Origins of the Building Blocks for Life: Soluble Organics in Meteorites

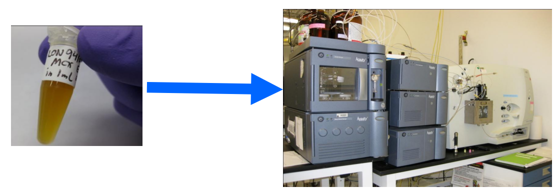
Jamie Elsila
NASA Goddard Space Flight Center

2012 Santander Summer School

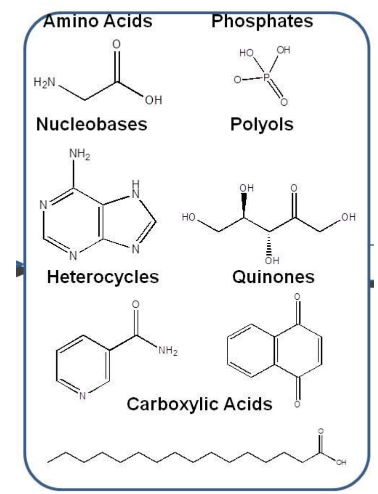
Outline

- Meteoritic delivery of organic compounds

- Meteorite samples
- Meteorite classification



- Analytical procedures
- Observed meteoritic soluble organic compounds

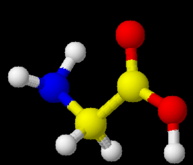


The Requirements for Life (as we know it)

Major Biogenic Elements + Energy + Water = **habitable environment**

Building Blocks:

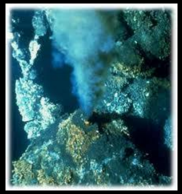
Carbon C
Hydrogen H
Oxygen O
Nitrogen N
Phosphorus P
Sulfur S




e.g. Sunlight (photosynthesis)

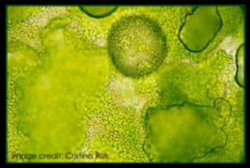
Chemical

Thermal

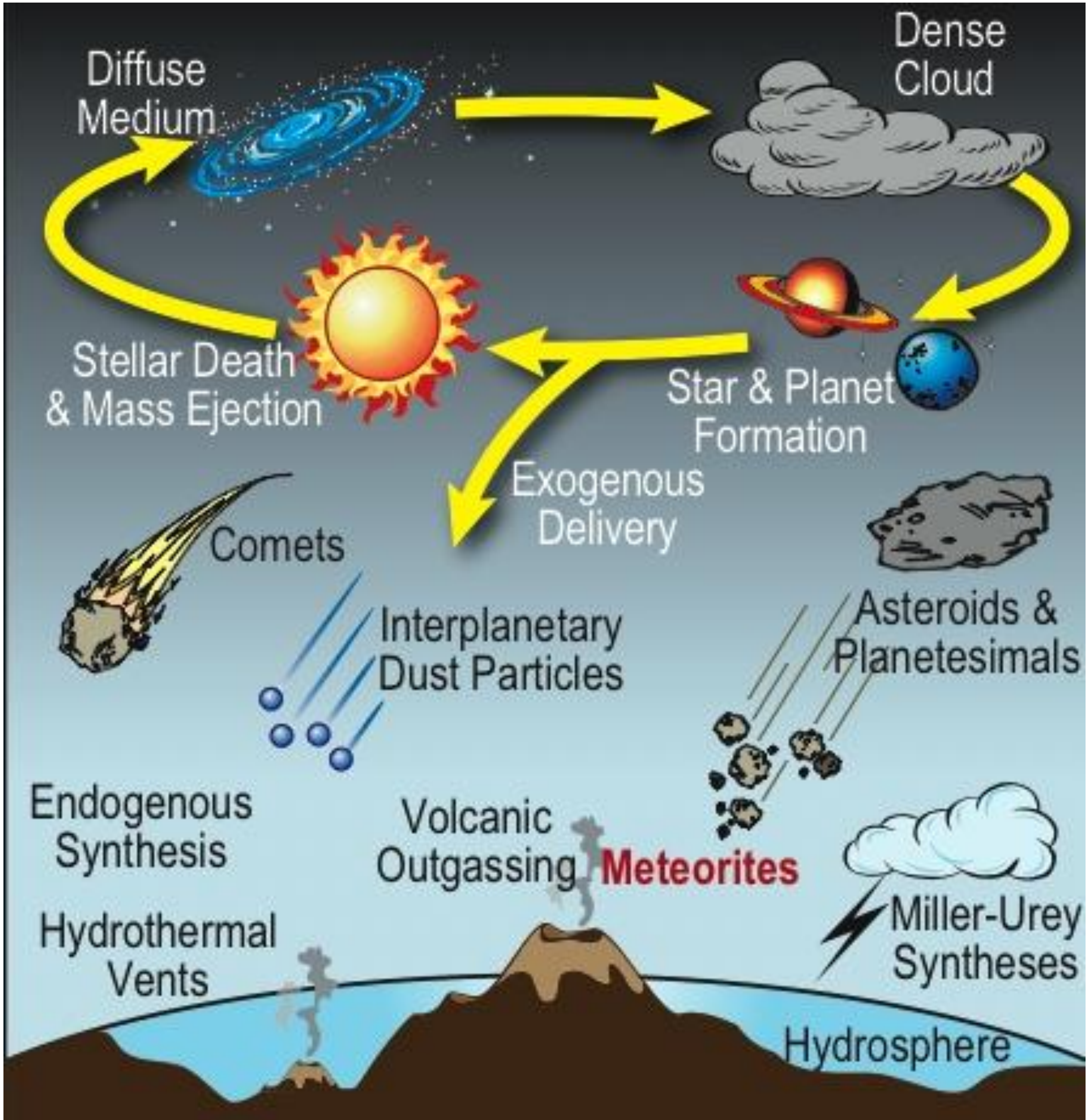



Liquid (chemistry)

Life?



Prebiotic Chemical Environments



Remote Observations & Simulations

Lab Analyses

Simulations

Cosmic Dust Raining from Space

Cosmic dust includes interplanetary dust particles, micrometeorites, and meteorites

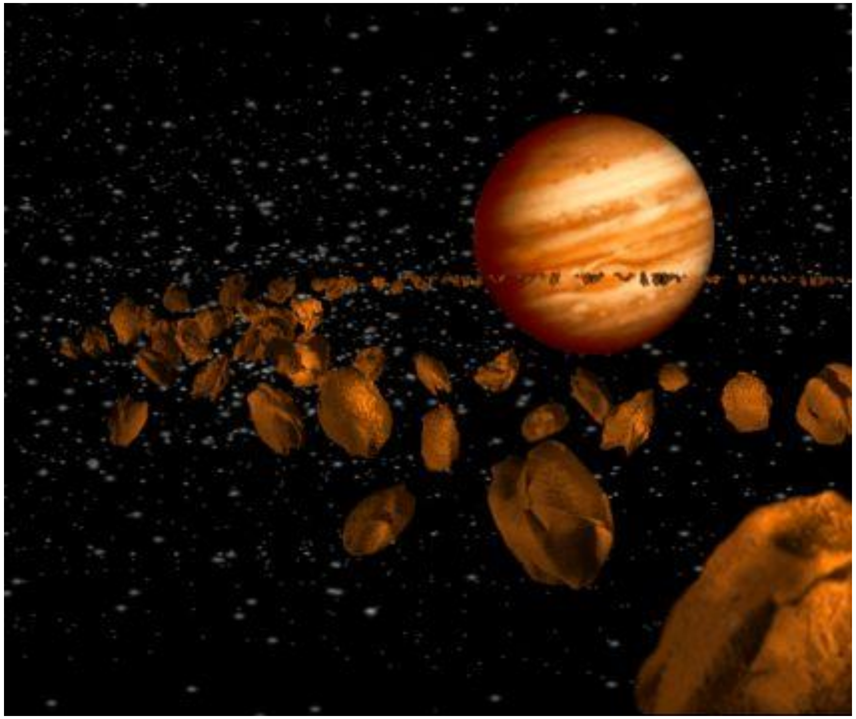
~30,000 tons of cosmic dust falling to Earth each year today

During heavy bombardment period (>3.8 bya), more than1000 times this amount falling to Earth

Extraterrestrial material could have been a major source of prebiotic organic material needed for the origin of life

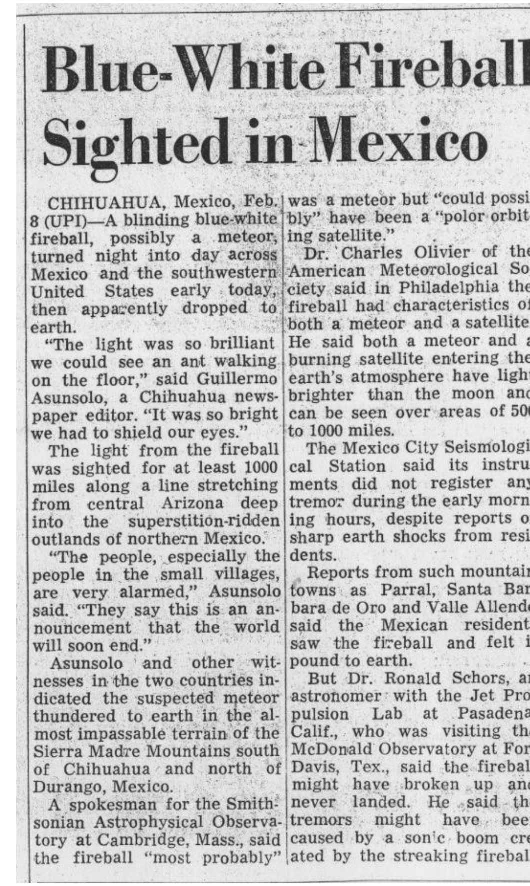
Meteorites as a Prebiotic Record

- Many meteorites come from parent bodies that remained relatively small in size
- Avoided most of the heating that inner planets experienced
- Contain a record of the chemistry taking place at this time, as well as subsequent processing



Meteorite Organic Analysis

- Early organic analysis of meteorites such as Orgueil (1864) were hampered by contamination
- Fortuitous falls of Allende and Murchison in 1969, coinciding with preparations for lunar material
- Expansion in recent years beyond Murchison to Tagish Lake, CR chondrites and others



Blue-White Fireball Sighted in Mexico

CHIHUAHUA, Mexico, Feb. 8 (UPI)—A blinding blue-white fireball, possibly a meteor, turned night into day across Mexico and the southwestern United States early today, then apparently dropped to earth.

"The light was so brilliant we could see an ant walking on the floor," said Guillermo Asunsolo, a Chihuahua newspaper editor. "It was so bright we had to shield our eyes."

The light from the fireball was sighted for at least 1000 miles along a line stretching from central Arizona deep into the superstition-ridden outlands of northern Mexico.

"The people, especially the people in the small villages, are very alarmed," Asunsolo said. "They say this is an announcement that the world will soon end."

Asunsolo and other witnesses in the two countries indicated the suspected meteor thundered to earth in the almost impassable terrain of the Sierra Madre Mountains south of Chihuahua and north of Durango, Mexico.

A spokesman for the Smithsonian Astrophysical Observatory at Cambridge, Mass., said the fireball "most probably" was a meteor but "could possibly" have been a "polor orbiting satellite."

Dr. Charles Olivier of the American Meteorological Society said in Philadelphia the fireball had characteristics of both a meteor and a satellite. He said both a meteor and a burning satellite entering the earth's atmosphere have light brighter than the moon and can be seen over areas of 500 to 1000 miles.

The Mexico City Seismological Station said its instruments did not register any tremor during the early morning hours, despite reports of sharp earth shocks from residents.

