Organic Compounds in Meteorites, Comets, and Cosmic Dusts: Building Blocks of Planets and Life

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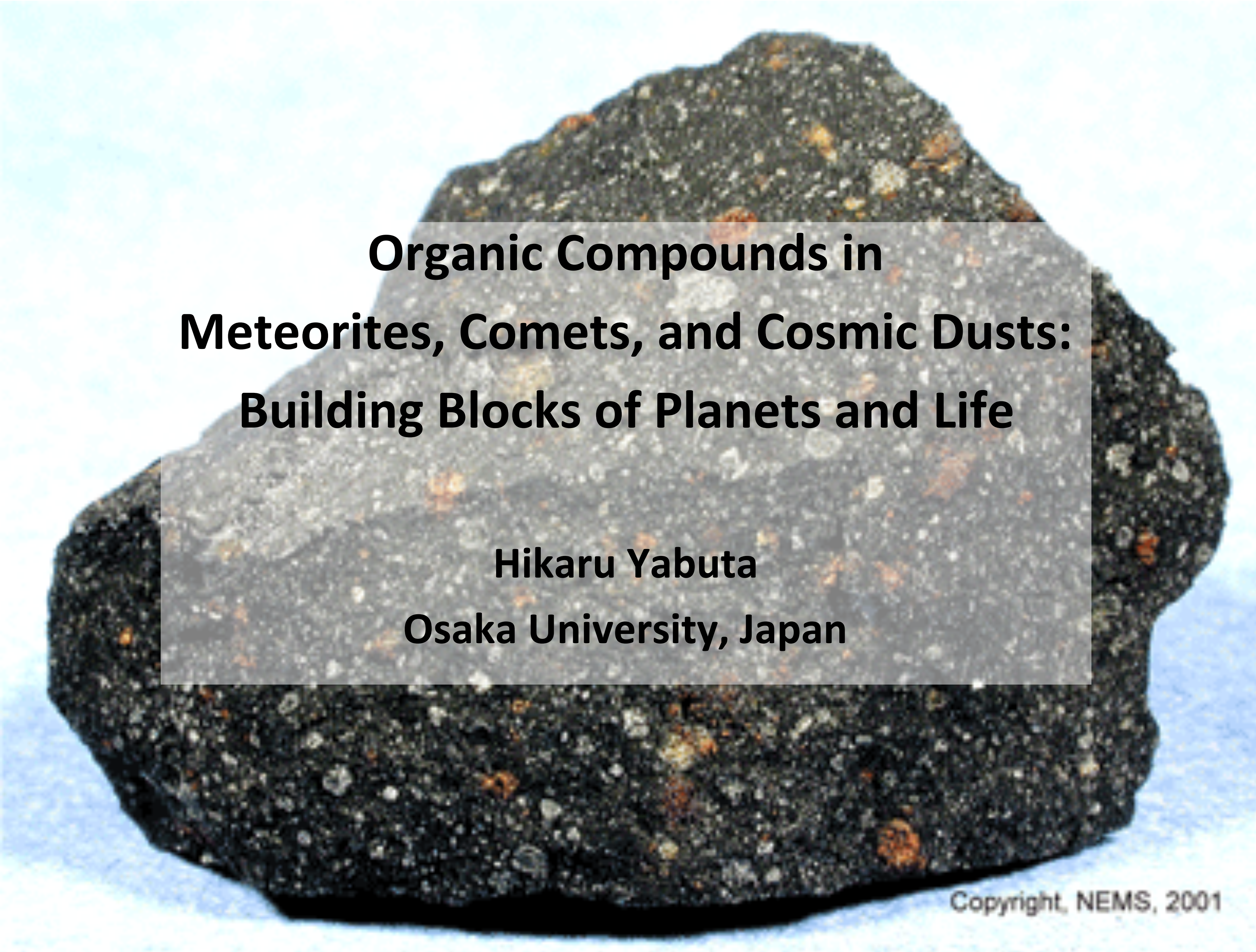
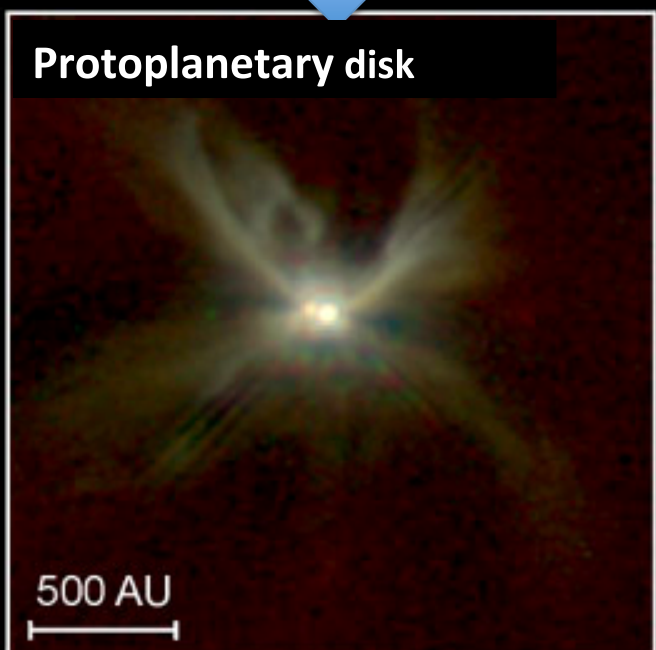
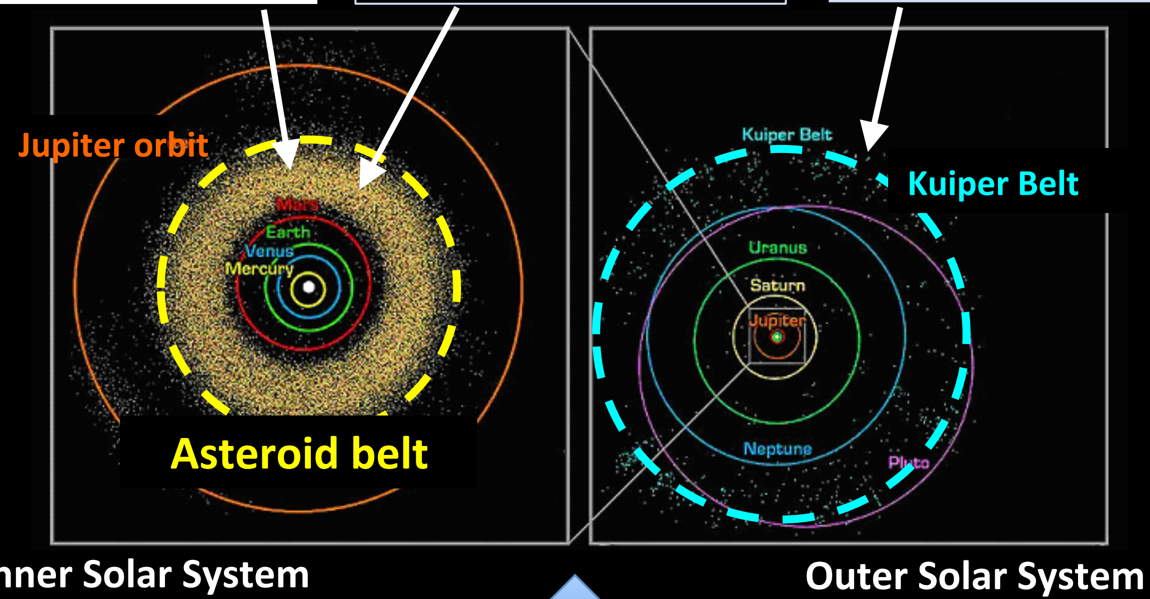


Primitive small bodies (comets, asteroids, meteorites) are 4.5 billion-year-old "fossils" of the early Solar System





Significant roles of organic compounds in the early Solar System

- High abundances of C, H, O, N in the Solar System

- Major components of dusts (silicates, ice, organics) in interstellar clouds

- Highly reactive to heat, light, shock, water, and minerals (Chemical indicator recording the processes in the Solar System)

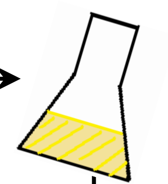
- Possible contribution to accretion of dusts, due to their stickiness

- Possible contribution to redox imbalance in solar nebula (that determined the chemical compositions of chondrules)

Organic compounds in meteorite (carbonaceous chondrite)

10 – 1000 mg

Solvent / Water extraction



Carbonaceous CM chondrite contains ca. **2 wt%** total organic carbon

ca. **1 wt%**

Soluble organic compounds

Acid-Insoluble macromolecular organic solid (IOM)

