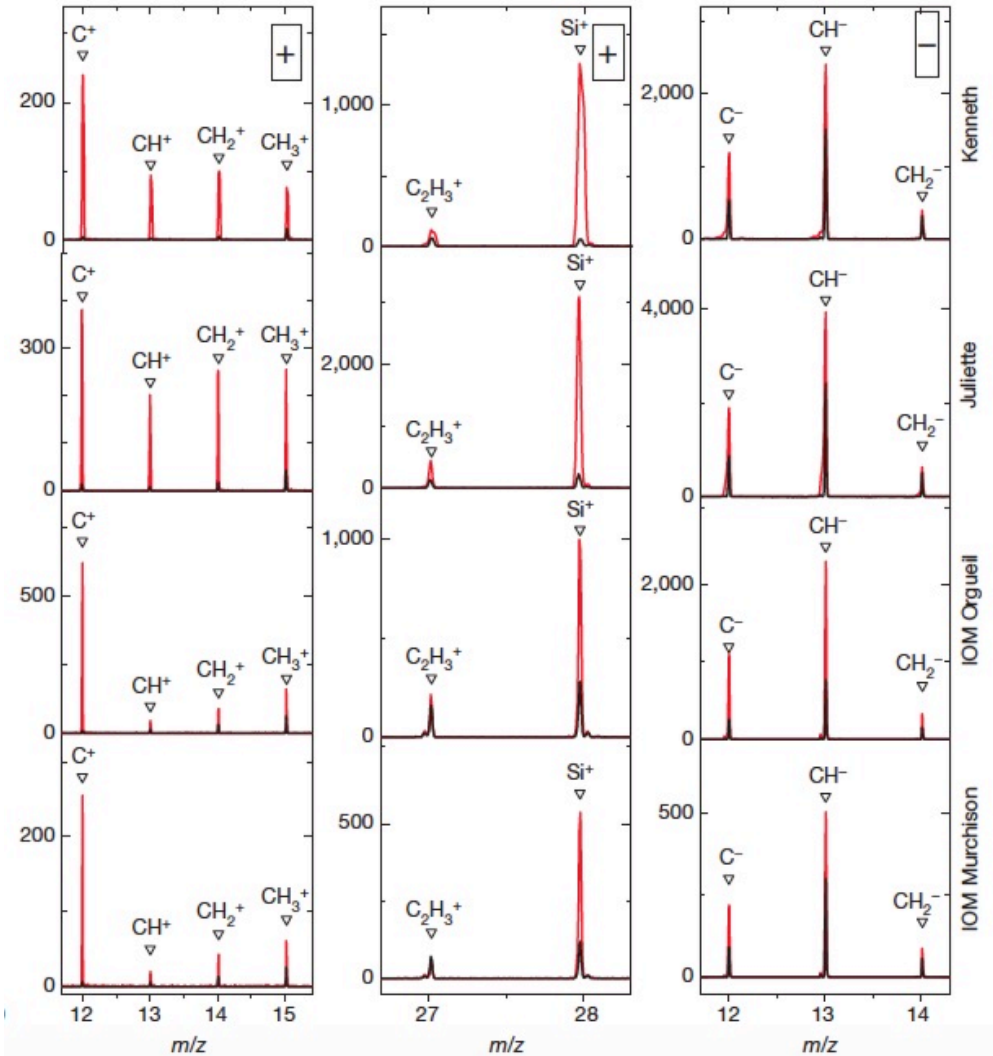
- $C_{100}H_{80}N_4O_{20}S_2$ comet Halley CHON (Kissel and Krueger, 1987).

- $C_{100}H_{79}N_{3.8}O_{15}S_3$ in CR chondrite IOM (Alexander et al. 2007).



Messenger (2000) + Busemann et al. (2006)

A comet-chondrite connection



(Fray et al. 2016)

- Fray et al. (2016) concluded that the refractory C in comet 67P dust is macromolecular and similar to chondritic IOM.
- Its N/C≈0.035, also very similar to Halley CHON and chondritic IOM (Fray et al. 2017).
- However, the C content of 67P dust is ≥7 times chondrites (Bardyn et al. 2017).