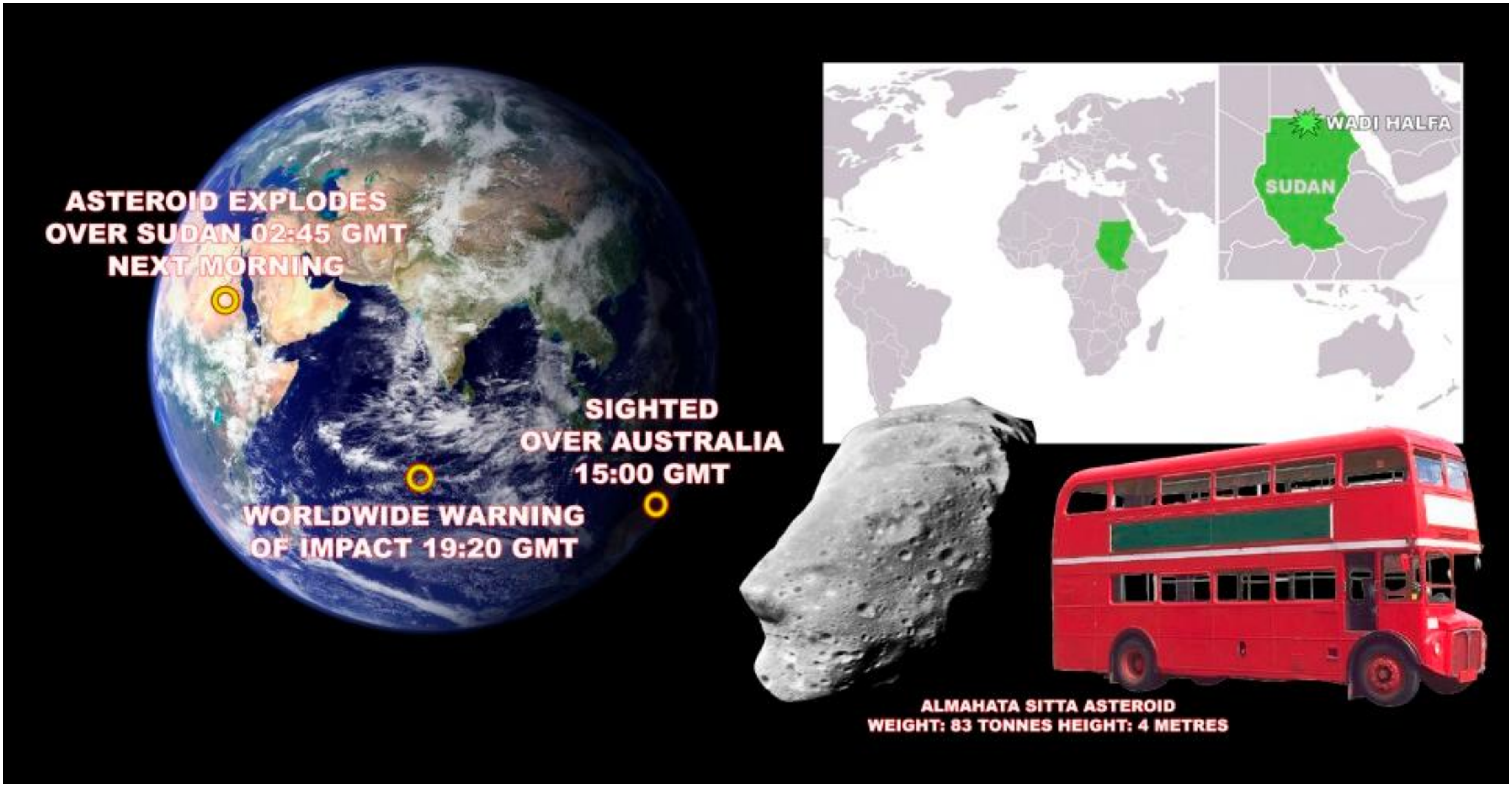
Reports from such mountain towns as Parral, Santa Barbara de Oro and Valle Allende said the Mexican residents saw the fireball and felt it pound to earth.

But Dr. Ronald Schors, an astronomer with the Jet Propulsion Lab at Pasadena, Calif., who was visiting the McDonald Observatory at Fort Davis, Tex., said the fireball might have broken up and never landed. He said the tremors might have been caused by a sonic boom created by the streaking fireball.

Meteorite samples

Falls

Asteroid 2008 TC_3



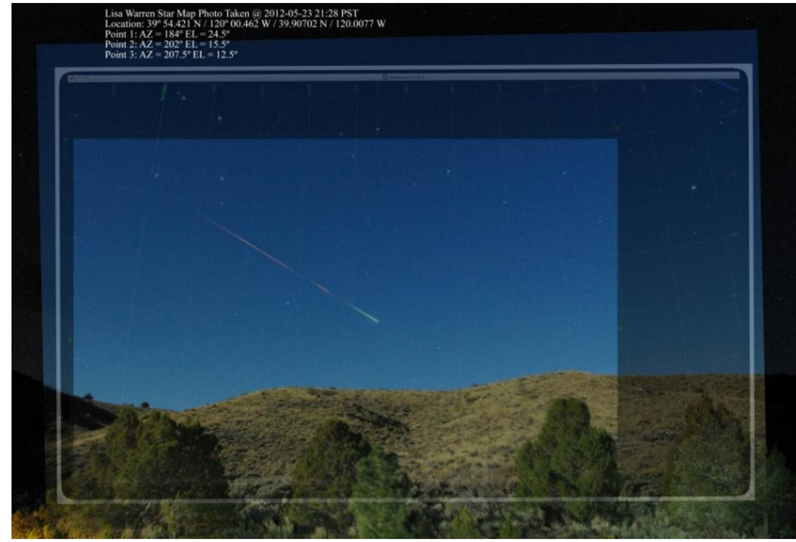
Almahata Sitta TC_3 Ureilite (2008)

*first asteroid to be followed from detection in space to landing on Earth
-meteorites were linked to their asteroid parent body

*estimated at 80 tons (73 Mg or 73,000 kg) and $28m^3$

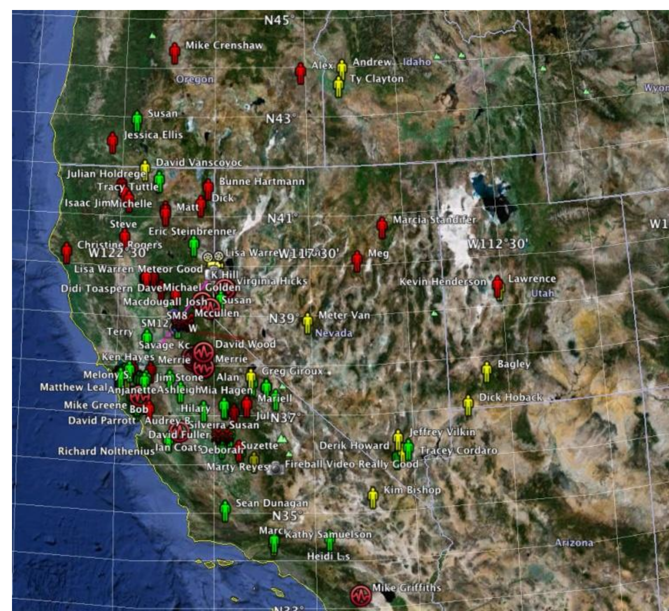
*39 kg survived fall (0.05%), spread over 30km * 7 km fall zone

Sutter’s Mill meteorite



Fell April 22, 2012

- Recovery by scientists, general public, and meteorite hunters/collectors
- Scientific consortium to get initial results quickly



Meteorite samples

Falls

and

Finds

The Advantages of Sample Return Missions

- Allows for use of state-of-the-art analytical techniques and equipment, providing for the ultimate current precision, sensitivity, resolution, and reliability
- The returned samples are a resource for current and *future* studies by a broad international community
- Analyses are iterative and fully adaptive - results are not limited by "instrument' design or current ideas
- Avoids limitations associated with cost, power, mass, and reliability
- Analyses can be replicated, verified, done with multiple techniques and instruments, fully calibrated, and contamination can be fully evaluated

OSIRIS-REx

Asteroid Sample Return Mission

OSIRIS-REx

EXPLORING OUR PAST
SECURING OUR FUTURE

Starring a multi-generational team led by

Principal Investigator: Dante Lauretta
Lunar and Planetary Laboratory
University of Arizona

Partners: Goddard Space Flight Center and
Lockheed Martin

and with researchers around the country and in other countries

THE UNIVERSITY OF ARIZONA • NASA GODDARD SPACE FLIGHT CENTER • LOCKHEED MARTIN

FROM LAUNCH IN 2016 TO SAMPLE RETURN IN 2023… *AND BEYOND*

= sample **return mission**

= **at least 2.1 ounces or 60 g**

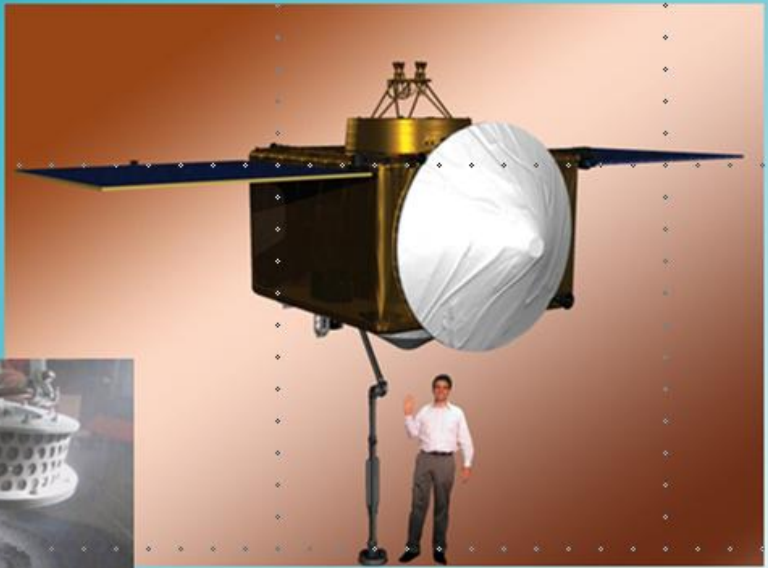
(and as much as 4.4 pounds or 2 kg)

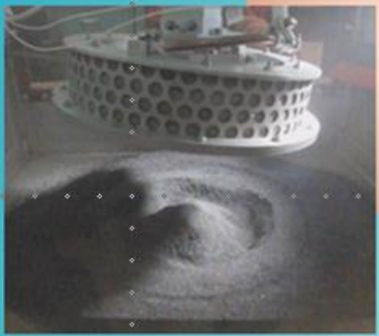
= **pristine carbonaceous material**

= **a *time capsule from the early Solar System*!**

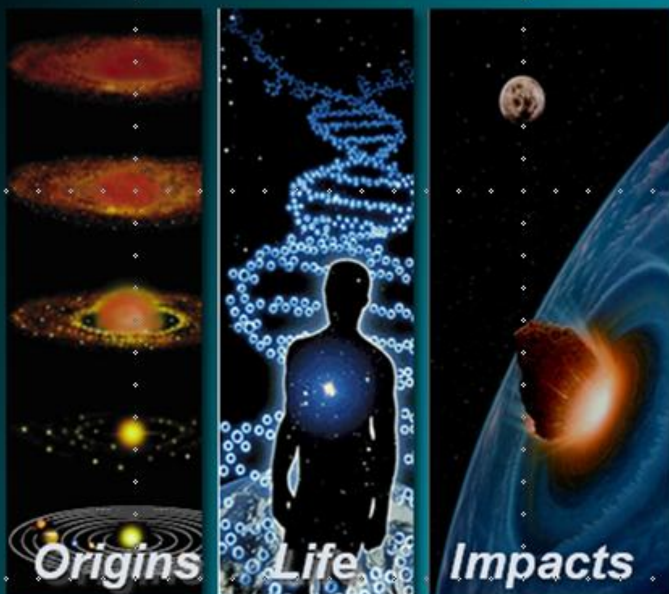
<u>*FAST FACTS*</u>

- 16.6 feet per side (2 meters)
- 91 square feet of solar panels ($8.5\ m^2$)
- Lithium ion batteries
- 8 Instruments
- Touch-and-Go Sampler
- Sample Return Capsule





GENERATIONS OF SCIENTISTS WILL EXPLORE FUNDAMENTAL QUESTIONS



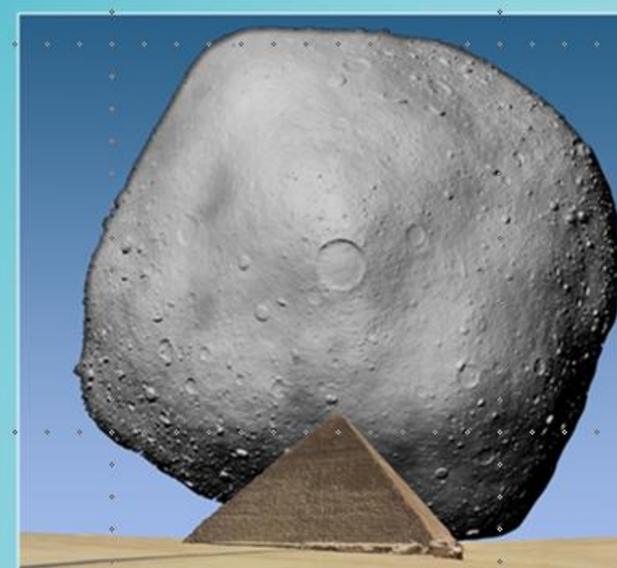
How did the Solar System form and what kinds of materials exist in the Solar System?

How did life evolve in the Solar System?

Are asteroids bringers of life or death – *or both*?