Carboxylic acids +++ (mono-, di-, hydroxy-)

Amino acids ++

Alcohols ++
Aldehydes ++
Ketones ++
Amides ++
Amines ++
PAHs ++
Aliphatic hydrocarbons ++

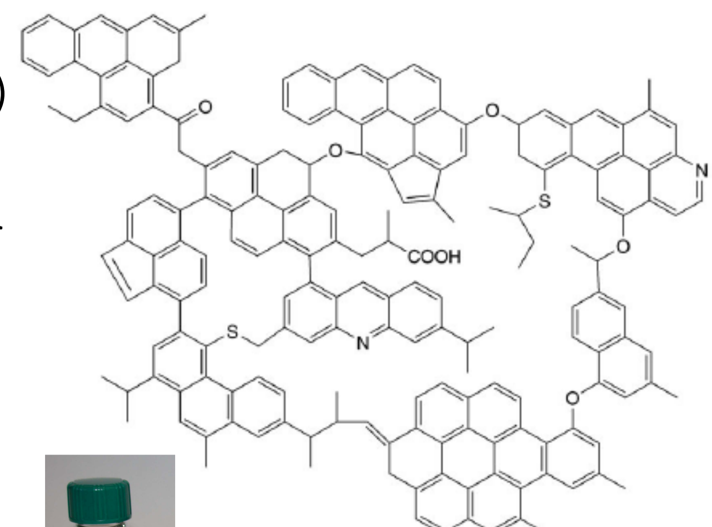
Purines ++
Pyrimidines ++
Phosphoric acids ++
Sulfonic acids ++

Unidentified soluble compounds
(Schmitt-Kopplin et al. 2010)

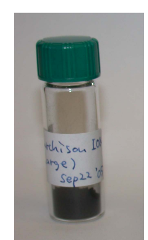
(+++ > 100 ppm, ++ > 10 ppm, + > 1 ppm)

$C_{100}H_{75}N_4O_{17}S_3$
(Alexander et al. 2007)

$C_{100}H_{80}N_4O_{20}S_2$
(Halley CHON, Kissel & Krueger, 1987)



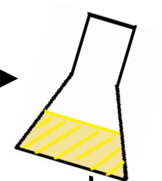
(Pizzarello et al. 2008)



Meteoritic "Anatomy" – Improvement of Analytical Techniques

10 – 1000 mg

Solvent / Water extraction



Carbonaceous CM chondrite contains ca. **2 wt%** total organic carbon

ca. **1 wt%**

Soluble organic compounds

- **Molecules, Homochilarity**
  - Chromatography-Mass spectrometry (GC-MS, LC-FD/ToF-MS, 2D-HPLC)
- **Isotope**
  - GC/Combustion/ Isotope Ratio MS

- Fourier transform ion cyclotron resonance (FTICR) MS

Acid-Insoluble macromolecular organic solid (IOM)

- **Elemental**
  - Combustion
- **Functional groups**
  - Degradation (Pyrolysis, Chemolysis)
  - Non-degradation (NMR, Infrared, Raman, X-ray absorption spectroscopy)
- **Isotope**
  - Combustion-IRMS
  - Ion-probe mass spectrometry (SIMS)
- **Structure**
  - Electron microscopy (TEM)

Evidences of extraterrestrial organics: Amino acids

(Cronin and Chang, 1993)

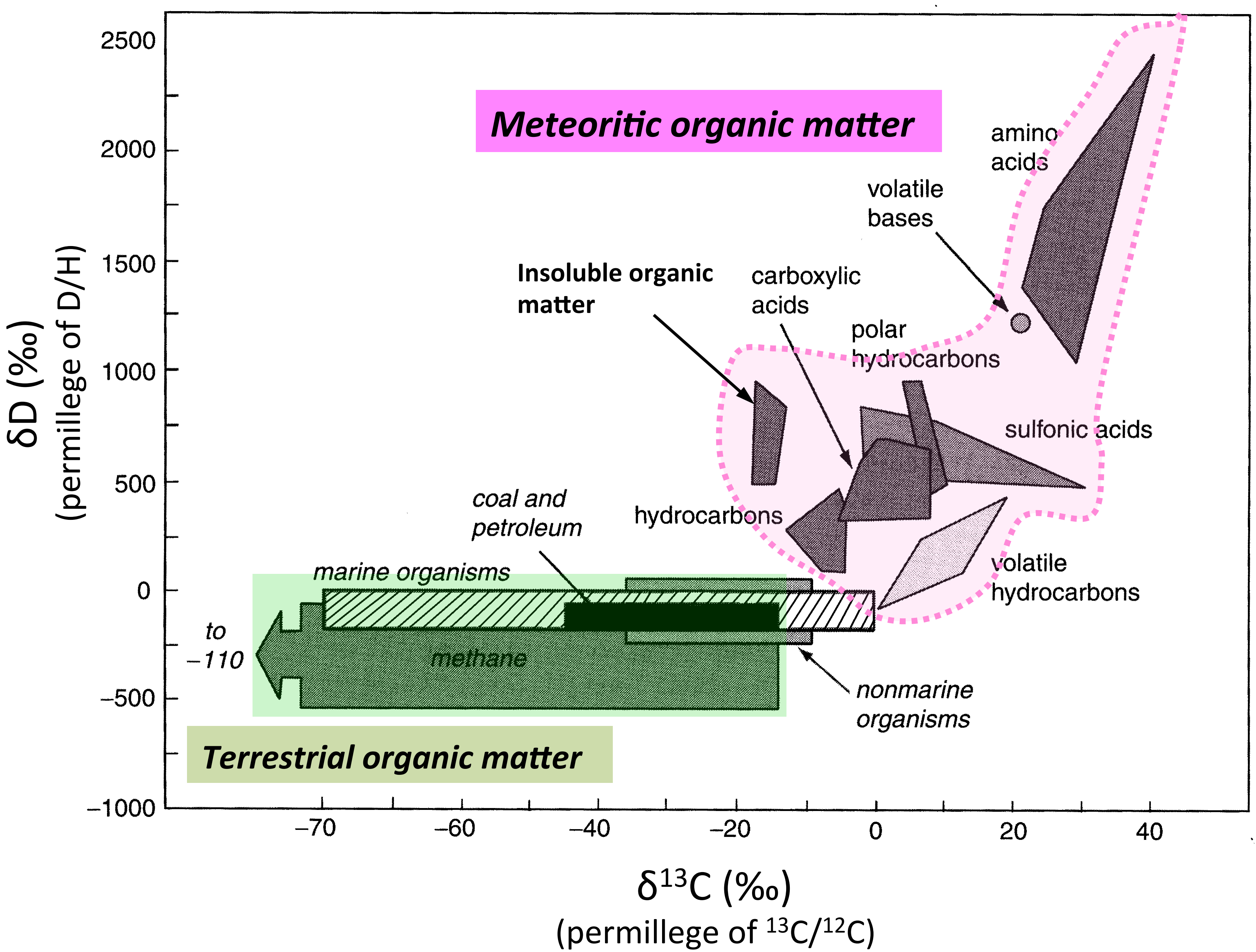
1. More than **70 kinds** of amino acids **including those which have not been reported to occur in terrestrial material** (e.g., isovaline, **α-**aminoisobutyric acid) have been identified

2. **Decrease in abundance with increasing carbon number**
-> The pattern of prebiotic synthesis from smaller molecules to larger molecules

3. **Enantiomer ratios for most of amino acids are racemic (D:L = 1 : 1)**
For several α-methylamino acids, L-enantiomeric excesses (9 – 18.5%) are reported (Cronin and Pizzarello, 1997; Glavin and Dworkin, 2009)

Possible sources are Circular Polarized Light, water-mineral interaction or crystal growth of amino acids on the asteroid parent bodies

4. **Very high isotopic compositions** of carbon ($^{13}C/^{12}C$), hydrogen (D/H), and nitrogen ($^{15}N/^{14}N$)



Sephton and Botta (2005) modified

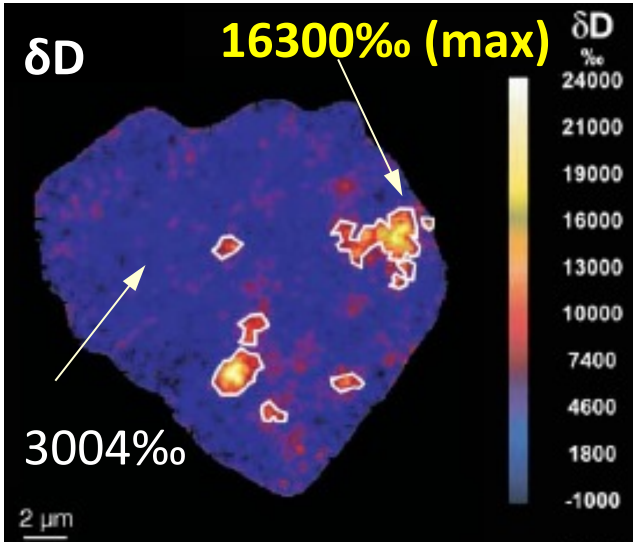
The conditions for Deuterium and Nitrogen-15 enrichments occur in cold environments