Interstellar or Solar?

- Ice in comet 67P is consistent with a largely interstellar origin.
- Abundance of refractory C in Halley and 67P ~50-70 % cosmic C.
- In the diffuse ISM, ~50% of the C is in dust (e.g., Compiègne et al. 2011), probably higher in molecular clouds.
- Is IOM diffuse ISM dust that was modified in the protosolar MC (high D, ^{15}N, O and N functionality, etc.)?

Why no Life in Meteorites?

- Primitive meteorites had many of the conditions that would seem necessary for life:

    Liquid water.

    Fairly abundant organic C, including many N-rich compounds (e.g., amino acids).

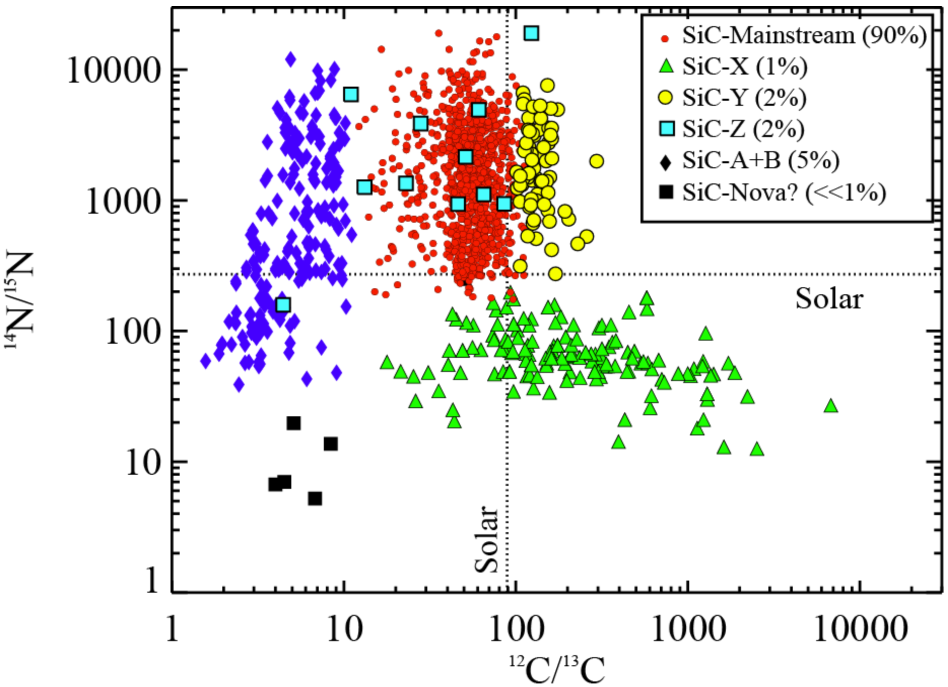
    A source of enantiomeric excesses.

    Disequilibrium inorganic systems (serpentinization).

- Why no life? A lack of time or abundant organic P?