FAST FACTS

- About 1/3 mile diameter
- 4.5-hour rotation period
- 436.6-day orbit of Sun
- Ancient carbon, volatiles
- Potential hazard to Earth

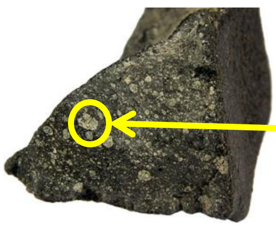


Meteorite Classification

Irons (~ 5% falls)

Stony Meteorites (> 90% falls)

Stony-Irons (~1% falls)



Chondrites (with chondrules)

Achondrites (lack chondrules)

Ordinary (~75% falls)

Carbonaceous (~4% falls)

Enstatite (~2% falls)

Other (K and R type)

CI Ivuna

CM Mighei

CR Renazzo

CV Vigarano

CO Ornans

CK Karoonda

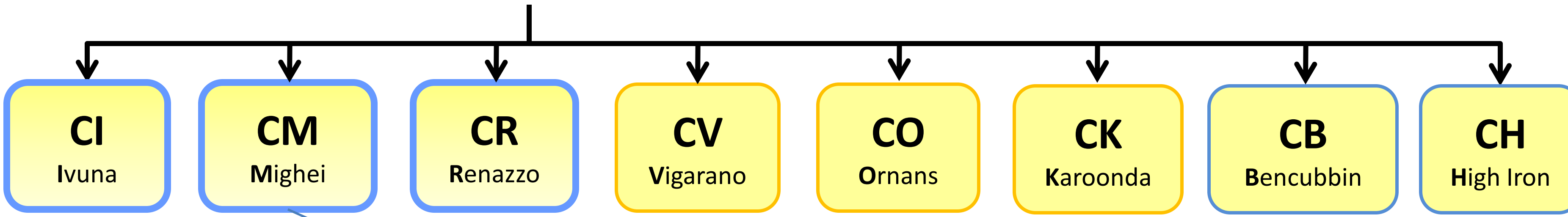
CB Bencubbin

CH High Iron

Petrographic Type (Chondrites)

1	2	3	4	5	6

More aqueous alteration ← → *More thermal metamorphism*



Murchison meteorite
Fell in Murchison, Australia, in 1969
Extensively analyzed

CM2 – moderate aqueous alteration

~30% soluble organics

~70% insoluble organics

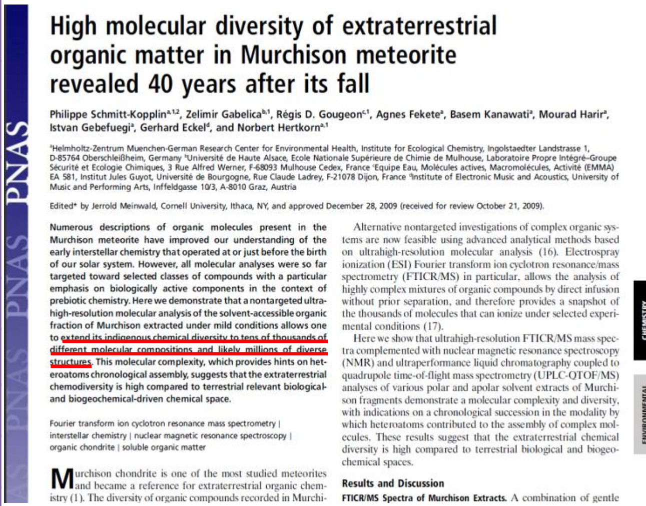
George Cody's lectures

More recent analyses show that Murchison is not representative of all carbonaceous chondrites. For example, CR chondrites have more water-soluble organics and more N-containing compounds.

Lots of Organics in Murchison!

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 (83 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


PNAS

High molecular diversity of extraterrestrial organic matter in Murchison meteorite revealed 40 years after its fall

Philippe Schmitt-Kopplin[a,1,2], Zelimir Gabelica[b,1], Régis D. Gougeon[c,1], Agnes Fekete[a], Basem Kanawati[a], Mourad Harir[a], Istvan Gebefuegi[a], Gerhard Eckel[d], and Norbert Hertkorn[a,1]

[a]Helmholtz-Zentrum Muenchen-German Research Center for Environmental Health, Institute for Ecological Chemistry, Ingolstaedter Landstrasse 1, D-85764 Oberschleißheim, Germany [b]Université de Haute Alsace, Ecole Nationale Supérieure de Chimie de Mulhouse, Laboratoire Propre Intégré–Groupe Sécurité et Ecologie Chimiques, 3 Rue Alfred Werner, F-68093 Mulhouse Cedex, France [c]Equipe Eau, Molécules actives, Macromolécules, Activité (EMMA) EA 581, Institut Jules Guyot, Université de Bourgogne, Rue Claude Ladrey, F-21078 Dijon, France [d]Institute of Electronic Music and Acoustics, University of Music and Performing Arts, Inffeldgasse 10/3, A-8010 Graz, Austria

Edited* by Jerrold Meinwald, Cornell University, Ithaca, NY, and approved December 28, 2009 (received for review October 21, 2009).

Numerous descriptions of organic molecules present in the Murchison meteorite have improved our understanding of the early interstellar chemistry that operated at or just before the birth of our solar system. However, all molecular analyses were so far targeted toward selected classes of compounds with a particular emphasis on biologically active components in the context of prebiotic chemistry. Here we demonstrate that a nontargeted ultra-high-resolution molecular analysis of the solvent-accessible organic fraction of Murchison extracted under mild conditions allows one to extend its indigenous chemical diversity to tens of thousands of different molecular compositions and likely millions of diverse structures. This molecular complexity, which provides hints on heteroatoms chronological assembly, suggests that the extraterrestrial chemodiversity is high compared to terrestrial relevant biological- and biogeochemical-driven chemical space.

Fourier transform ion cyclotron resonance mass spectrometry | interstellar chemistry | nuclear magnetic resonance spectroscopy | organic chondrite | soluble organic matter

Murchison chondrite is one of the most studied meteorites and became a reference for extraterrestrial organic chemistry (1). The diversity of organic compounds recorded in Murchi-

Alternative nontargeted investigations of complex organic systems are now feasible using advanced analytical methods based on ultrahigh-resolution molecular analysis (16). Electrospray ionization (ESI) Fourier transform ion cyclotron resonance/mass spectrometry (FTICR/MS) in particular, allows the analysis of highly complex mixtures of organic compounds by direct infusion without prior separation, and therefore provides a snapshot of the thousands of molecules that can ionize under selected experimental conditions (17).

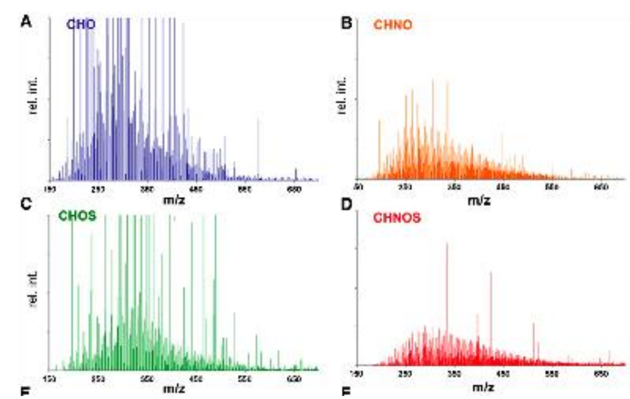
Here we show that ultrahigh-resolution FTICR/MS mass spectra complemented with nuclear magnetic resonance spectroscopy (NMR) and ultraperformance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry (UPLC-QTOF/MS) analyses of various polar and apolar solvent extracts of Murchison fragments demonstrate a molecular complexity and diversity, with indications on a chronological succession in the modality by which heteroatoms contributed to the assembly of complex molecules. These results suggest that the extraterrestrial chemical diversity is high compared to terrestrial biological and biogeochemical spaces.

Results and Discussion

FTICR/MS Spectra of Murchison Extracts. A combination of gentle

CHEMISTRY

ENVIRONMENTAL SCIENCES

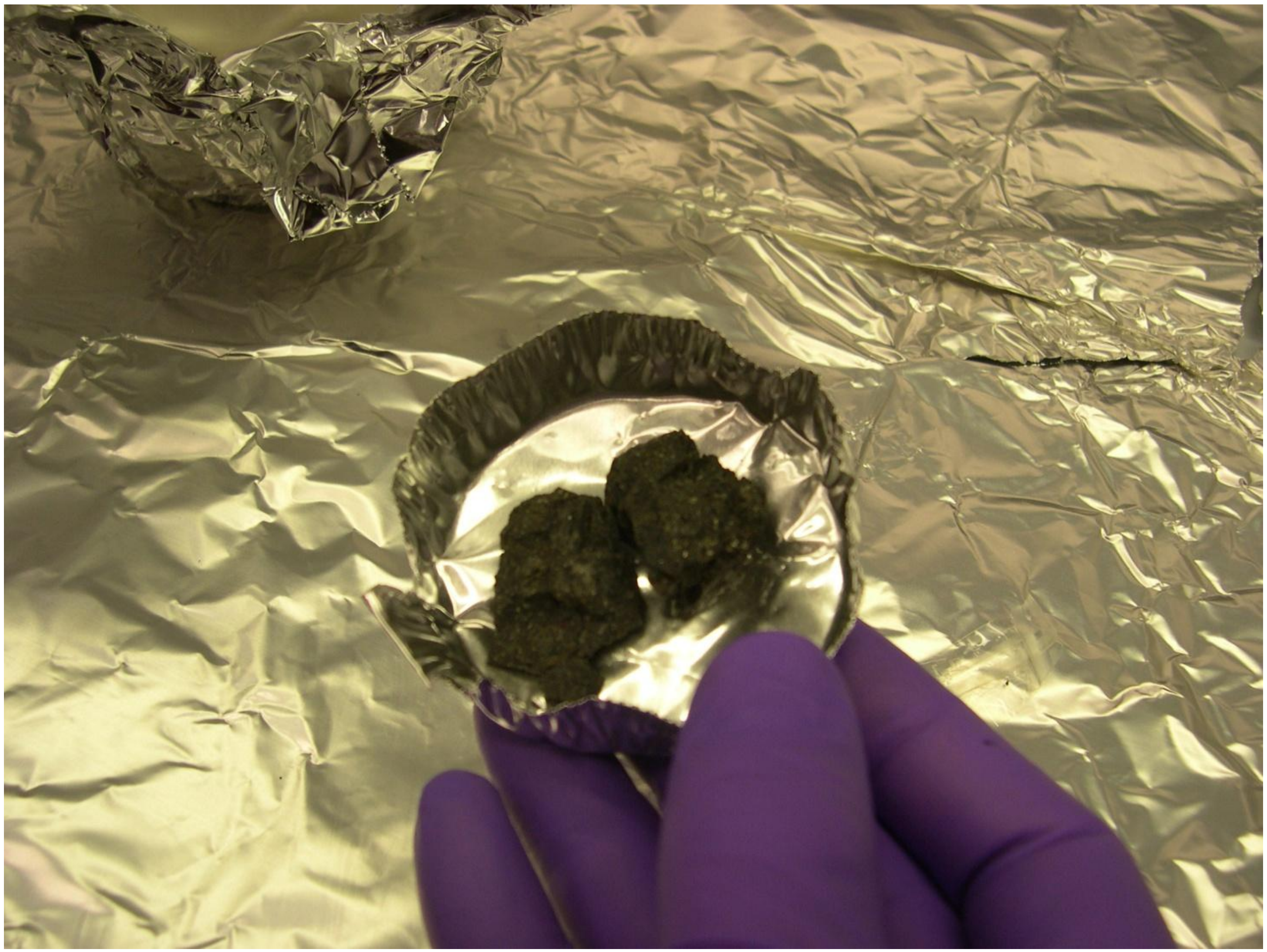


High resolution mass spectrometry analysis revealed millions of diverse chemical structures
(Schmitt-Kopplin et al. 2010)