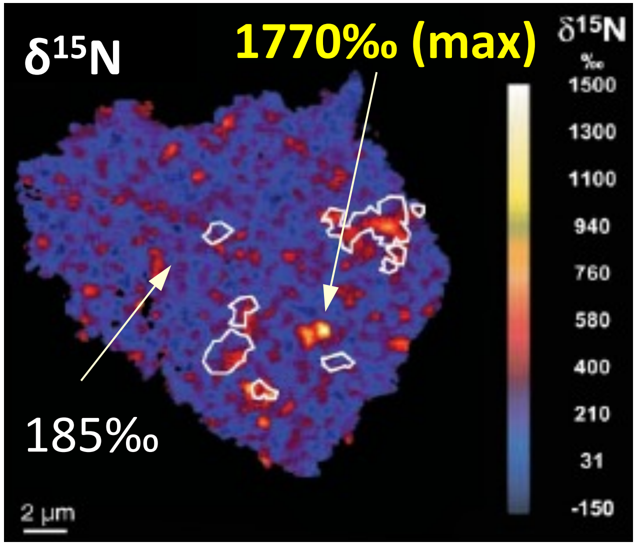
For example, $H_2 + H_2^+ \longrightarrow H_3^+ + H$

$$H_3^+ + HD \longrightarrow \underline{H_2D^+} + H_2$$

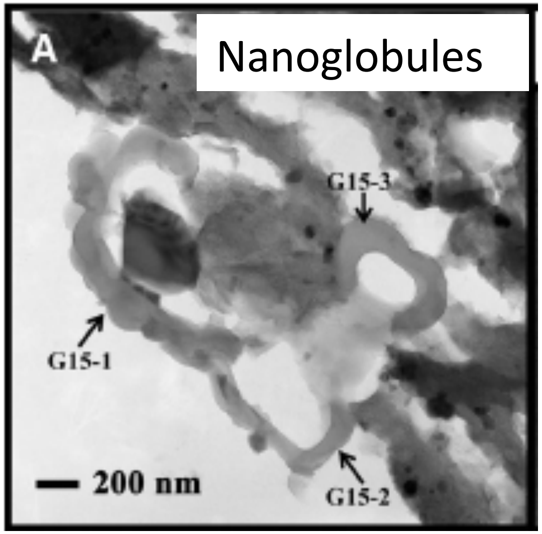
Isotopic anomalies in insoluble organic material preserve organics formed in molecular cloud or outer regions of protosolar disk

Macromolecular solids from CR chondrite（EET92042）





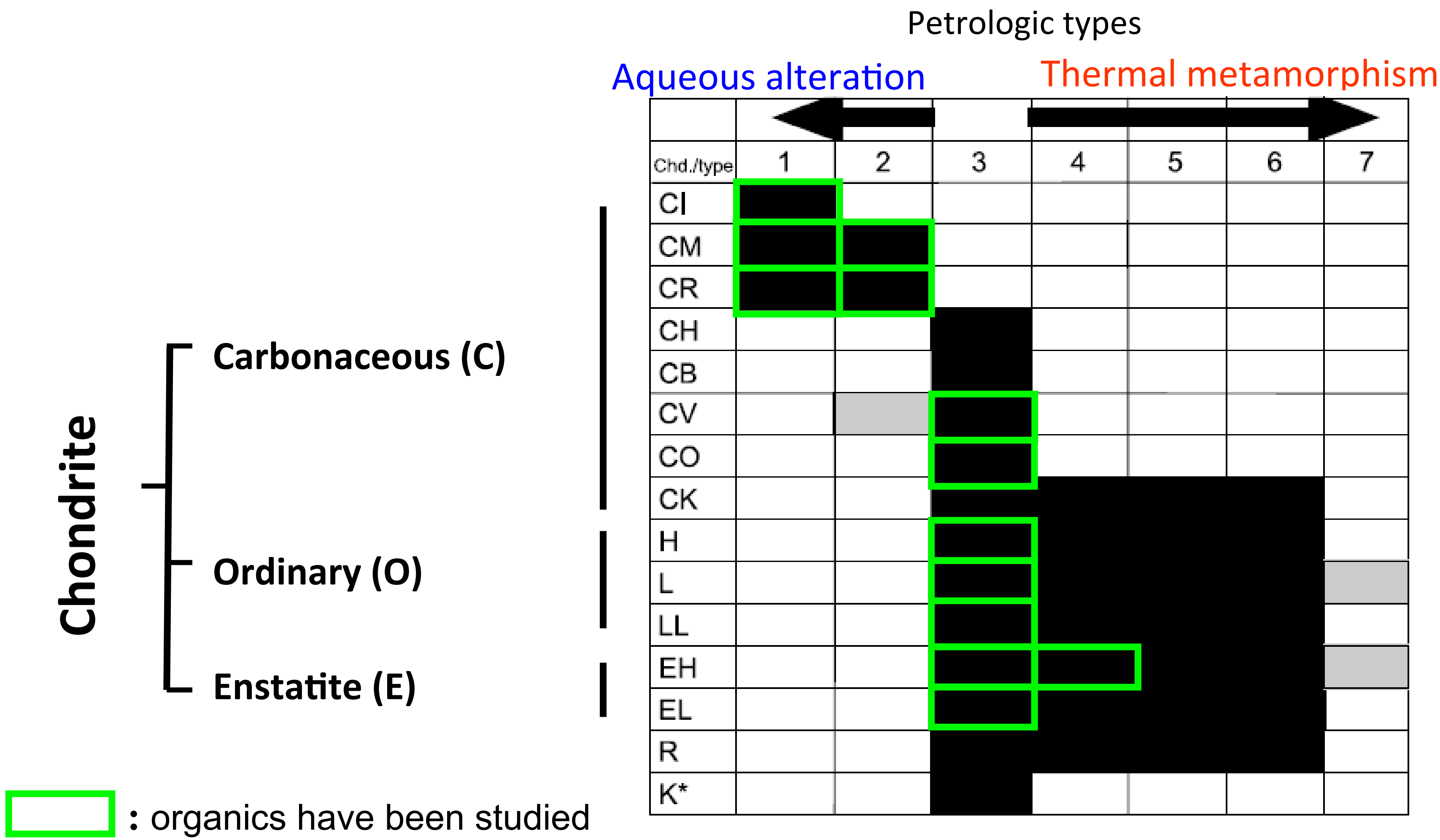
Busemann et al. (2006)



Nakamura-Messenger et al. (2006)

Comparative meteorite organic chemistry

Chemical history of the early solar system is recorded in <u>the variations of molecular and isotopic compositions of organic matter</u> in wide ranges of meteorite groups and petrologic types



Weisberg et al (2006)

Comparative meteorite organic chemistry

- Aqueous alteration on parent bodies-

Soluble OM (amino acids)

• Amino acids are the most abundant in less altered CR2 (EET92042), while they are depleted in more altered CR1
(Martins et al. 2007)