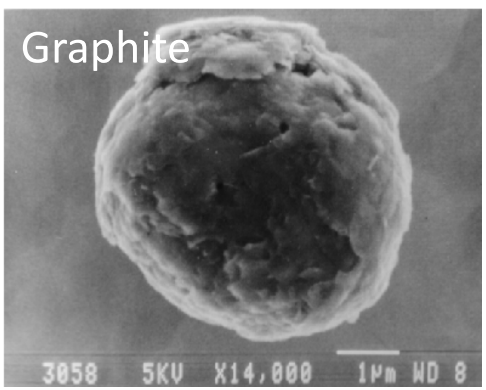
A mixed solar and interstellar heritage

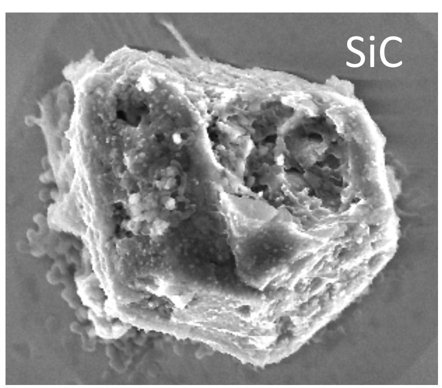
- Circumstellar grains in meteorites demonstrate that some interstellar material survived.
- Non-solar D/H of water and presence of CO_2/CO/CH_4 and HCN/NH_3 suggest a link to cometary ices.
- The IOM has chemical affinities to refractory C in comets Halley and 67P. D and ^{15}N enrichments suggest low T formation or modification in proto-solar MC or outer Solar System.
- The soluble organics reflect a rich abiotic chemistry, much of which probably occurred in their asteroidal parent bodies. D and ^{15}N enrichments suggest low T formation of precursors in interstellar or outer Solar System.