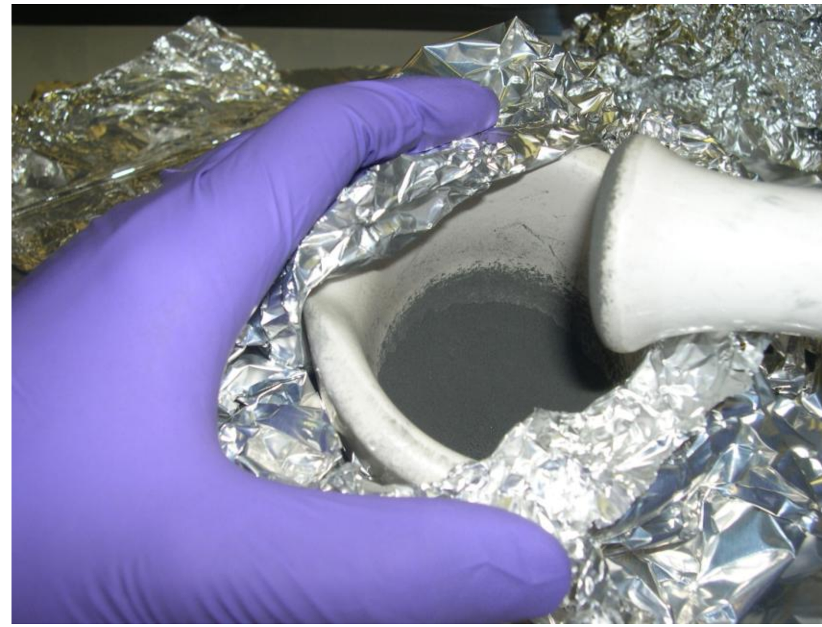
Table modified from:
*Meteorites and the Early Solar System II, (*2006) Pizzarello, S., Cooper, G. W., and Flynn, G. J., pp. 625-651, eds. D. S. Lauretta and H. Y. McSween

A meteorite's life in the lab

LON 94102
(CM2 carbonaceous chondrite)



1. Meteorite Grinding



2. Meteorite extraction and acid hydrolysis

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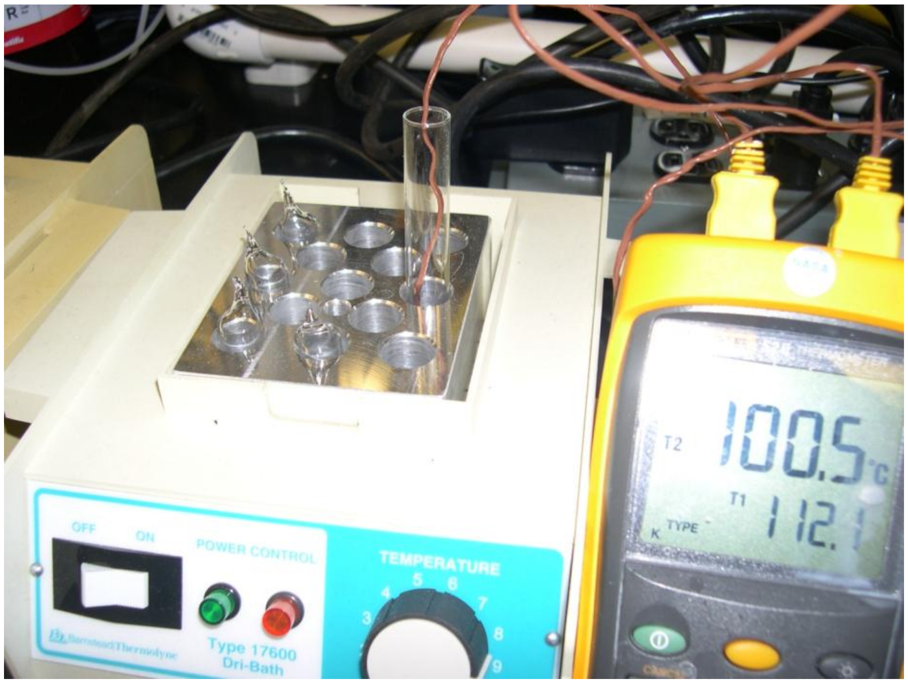
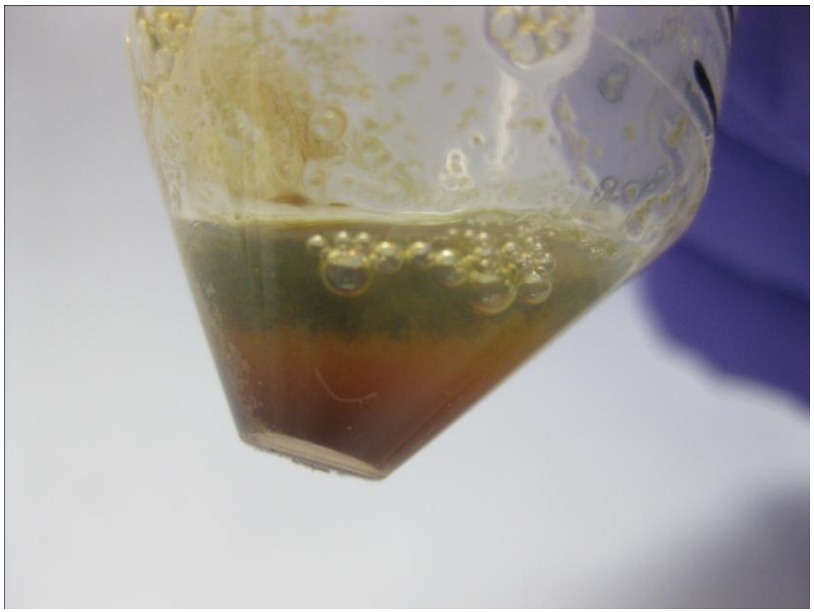
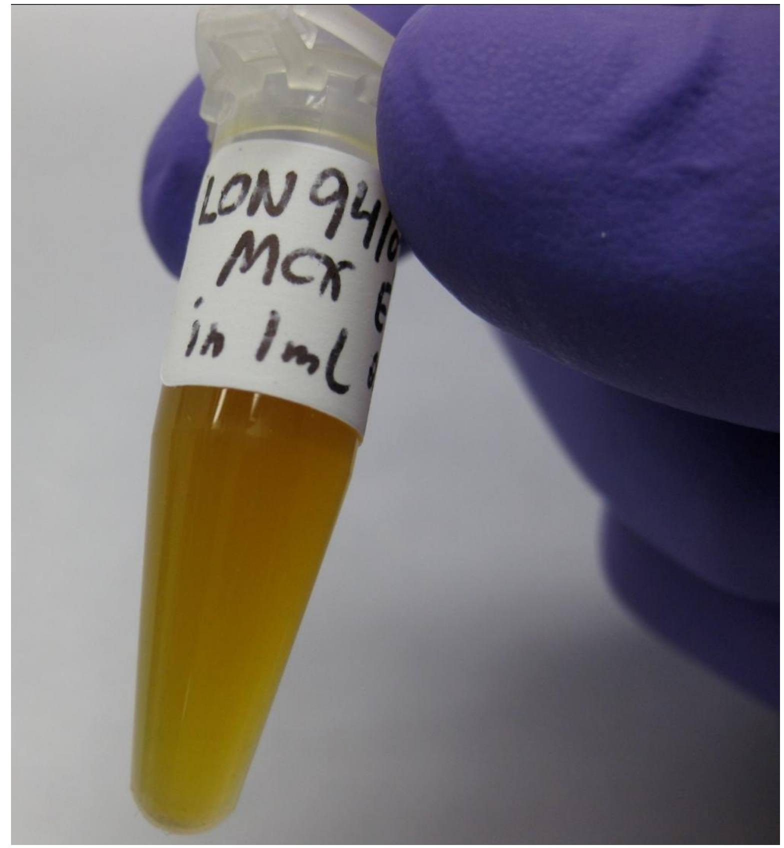


3. Clean up samples with cation-exchange resin

4. Dry Down and Concentration





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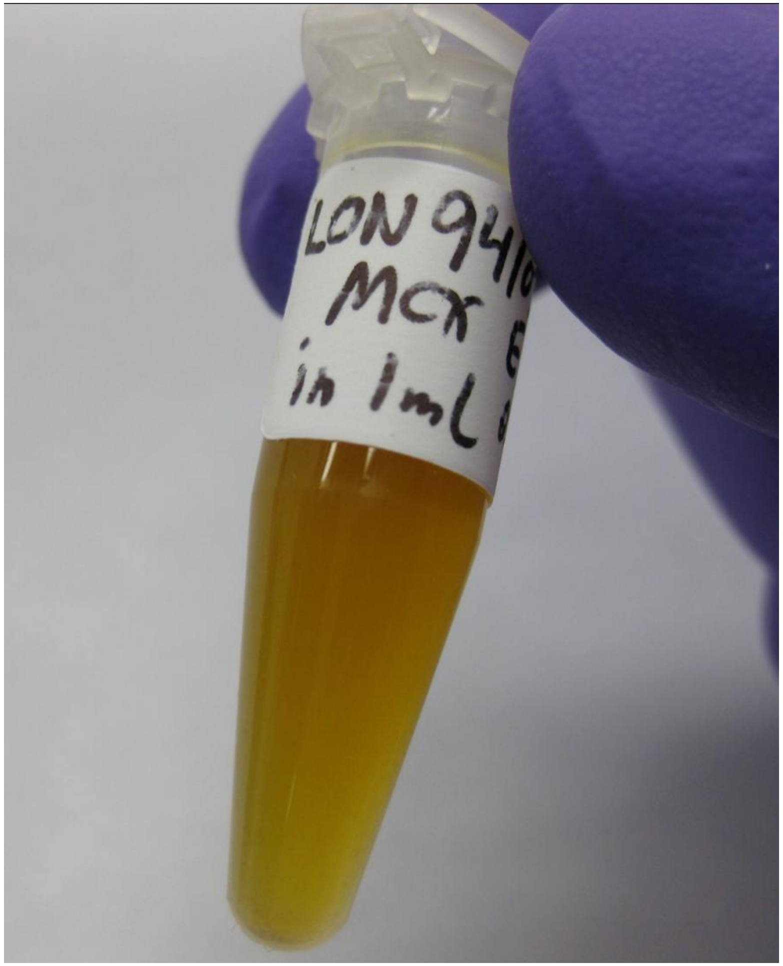
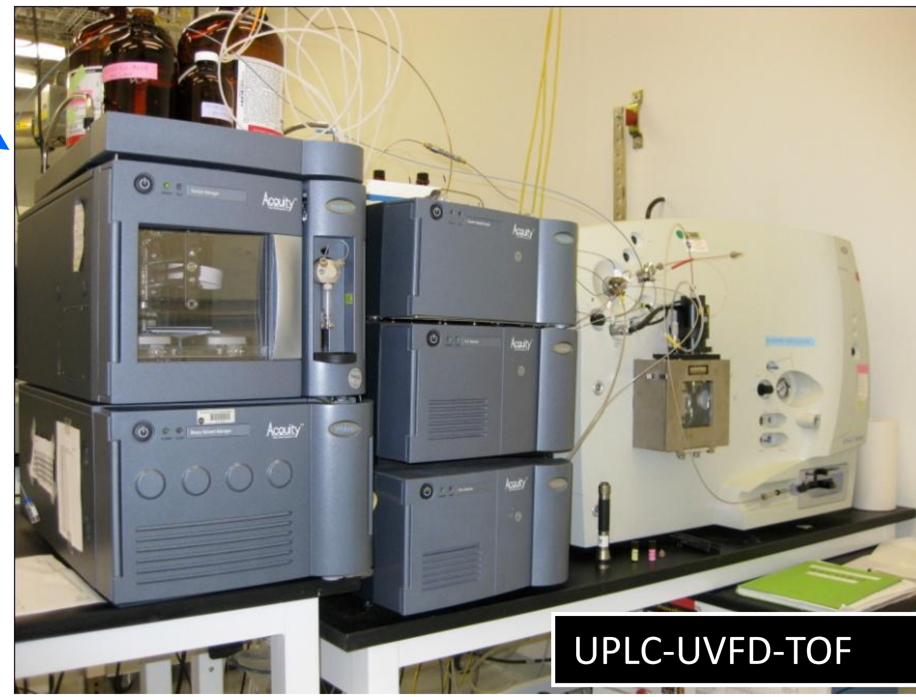
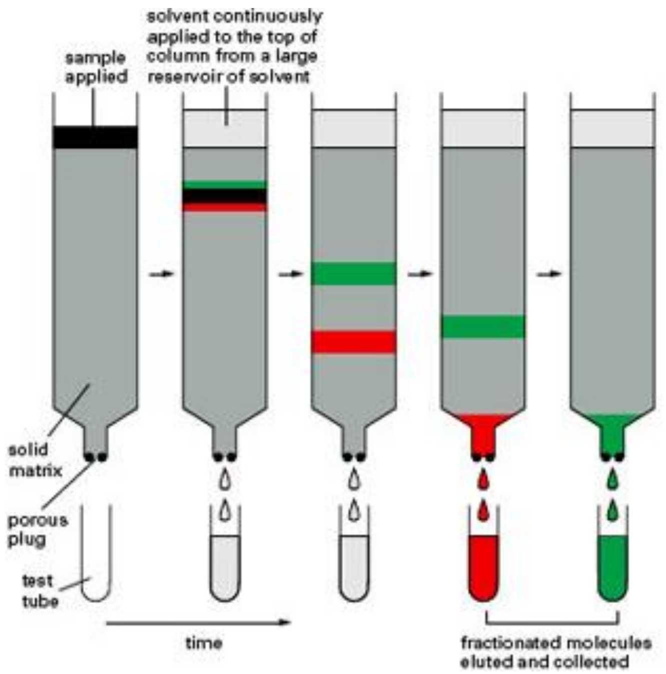


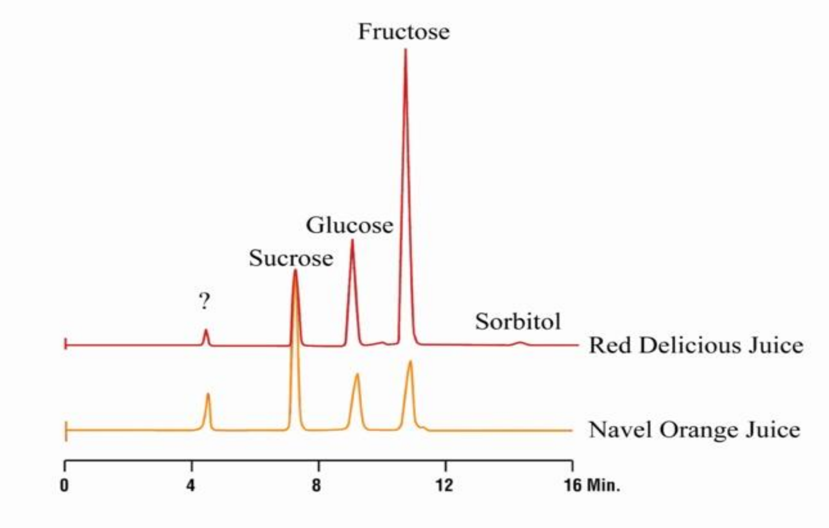
5. Analysis



Common analytical techniques

- Chromatography (gas or liquid)





Chudy & Young (1999) Carbohydrate profiles of orange juice and apple juice by HPLC and evaporative light scattering detection.