• Large L-enantiomeric excess (Lee) of isovaline was observed for altered CI1 and CM2, but for pristine CR2

more altered

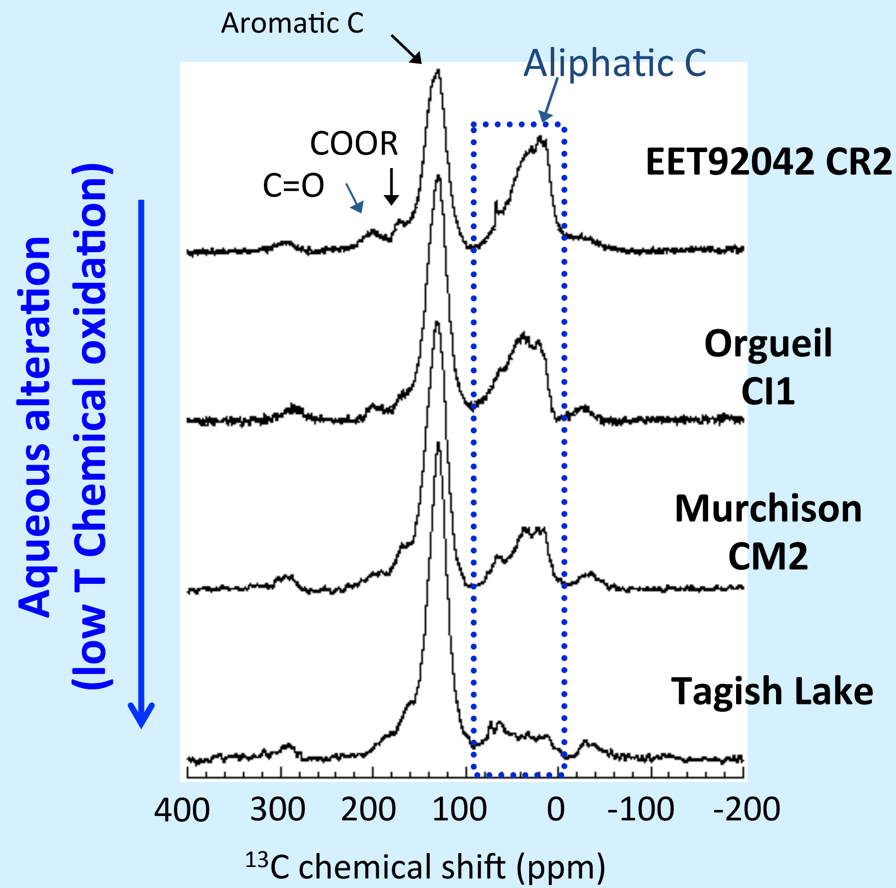
less altered

		Isovaline
Sample	Lee, %	δx (n)
Orgueil (CI1)	15.2	±4.0 (8)
Murchison (CM2)	18.5	±2.6 (20)
	15.2*	±0.2 (8)*
LEW 90500 (CM2)	3.3	±1.8 (23)
LON 94102 (C2)	2.4	±4.1 (8)
QUE 99177 (CR2)	0.3	±2.1 (8)
EET 92042 (CR2)	−1.0	±4.3 (8)
Racemic standard†	−2.3	±1.3 (14)

Glavin and Dworkin (2009)

Insoluble OM

Solid state ^{13}C NMR

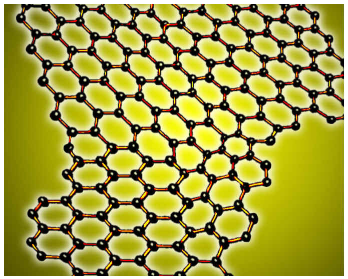


Cody and Alexander (2005)

Comparative meteorite organic chemistry

- Thermal metamorphism on parent bodies -

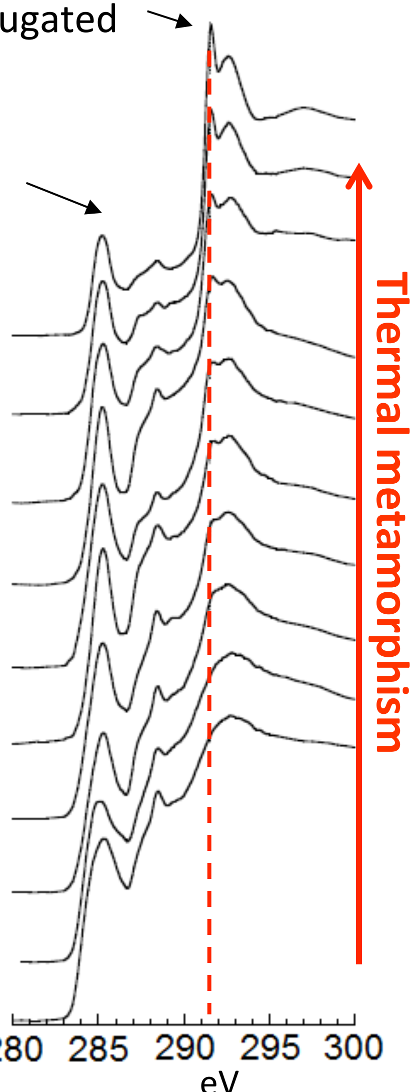
Carbon-XANES of IOM



Highly conjugated sp^2 C 1s-*σ

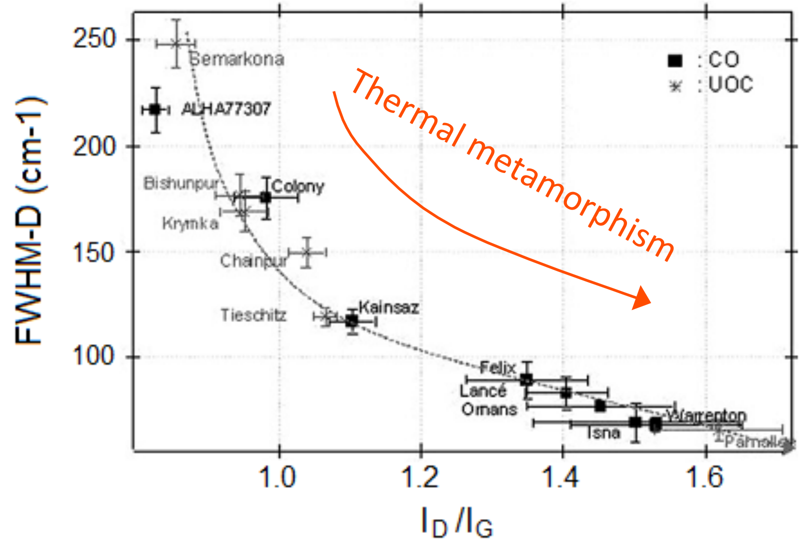
Aromatic C 1s-π*

Graphite	
Indarch (EH**4**)	948°C
Isna (CO**3.7**)	700°C
Allende (CV**3.6**)	554°C
Bishunpur (LL**3.15**)	551°C
ALHA77003 (CO**3.5**)	425°C
Mokoia (CV**3.2**)	423°C
Kaba (CV**3.1**)	371°C
Semarkona (LL**3.0**)	203°C
ALHA77307 (CO**3.0**)	203°C



Cody, Yabuta, Alexander et al. (2008)

Raman of IOM



Bonal et al. (2007)

X ray absorption feature of highly conjugated sp^2 carbon (e.g., graphene) can be used as a **thermometer** of parent bodies (Cody et al. 2008)

Small bodies sample return missions

STARDUST (2006)
Comet 81P/Wild 2

- Investigate more primitive materials than meteorites

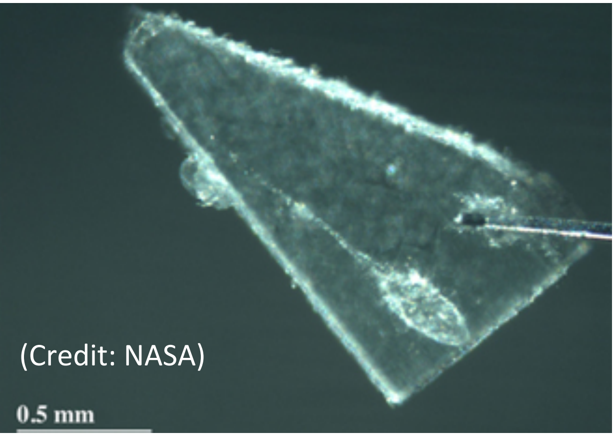
HAYABUSA (2010)
S-type asteroid Itokawa

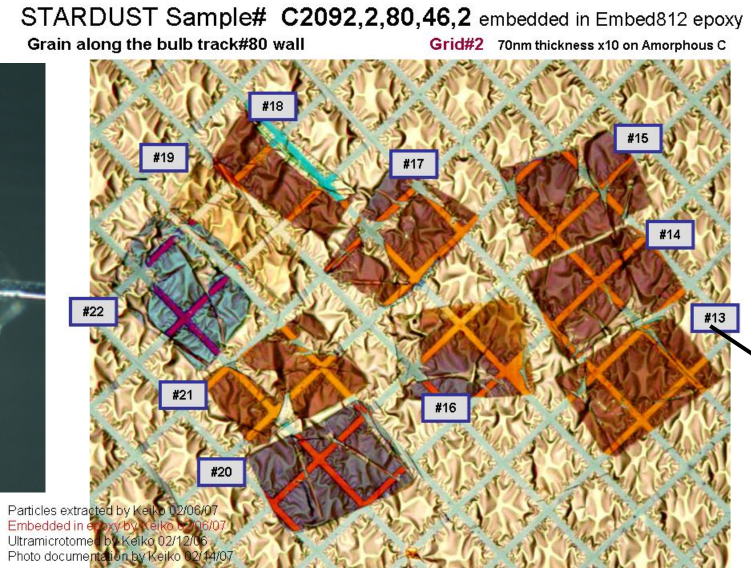
- Unveil the information which meteorites might have lost （locality, volatiles, etc）
- Understand the intact compositions without terrestrial contamitaion/alteration