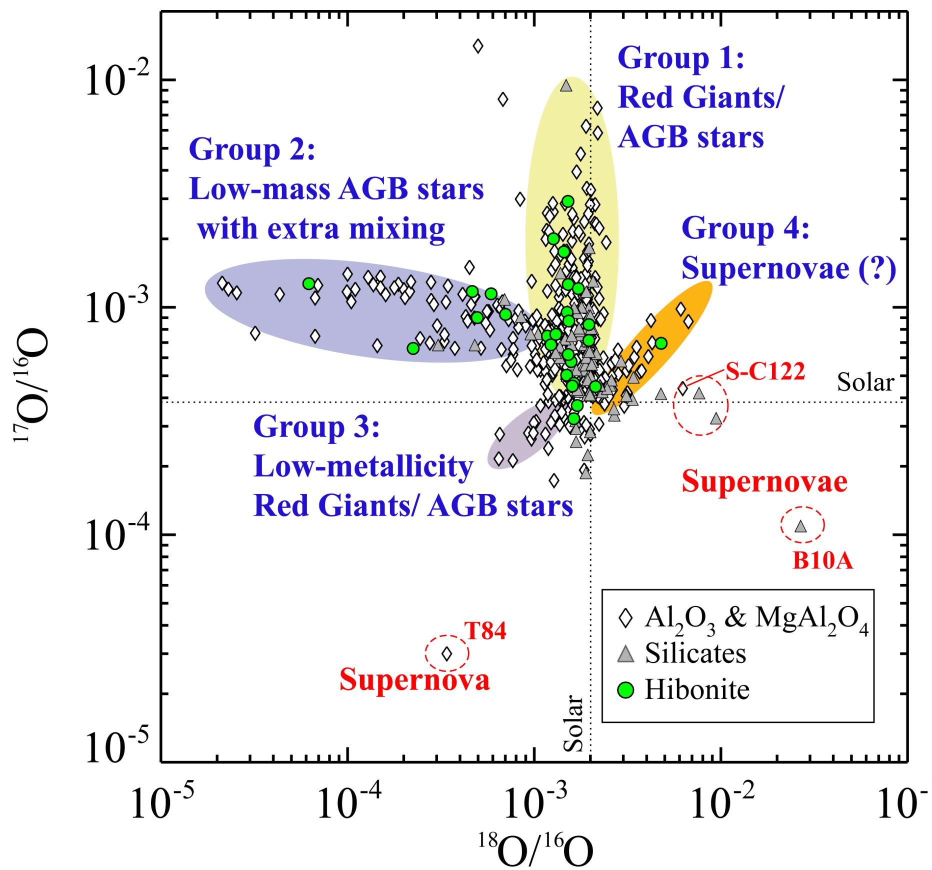


Presolar Grains

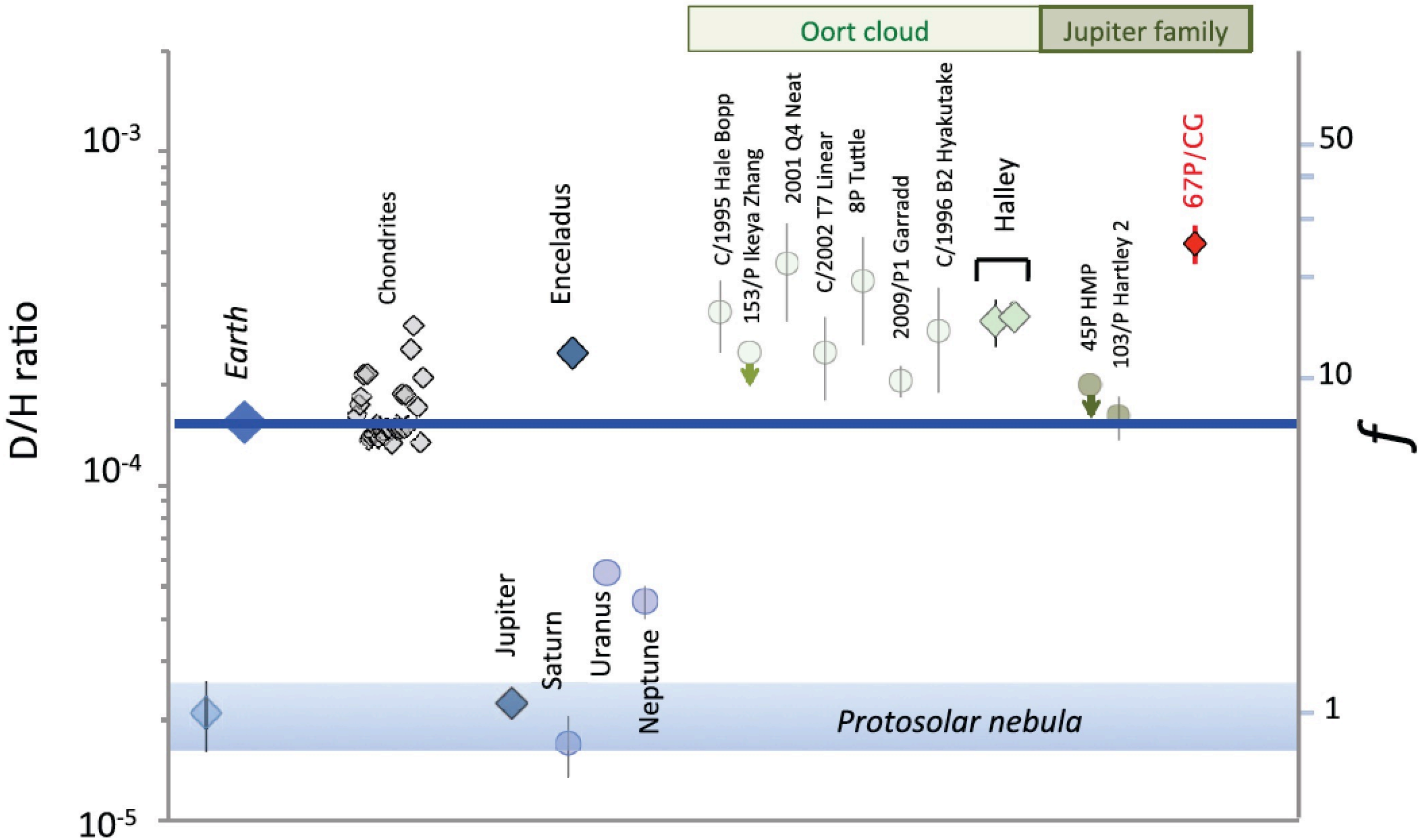
Not everything was processed!