Common analytical techniques

- Chromatography (gas or liquid)
- Mass spectrometry
- UV-Vis or Fluorescence detection
- Isotope ratio mass spectrometry

Extraterrestrial or Contamination?

- How can we be sure these compounds are indigenous?
  - Controls: procedures, equipment, soil, etc.
  - Molecular distribution
  - Chirality
    - Most non-biological processes produce equal handedness, whereas life on Earth is based on L-amino acids
  - Isotopic measurements

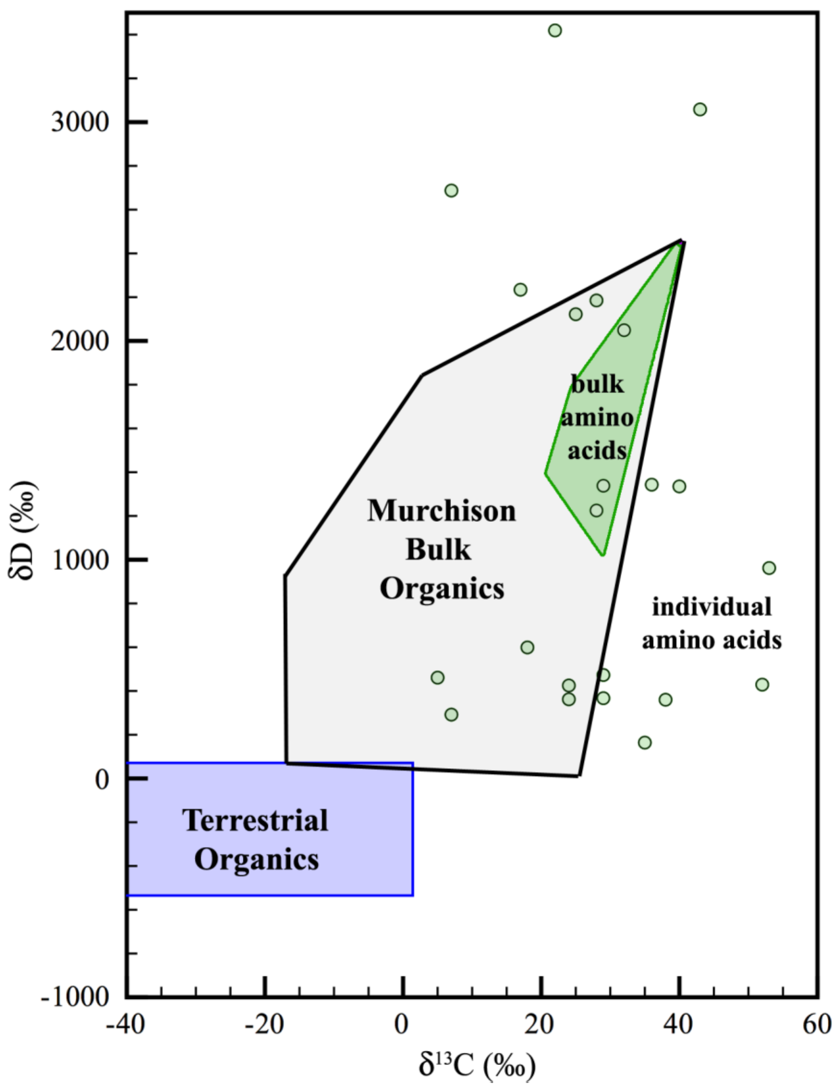
Meteoritic Stable Isotope Analysis

- Isotope ratios of interest in prebiotic organic chemistry: $^{13}C/^{12}C$, $^{15}N/^{14}N$, D/H
- Provide clues to chemical, physical, and biological processes.
- Expressed in delta notation:

$$\delta^{13}C = \frac{[(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{std}]}{(^{13}C/^{12}C)_{std}} \times 1000$$

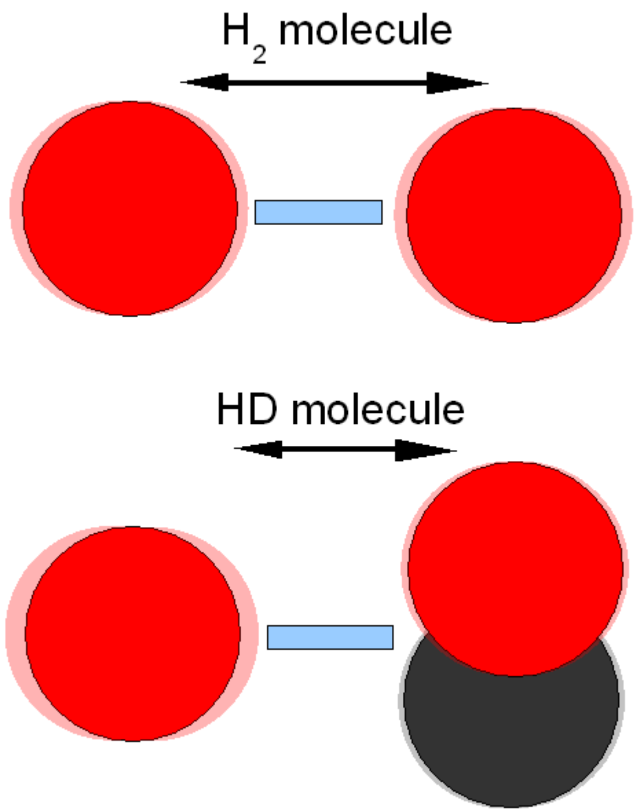
- "Enriched" = heavier (more positive)
- "Depleted" = lighter (more negative)

Meteoritic Stable Isotope Analysis



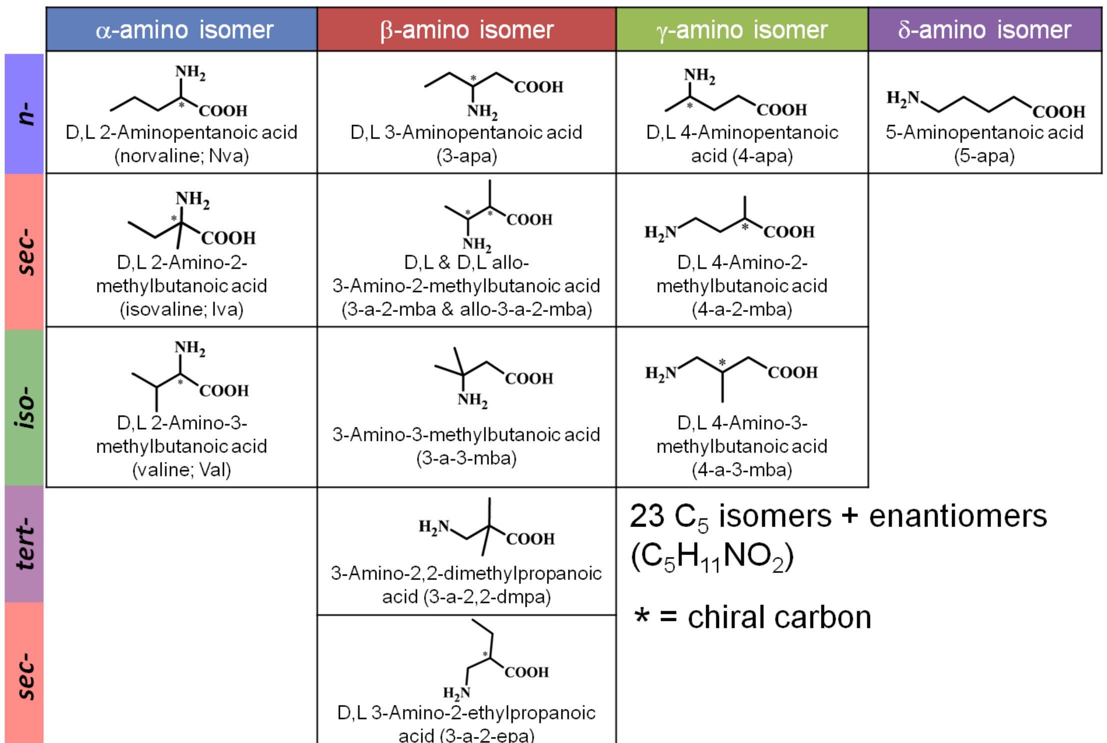
Isotopic enrichment in cold environments

- Differences in masses between isotopes cause differences in zero point energies
- Heavier atoms lead to lower zero-point energies, creating more stable bonds
- At low temperatures, this effect is magnified, preferentially incorporating heavy isotopes into bonds
- The effect depends on relative masses of the isotopes, so it is larger for D/H than for $^{13}C/^{12}C$



General characteristics of soluble meteoritic organics

- Homologous series (HCOOH, CH_3COOH, CH_3CH_2COOH)
- Structural diversity, especially compared to biological specificity (all possible isomers of a given formula)
- Enriched in heavier isotopes



Astrobiologically Important Compounds

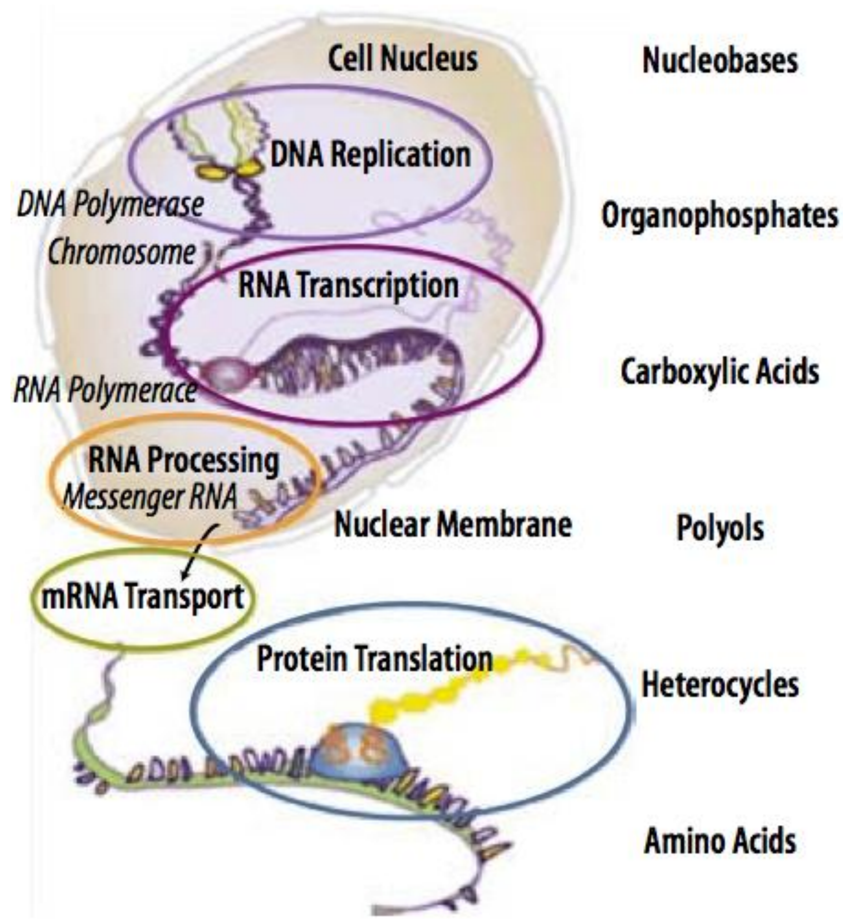
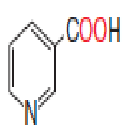
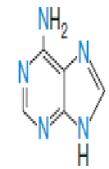
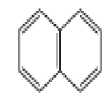
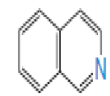
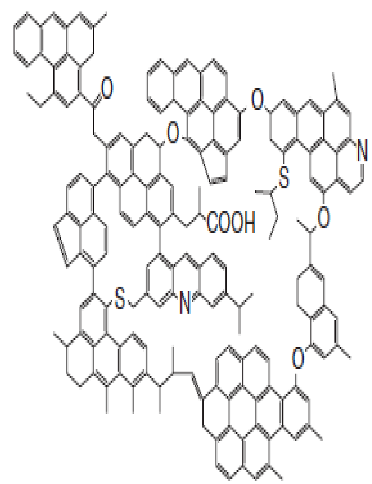
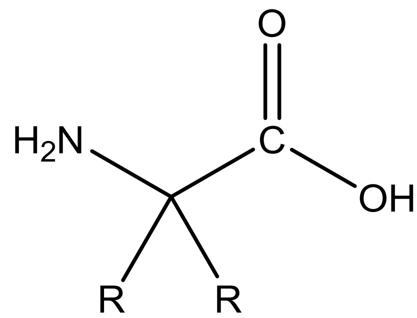


Table 1. Classes of organic compounds in the Murchison meteorite.