HAYABUSA2 (2014)
C-type asteroid 1999JU3

- Search for unknown extraterrestrial materials

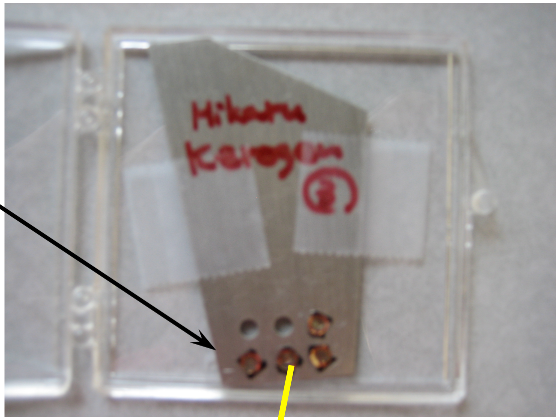
Organic analyses of comet Wild 2 dust particles collected by Stardust

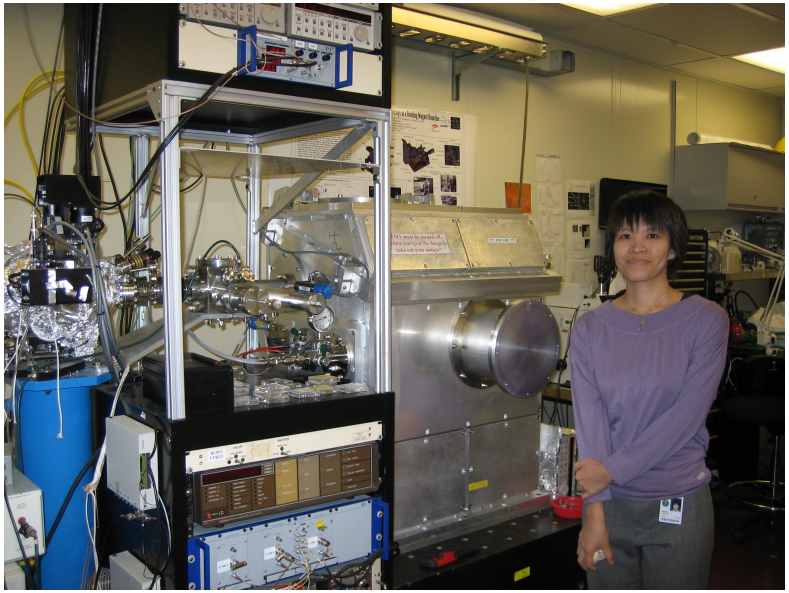




(Credit: Nakamura-Messenger, NASA-JSC)

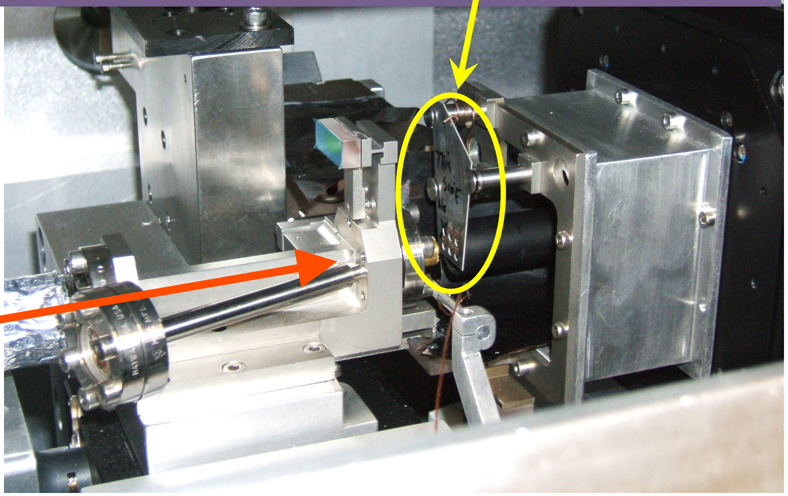
Thin sectioned samples on SiO-supported TEM grid





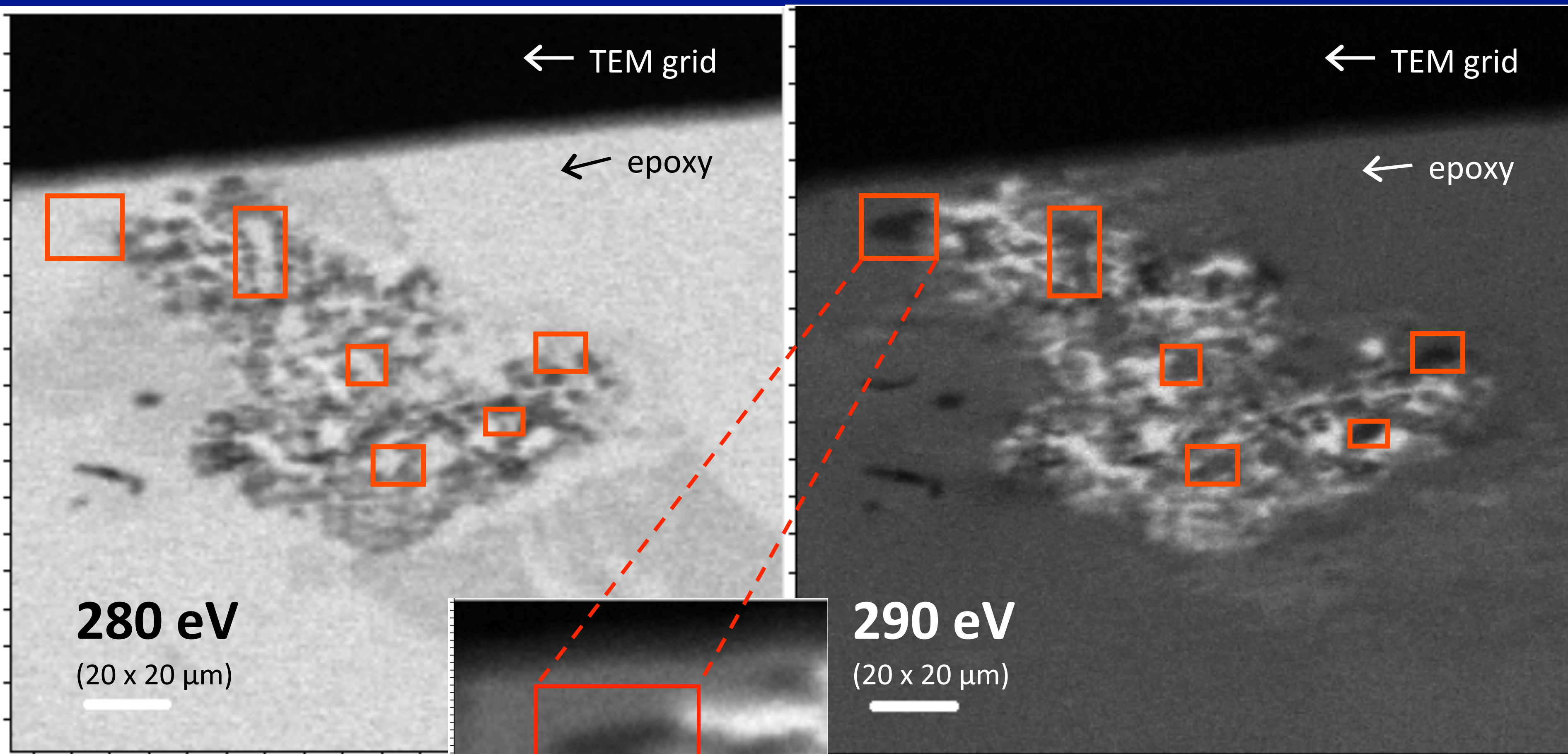
Synchrotron based
Scanning Transmission X ray microscopy

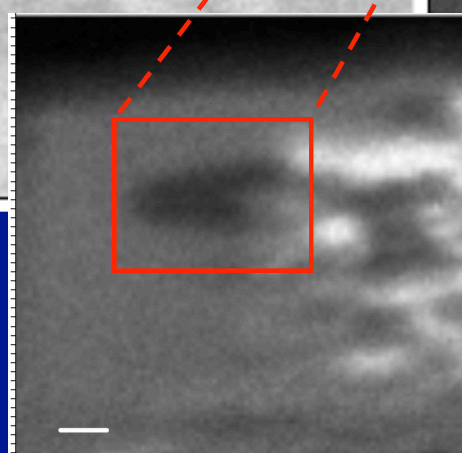
Soft X-ray



Cody, Alexander, Araki, Kilcoyne, Nakamura-Messenger, Sandford, Yabuta et al. (2008) *MAPS*