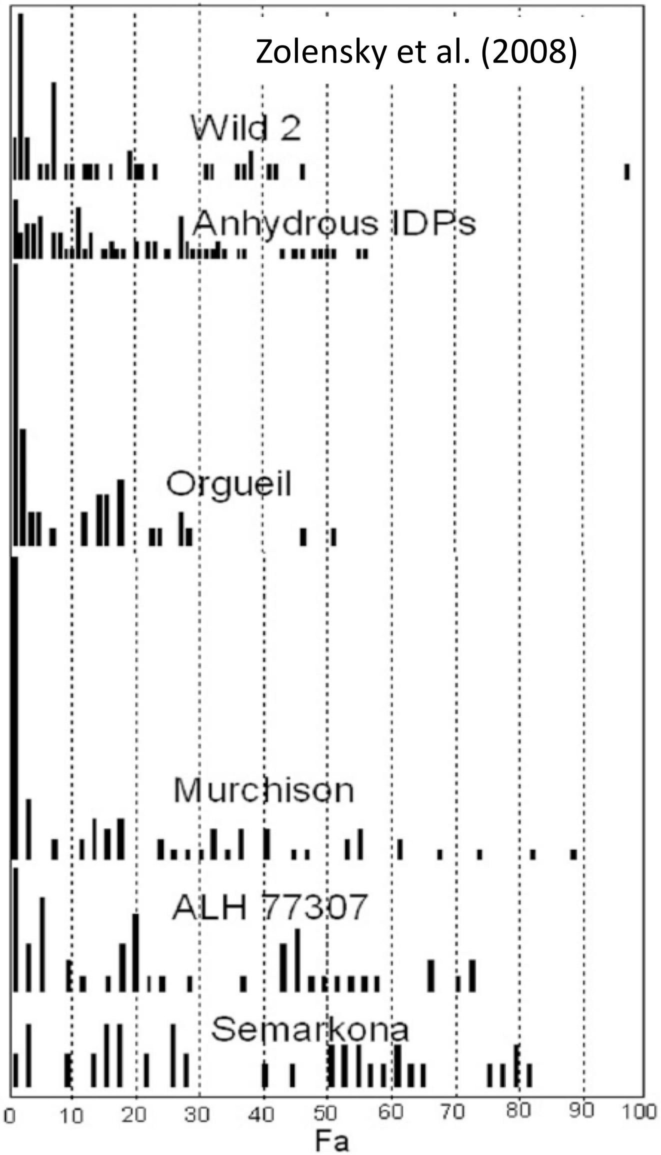
D/H in Solar System objects

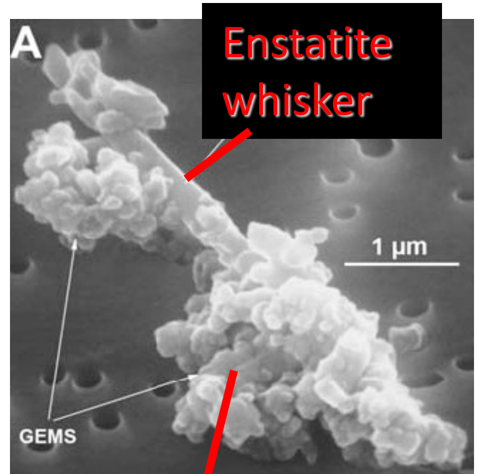


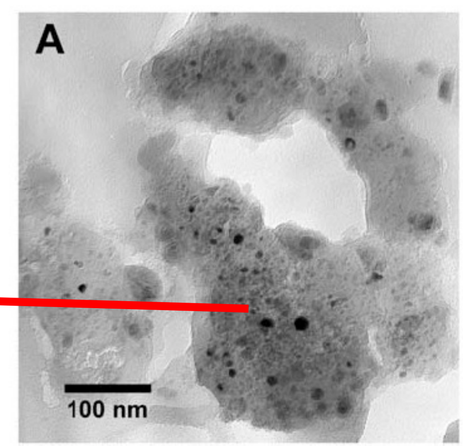
Altwegg et al. (2015)

Fine-grained Silicates

There are many similarities between fine silicates in Wild 2, IDPs and chondrite matrices (Ishii et al. 2008; Zolensky et al. 2008).







"GEMS" (Glass with Embedded Metals & Sulfides; J. Bradley)

Interstellar Organic Globules?