Compound Class	Structure	Example Molecule
Carboxylic acids	$H_3C-COOH$	Acetic acid
Amino acids	NH_2 $H_3C-C-COOH$ H	Alanine
Hydroxy acids	OH $H_3C-C-COOH$ H	Lactic acid
Ketoacids	O ‖ H_3C-C-H	Pyruvic acid
Dicarboxylic acids	H_2 $HOOC-C-COOH$	Succinic acid
Sugar alcohols & acids	OH OH $H_2C-C-CHO$ H	Glyceric acid
Aldehydes & Ketones	O ‖ H_3C-C-H	Acetaldehyde
Amines & Amides	$H_3C{\cdot}CH_2NH_2$	Ethyl amine
Pyridine carb. acids		Nicotinic acid
Purines & Pyrimidines		Adenine
Hydrocarbons:		
Alyphatic	$H_3C-CH_2-CH_3$	Propane
Aromatic		Naphthalene
Polar		Isoquinoline
		Insoluble Material (estimated)

From Pizzarello and Shock (2010) *Cold Spring Harbor Perspectives in Biology* ***2(3), a002105.***

Amino acids

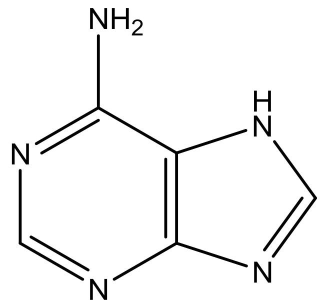


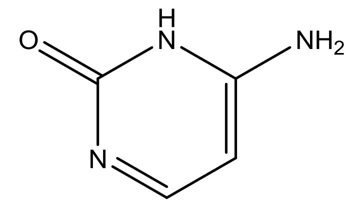
Astrobiological significance: Amino acids are the building blocks of proteins and essential to life as we know it.

Meteorites: Carbonaceous chondrites contain diverse and abundant suites of amino acids, with significant differences correlated to meteorite class and alteration type.

Will be discussed in detail in second lecture

Purines and Pyrimidines





Astrobiological significance: The nucleobases that are the structural bases of information storage in RNA and DNA are substituted purines and pyrimidines.

Meteorites:

• Reports of biologically common purines and pyrimidines in the Murchison meteorite in the 1970s; difficult to rule out contamination

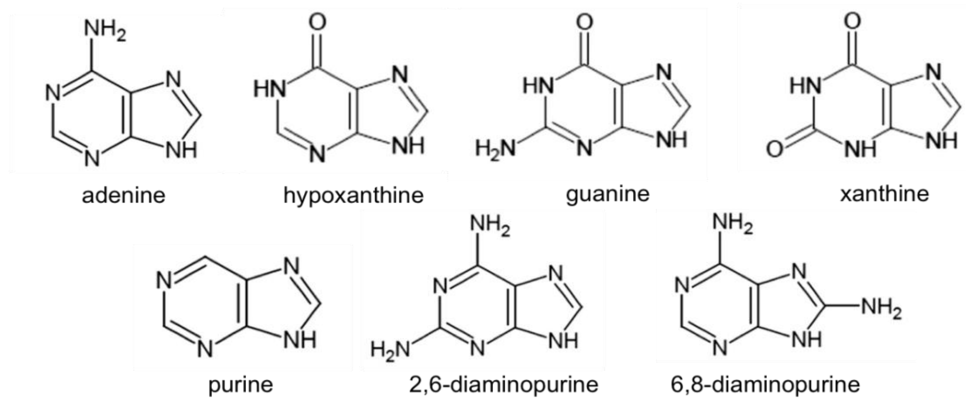
• Carbon isotopic measurements in 2008 suggested extraterrestrial origin

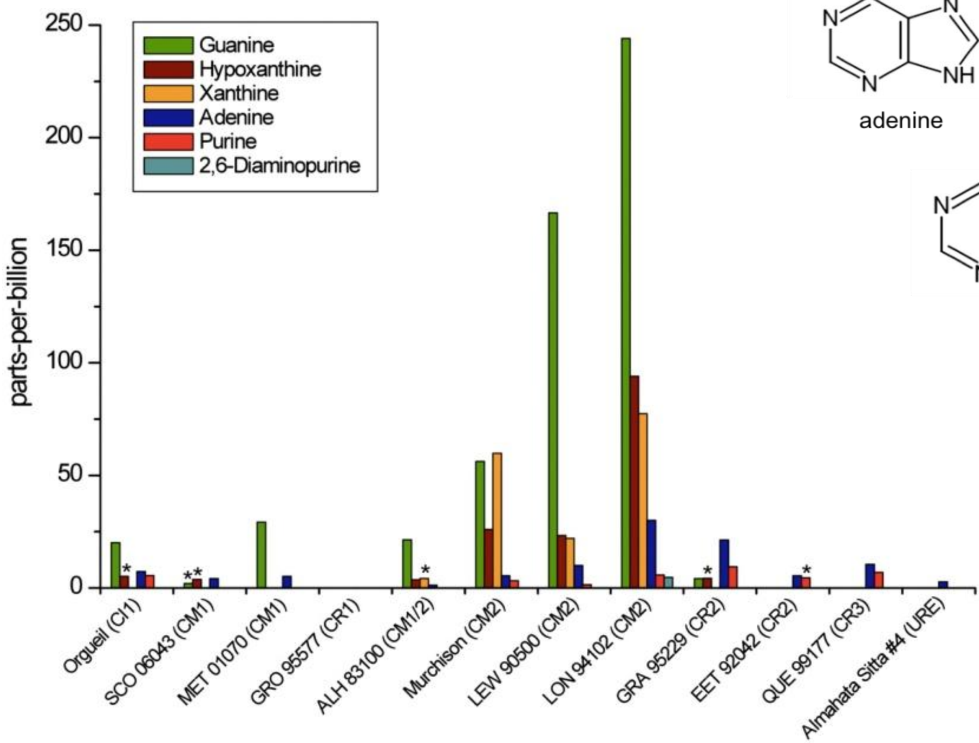
Vandervelden, W. & Schwartz, A. (1977) *GCA* **41**, 961–968.
Stoks, P. G. & Schwartz, A. W. (1979) *Nature* ***282,*** 709-710.
Martins Z., *et al.* (2008) *Earth and Planetary Science Letters* ***270,*** 130-136.

Purines and pyrimidines

Meteorites (cont'd):

•In 2011, nucleobases were detected in 11 carbonaceous chondrites, including terrestrially and biologically rare compounds, supporting a meteoritic origin.





Callahan et al. (2011) *PNAS* **108**, 13995-13998

Purines and pyrimidines

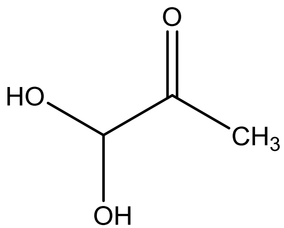
Meteorites (cont'd):

•Nucleobases may have formed from reactions of HCN and ammonia on parent bodies.

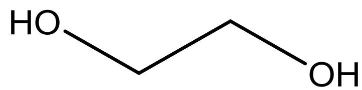
•Nonbiological (alternative) nucleobases could form Watson-Crick base pairs and serve a role in an alternate early genetic code (Benner and co-workers).

Callahan et al. (2011) *PNAS* **108**, 13995-13998

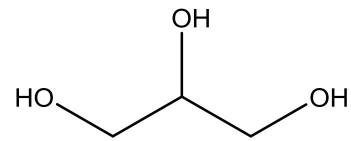
Sugar alcohols and acids



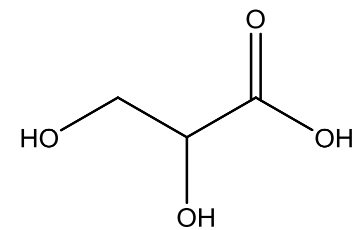
dihydroxyacetone



ethylene glycol



glycerol



glyceric acid

Astrobiological significance: Polyols are key components of DNA and RNA, cell membranes, and energy sources. Many are **chiral.**

Meteorites: Several polyols detected in water extracts of Murchison and Murray; carbon isotopes suggested extraterrestrial origin.

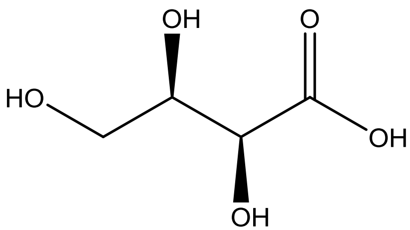
•Decreasing abundance with increasing carbon number; structural (isomeric) diversity

Cooper G. *et al.* (2001) *Nature* **414,** 879-883**.**

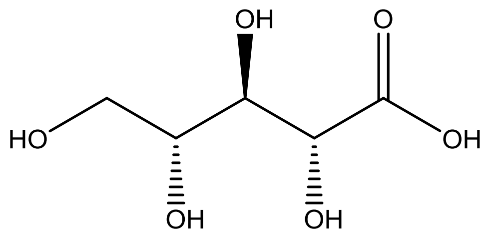
Sugar alcohols and acids

Meteorites (cont'd):

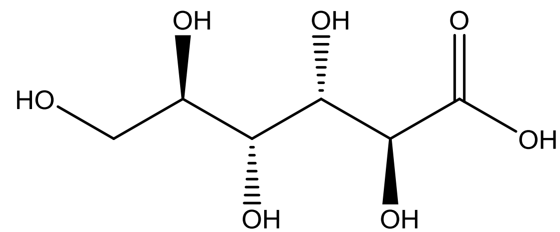
•Possible excess of D-enantiomers; still being investigated.



threonic acid



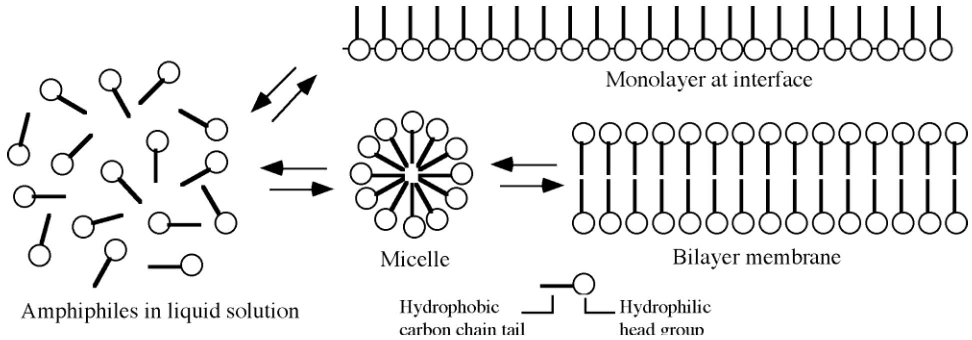
ribonic acid

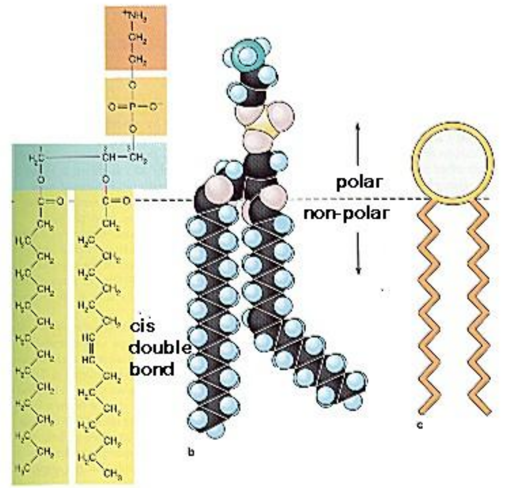


mannonic acid

•Potential formation through formaldehyde chemistry (formose reaction)