Identification of organics from the comet dust particle





Energy **below** the C1s edge

(X ray is not absorbed)

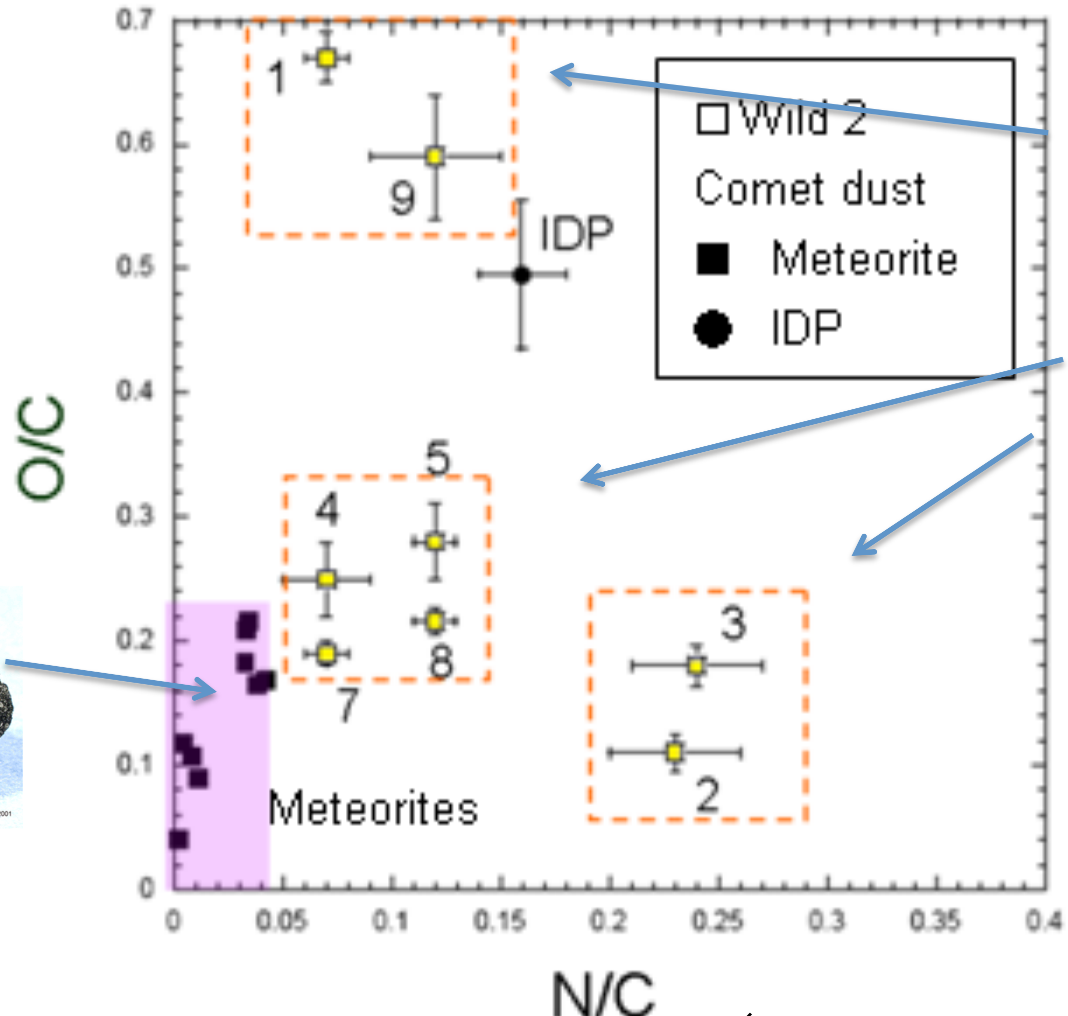
(5 x 5 µm)

Energy **above** the C1s edge

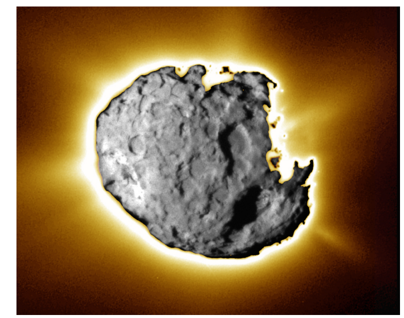
(X ray is absorbed)

Organic elemental compositions: Comet Wild 2 vs. Meteorites

Organic materials in 81P/Wild 2 comet dust particles are more heterogeneous and more abundant in N, O, and H than those in meteorites



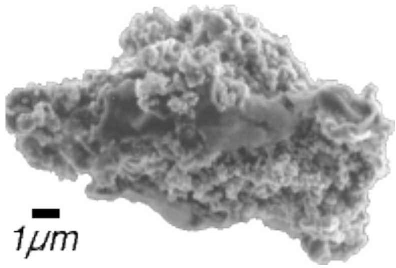
Comet Wild 2



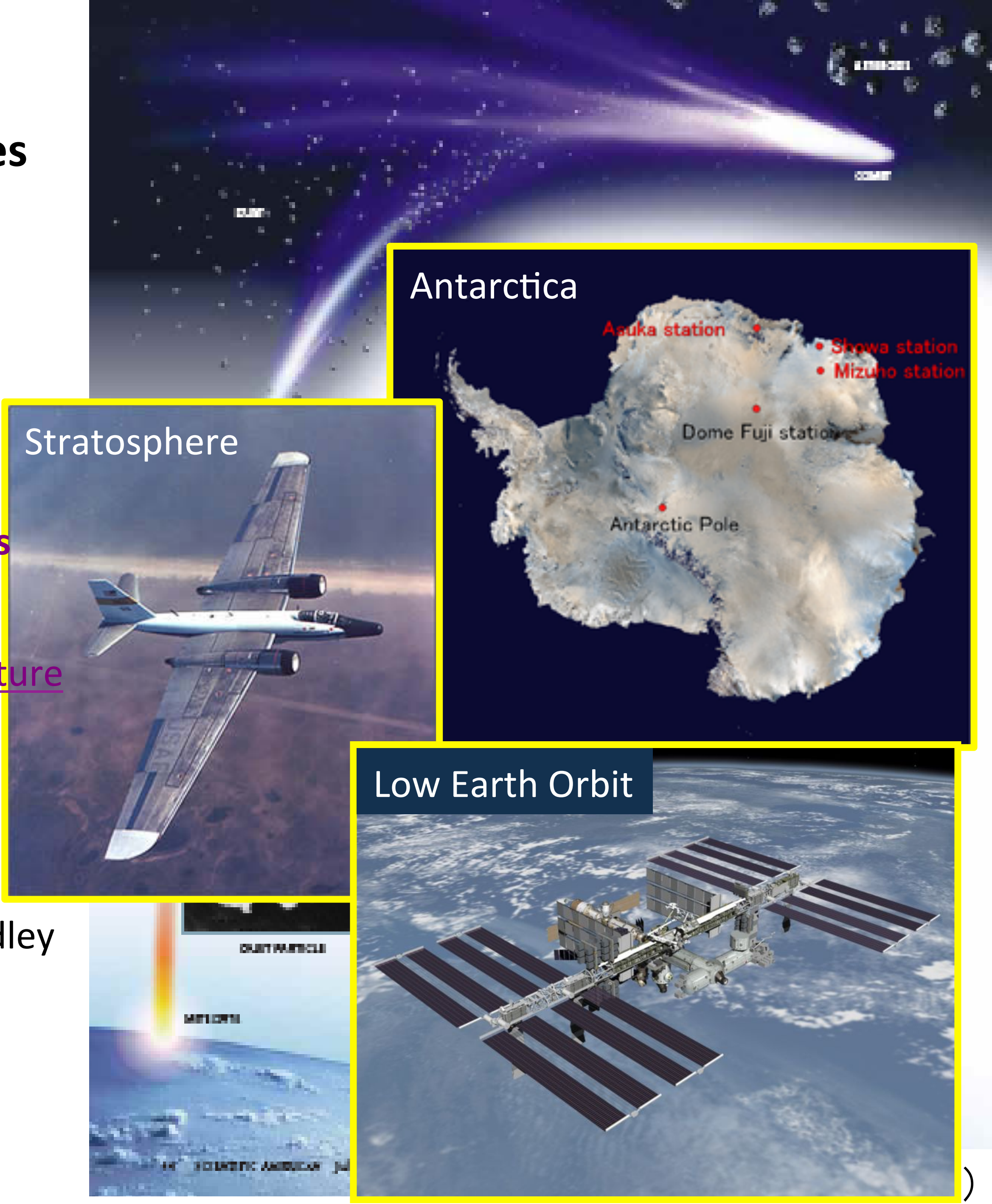
（Sandford et al. 2006; Cody et al. 2008）

Cosmic dusts

(Interplanetary dust particles (IDPs), Micrometeorites)



(Credit: Messenger,



- **The link with short-period comets** (Messenger et al. 2006)
- Fine grained, porous, fragile structure (Bradley and Brownlee, 1986)
- Highly enriched in Carbon (~12%, Thomas et al. 1993)
- Presolar mineralogy – GEMS (Bradley et al. 1999)
- D and ^{15}N enrichments (e.g., Messenger, 2000; Floss et al. 2004; Busemann et al. 2009)

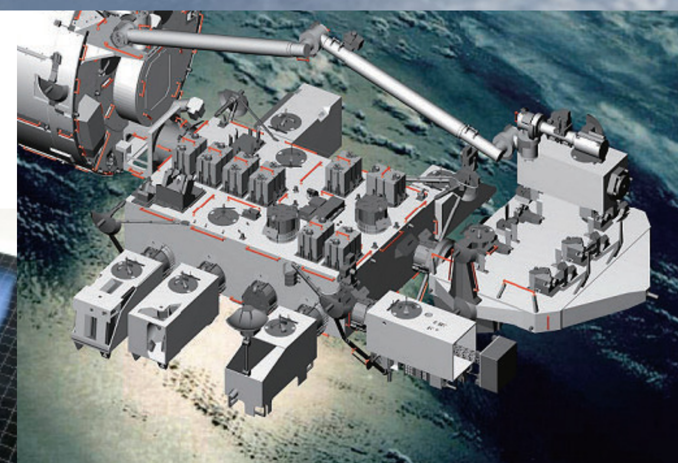
)

TANPOPO mission:

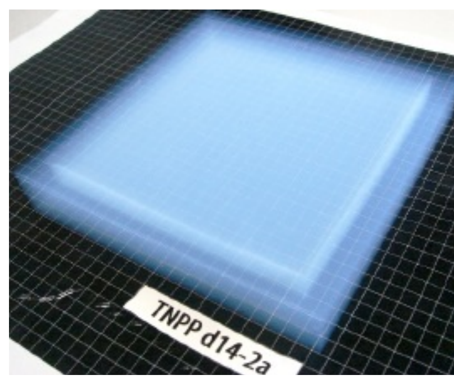
Japanese Astrobiology Exposure and Cosmic Dusts Capture on the International Space Station (ISS)

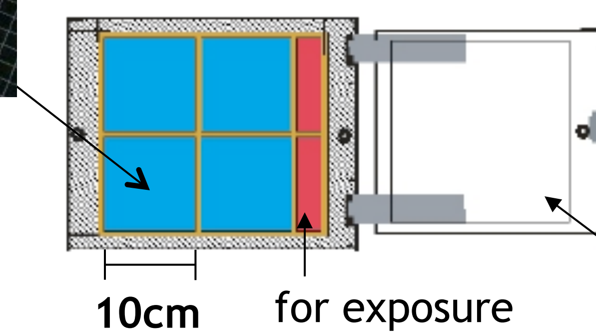
- Will be launched in 2013(?), returned in 2014, 2015, 2016

- Collection of the pristine IDPs without atmospheric entry heating and terrestrial contamination will be expected



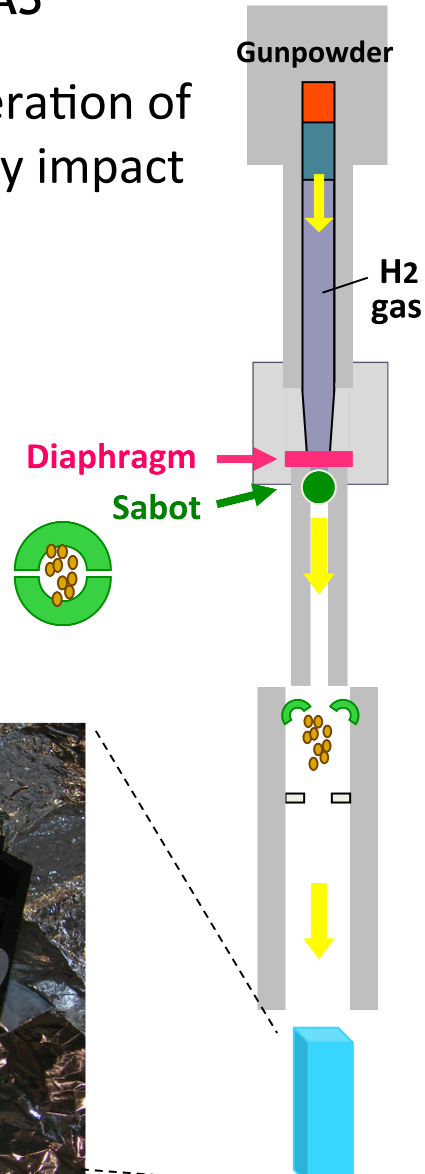
- Learning and improving from Stardust mission (Brownlee et al. 2006) – **A low-density silica aerogel (0.01 g/cm^3)** is used as a capture material (Tabata et al. 2011)



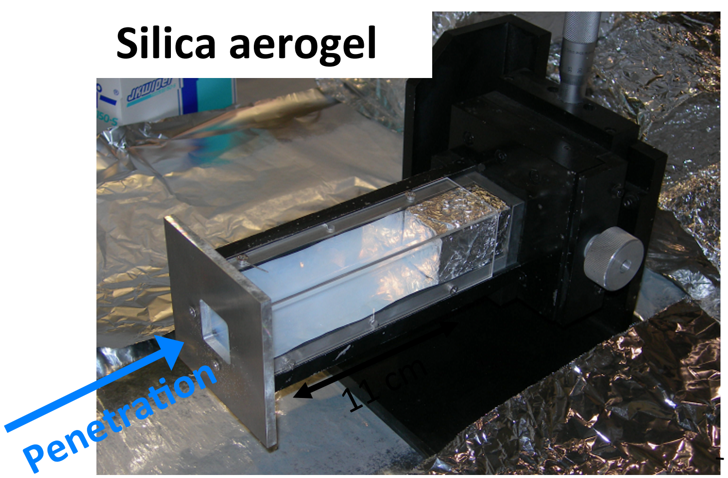


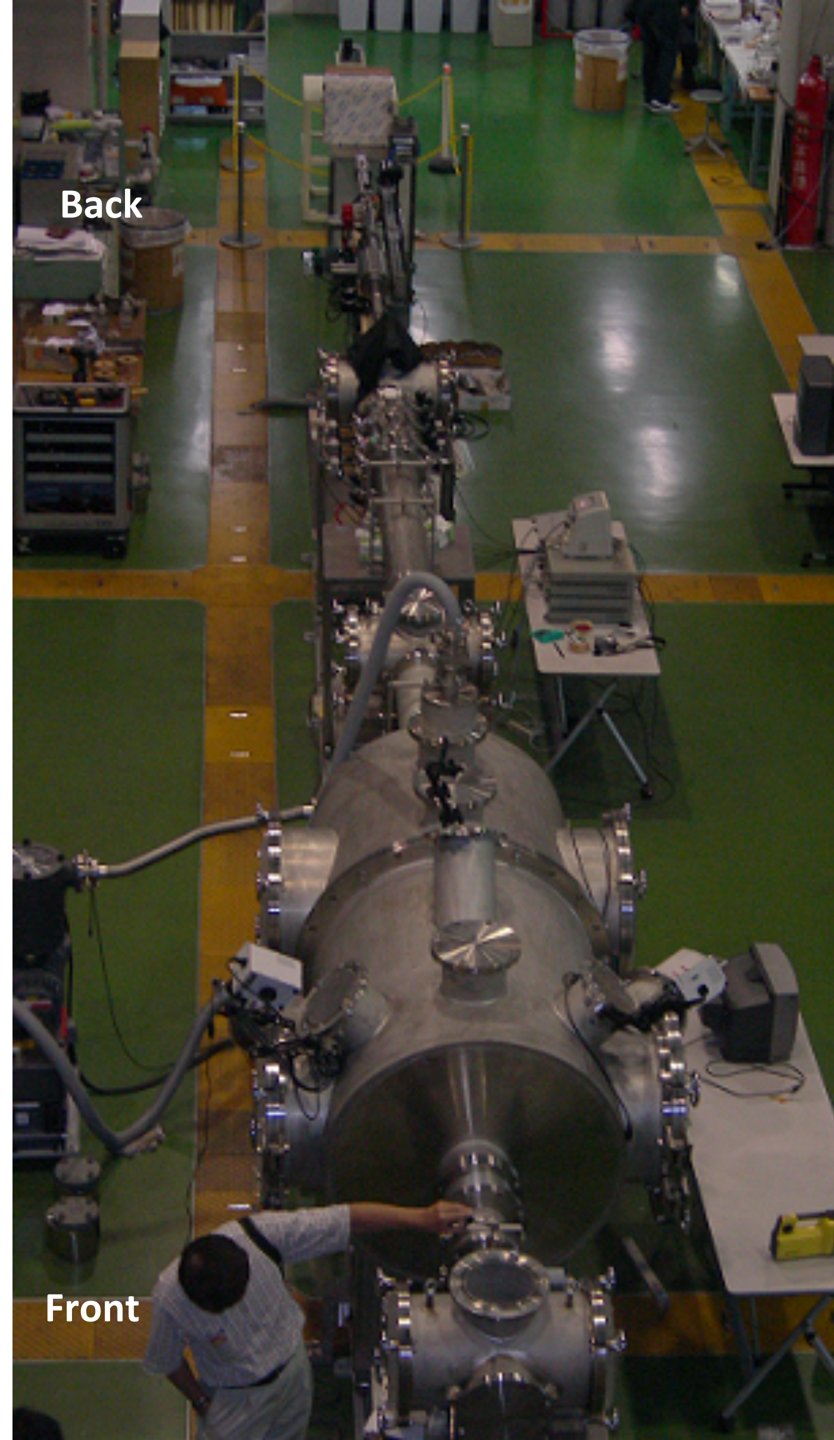
Hypervelocity impact experiment using a two stage light gas gun
at JAXA/ISAS