Amphiphiles





Astrobiological significance: Cell membranes

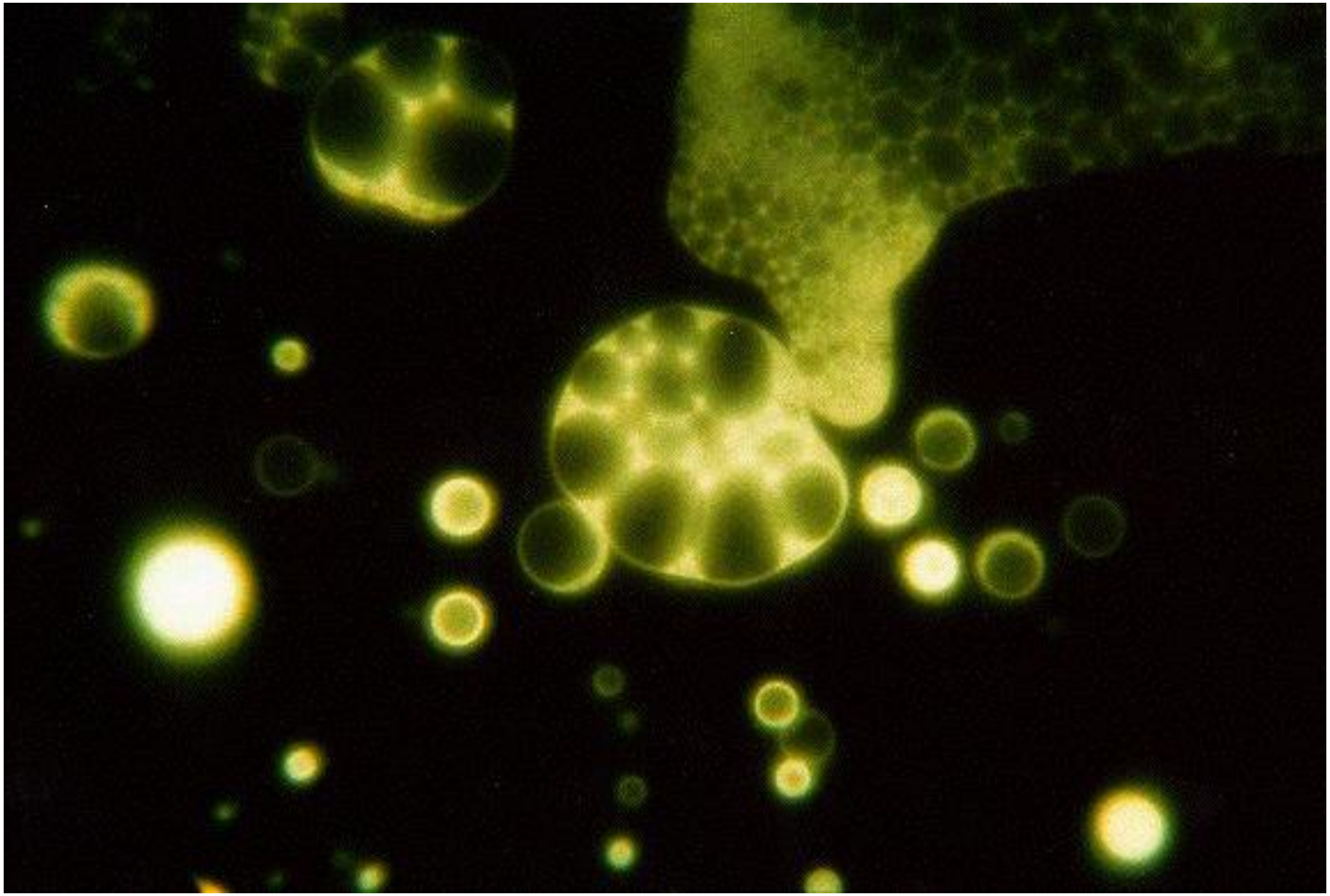
Meteorites:

•An amphiphilic component was extracted from CM2 meteorites with chloroform/methanol. Molecular identity of the amphiphiles is not known (long chain carboxylic acids?)

•The amphiphilic component could encapsulate other compounds and had some fluorescence

Deamer(1985), *Nature*, **317**, 792-794.

Murchison Extracts Form Fluorescent Droplets in Aqueous Media

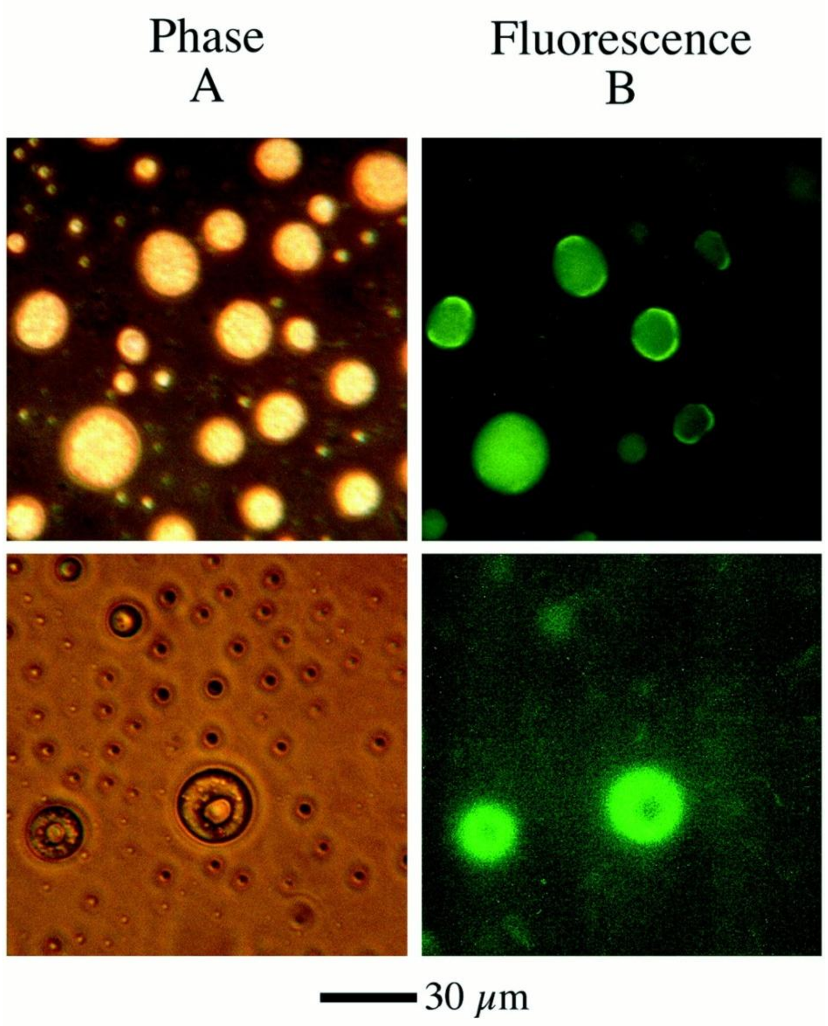


Fluorescence

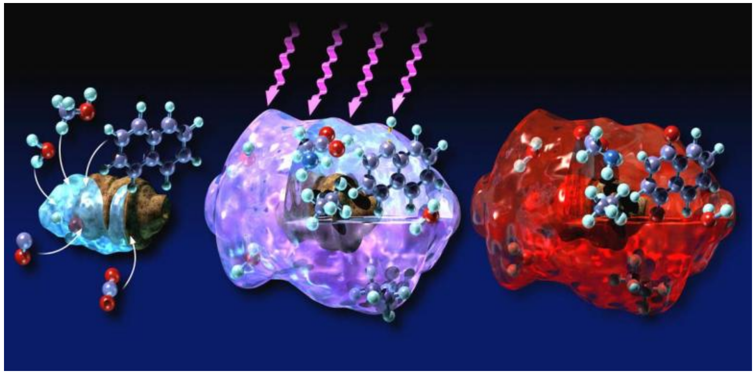
~10 μm

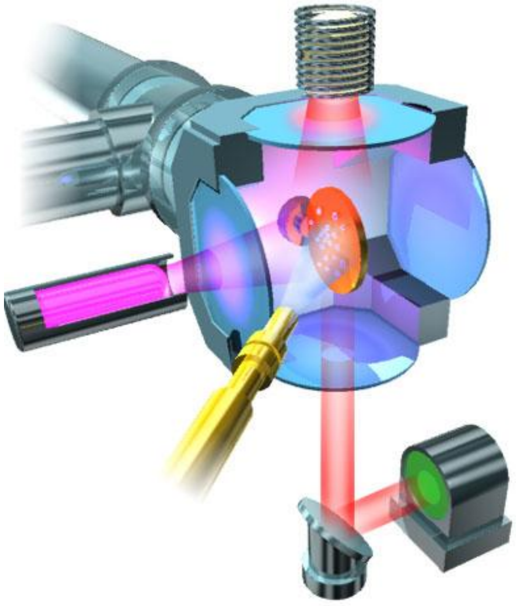
Deamer et al (1985) *Nature*, **317**, 792.

Residue droplets from UV irradiation of a $H_2O:CH_3OH:NH_3:CO$ = 100:50:1:1 interstellar ice analog viewed at ×400 via phase microscopy.

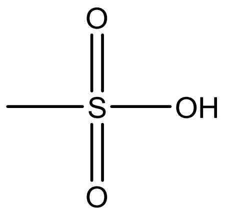


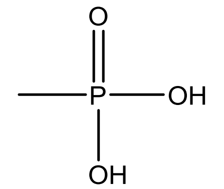
Dworkin J P et al. PNAS 2001;98:815-819





Phosphonic/sulfur acids





Astrobiological significance: Sulfur and phosphorus are important elements in biology.

Meteorites:

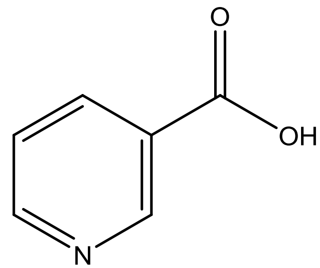
•Identified in Murchison as a homologous series that decreases in abundance with increasing carbon number.

• Structural diversity observed

• In Tagish Lake, only one sulfonic acid detected and no phosphonics.

Cooper et al. (1992) GCA, **56**, 4109-4115

Pyridine carboxylic acids



nicotinic acid

Astrobiological significance: Nicotinic acid is part of the co-factor of several enzymes that catalyze oxidation-reduction reactions in cell metabolism (NAD, NADP)

Meteorites:

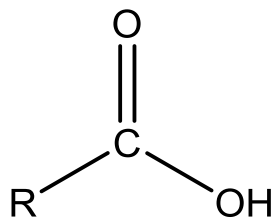
•Detected in Murchison and other meteorites.

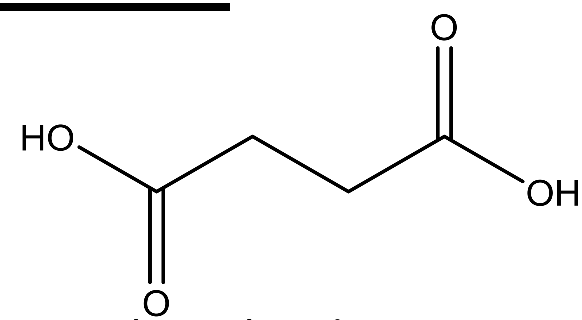
• Suite of pyrimidine monocarboxylic acids, isomers, and methyl/dimethyl homologs.

•Isotopic data indicates extraterrestrial origin, less enriched than amino acids.

Pizzarello S., *et al*. (2001) *Science* ***293***, 2236-2239***.***

Carboxylic acids





Astrobiological significance: Fatty acids play a role in lipids

Meteorites:

•Most abundant soluble organic compounds in Murchison; identified in others (Orgueil, CR2 chondrites, Tagish Lake, ...) .

•Isomerically diverse – branched and linear chains, declining abundance with increasing C number.