- Evaluation of possible alteration of IDPs upon their high velocity impact to the aerogel
- Impact velocity: **4 km/s**
- Multiple particle shot
- Sample: **Murchison meteorite powder** 500 μg (30–100 μm)



Silica aerogel





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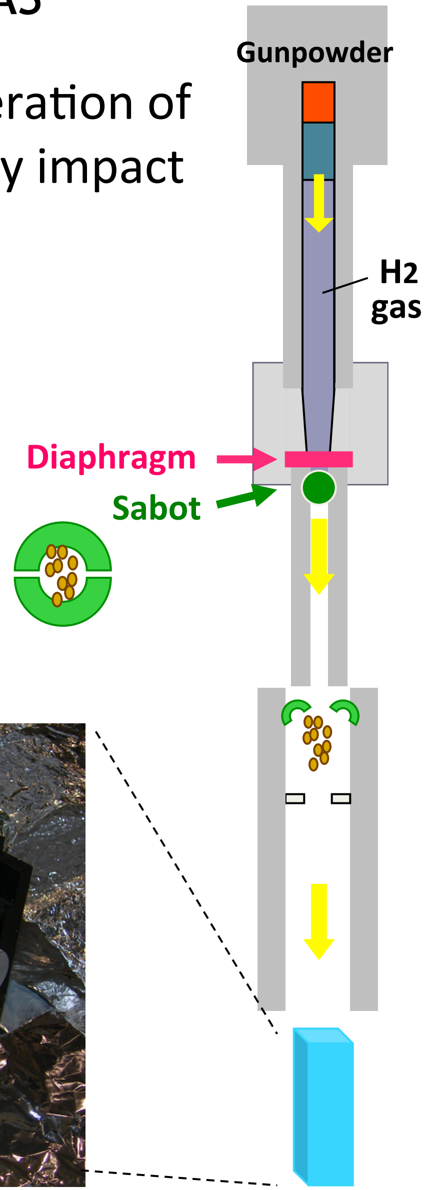

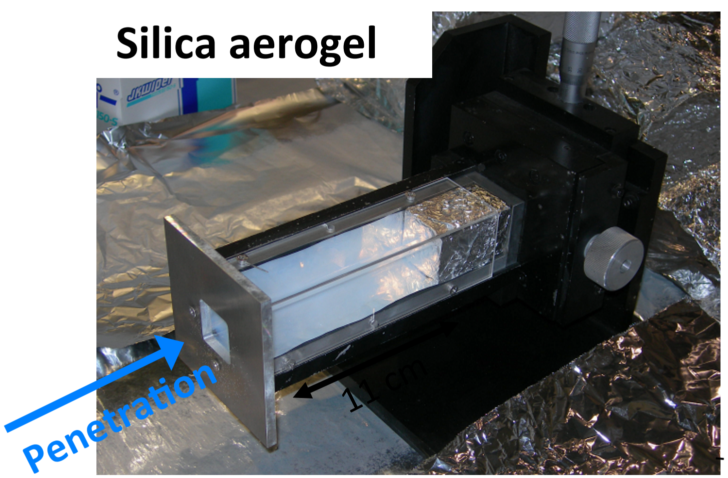

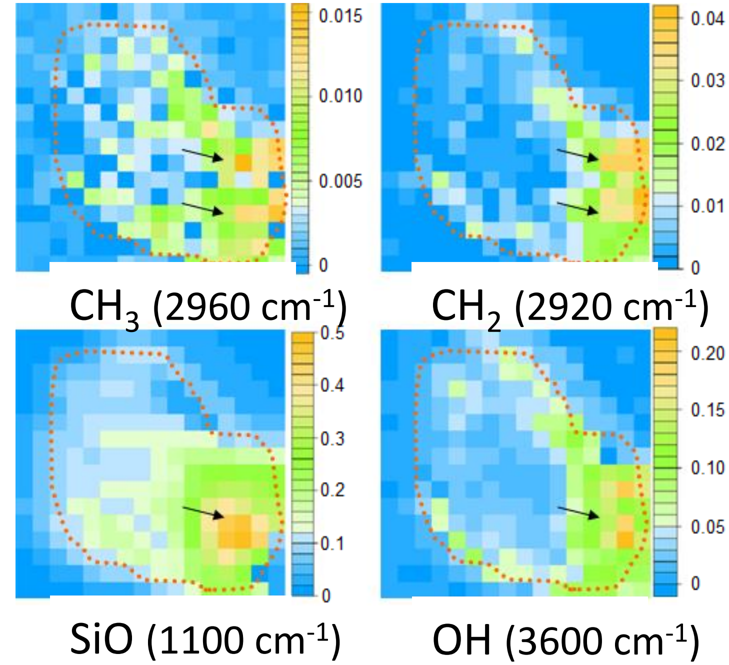

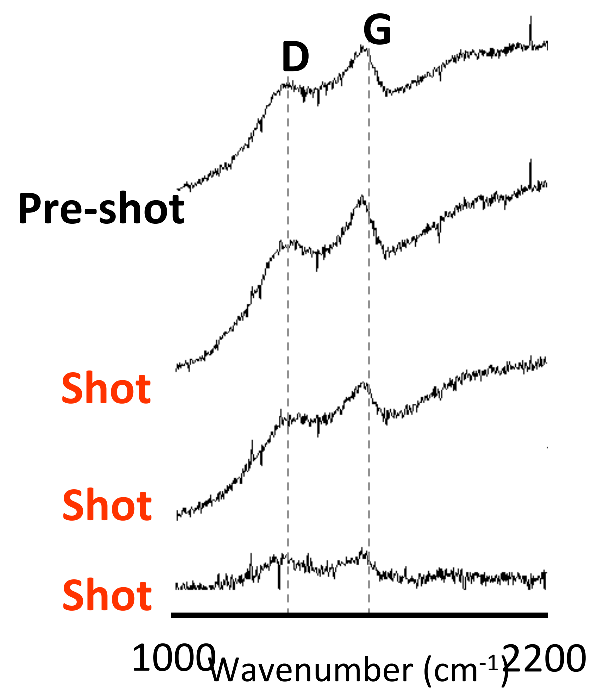

Conclusion

- **Molecular and isotopic compositions of organic compounds** in primitive small bodies are important indicators for origin and evolution of the solar system.

- **Sample return missions** provide the information which it is difficult to reveal only by meteorites study.
They will enhance our understanding of generality and diversity of organic chemistry in space.

- It is the **state-of-art analytical techniques that turn sample return missions to advantage**.

- It is necessary to understand **the genetic relationship between soluble and insoluble organic fractions**, as well as characterization of unidentified compounds.

Acknowledgments

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All my colleagues in Stardust, Hayabusa-2 & Tanpopo