•Isotopic measurements show $\delta^{13}C$ higher for branched chains; decreases with increasing length, indicating formation by addition to lower homologs

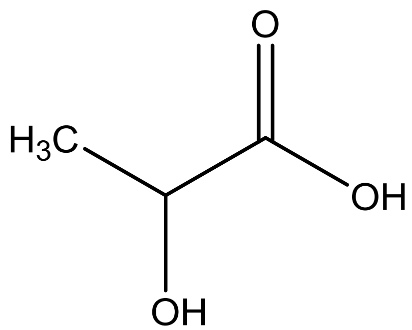
•Branched chains have δD significantly and consistently higher than linear species, indicating a cold, H-fractionating processes

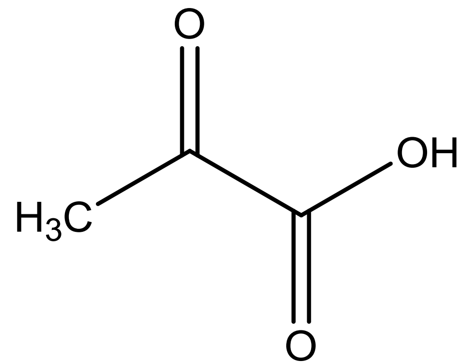
J. G. Lawless, et al. *Nature, 1974,* ***251, 40.***

J. R. Cronin, et al., *Geochim. Cosmochim. Acta, 1993,* ***57, 4745.***

Pizzarello S. and Huang Y. S. (2002) *Meteoritics and Planetary Science* ***37(5), 687-696.***

Hydroxy acids and keto acids



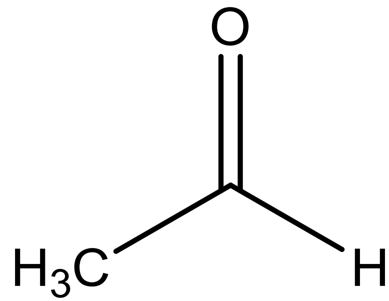


Astrobiological significance: May provide information on formation of amino acids via Strecker synthesis; chiral molecules may help understand origin of homochirality.

Meteorites: Detected in Murchison and CR chondrites, distributions of 2-H, 2-hydroxy acids similar to amino acids (but lower abundance).   Enantiomeric excesses of L-lactic acid were detected.

Pizzarello et al. (2010) *Geochimica et Cosmochimica Acta* ***74(21), 6206-6217.***
Cooper G. et al. (2005) *Lunar & Planetary Science Conference , 2381.*

Aldehydes and ketones

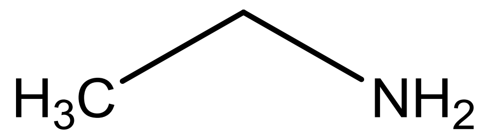


Astrobiological significance: Precursors to other molecules such as amino acids. Chiral molecules could lead to enantiomeric excesses.

Meteorites: Detected in various carbonaceous chondrites; acetone is the most abundant species**.** May be bound or chemisorbed, explaining the difficulty in their extraction.

Pizzarello S. and Holmes W. (2009) *Geochimica et Cosmochimica Acta 73(7), 2150-2162.*

Amines and amides

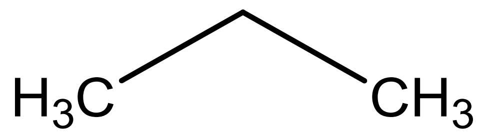


Astrobiological significance: Amines can form from decarboxylation of amino acids; amides and lactams form amino acids

Meteorites: Amines typically found with amino acids, often in comparable abundances.   Structurally diverse, decrease in abundance with increasing carbon number in Murchison, but not in some other meteorites.

Cooper G. W. and Cronin J. R. (1995) *Geochimica et Cosmochimica Acta* ***59,*** 1003-1015**.**
Pizzarello S. and Holmes W. (2009) *Geochimica et Cosmochimica Acta* ***73****,* 2150-2162*.*

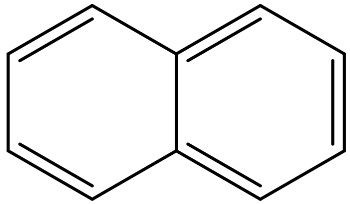
Aliphatic hydrocarbons

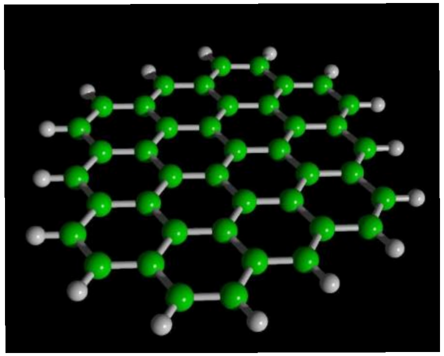


Meteorites: Easily contaminated by terrestrial hydrocarbons, particularly *n*-alkanes; useful in understanding how quickly contamination can occur. Depth profiles and isotopic measurements help distinguish terrestrial contamination.

Volatile hydrocarbons appear indigenous; decreasing $\delta^{13}C$ with increasing carbon number, indicating kinetic formation.

Aromatic hydrocarbons

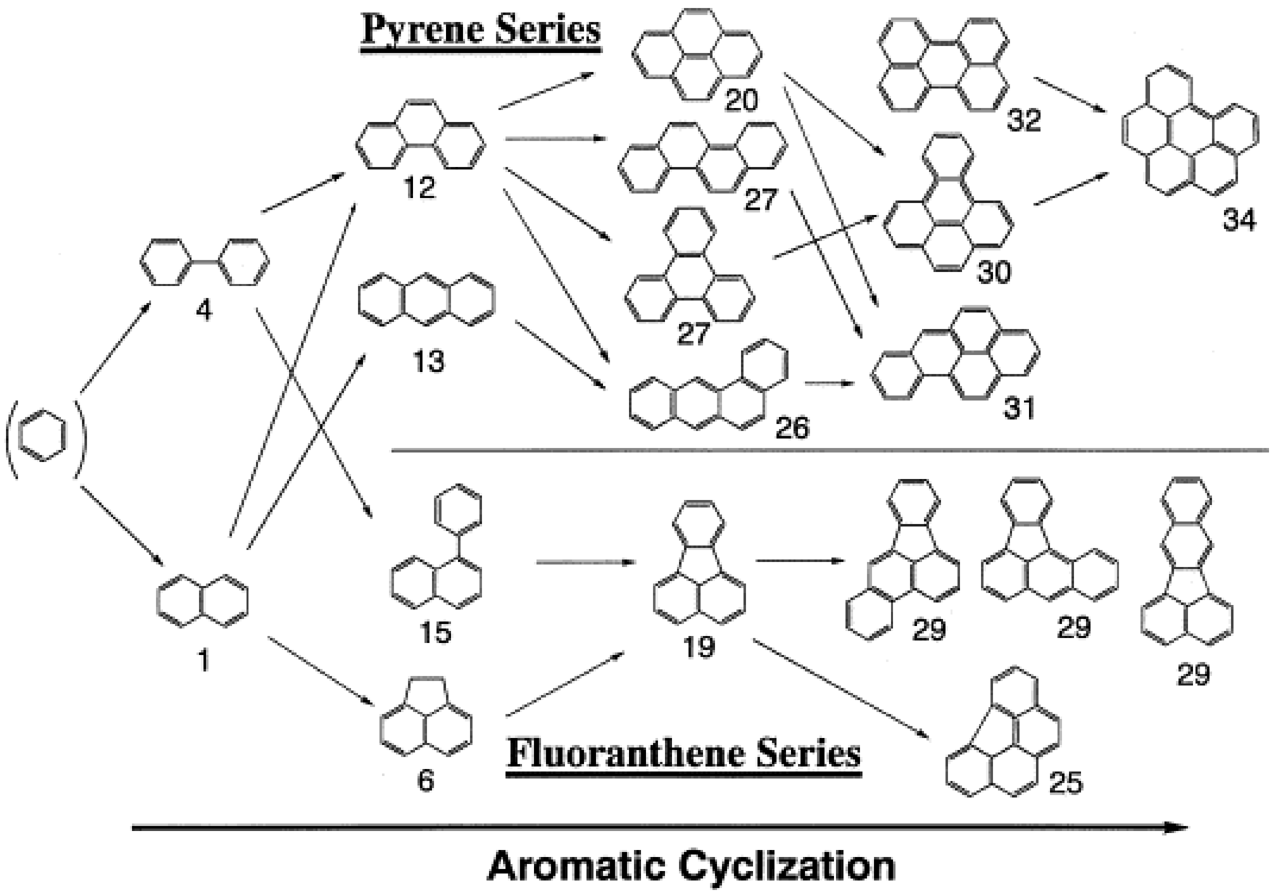




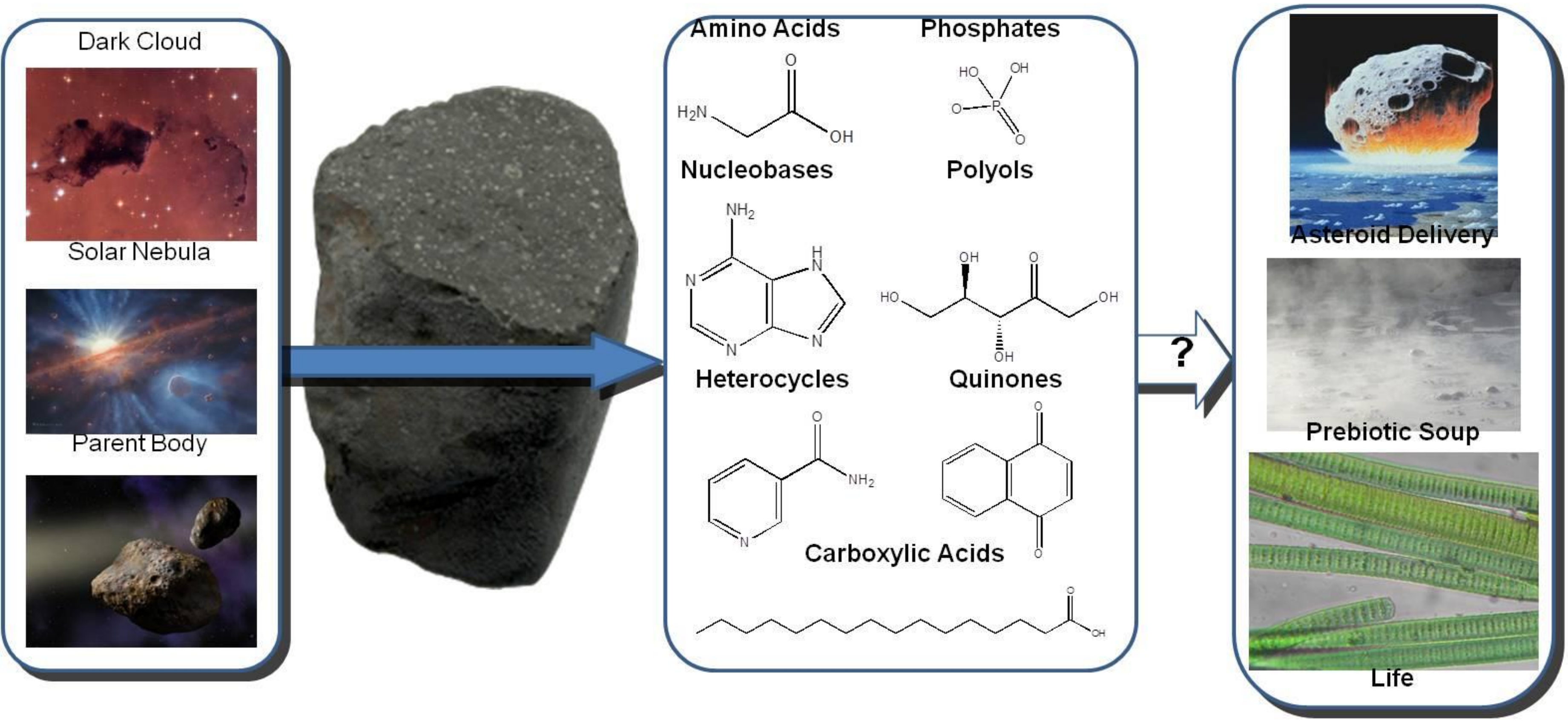
Astrobiological significance: Oxidized aromatics are important in terrestrial biochemistry, participating in electron transport and pigmentation.

Meteorites:

- Rich suites of PAHs detected in a variety of carbonaceous chondrites.
- Heterogeneous distributions. Correlation between concentration and volatility. Low petrographic types (more aqueous alteration) have more volatile aromatics
- . Differences in isomer (phenanthrene vs fluorene) $\delta^{13}C$ = different pathways to cyclization



Naraoka H., Shimoyama A., and Harada K. (2000) *Earth Planet. Sci. Lett.* ***184, 1-7.***


Dark Cloud
Solar Nebula
Parent Body
Amino Acids
Phosphates
Nucleobases
Polyols
Heterocycles
Quinones
Carboxylic Acids
?
Asteroid Delivery
Prebiotic Soup
Life