Organic molecules in primitive small bodies: From meteoritic studies toward asteroid sample return missions

Arrival of Hayabusa 2
at the asteroid Ryugu.
June 27, 2018

Sorry – the image is not shown

(Credit: JAXA, University of Tokyo & collaborators)

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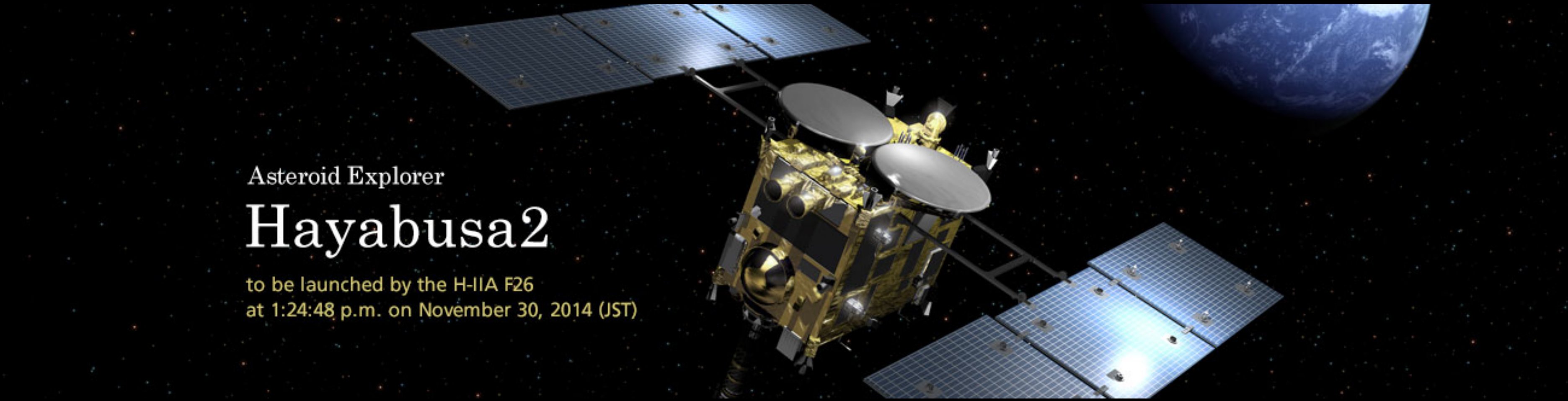
Hayabusa2
Carbonaceous (C-type) asteroid sample return mission

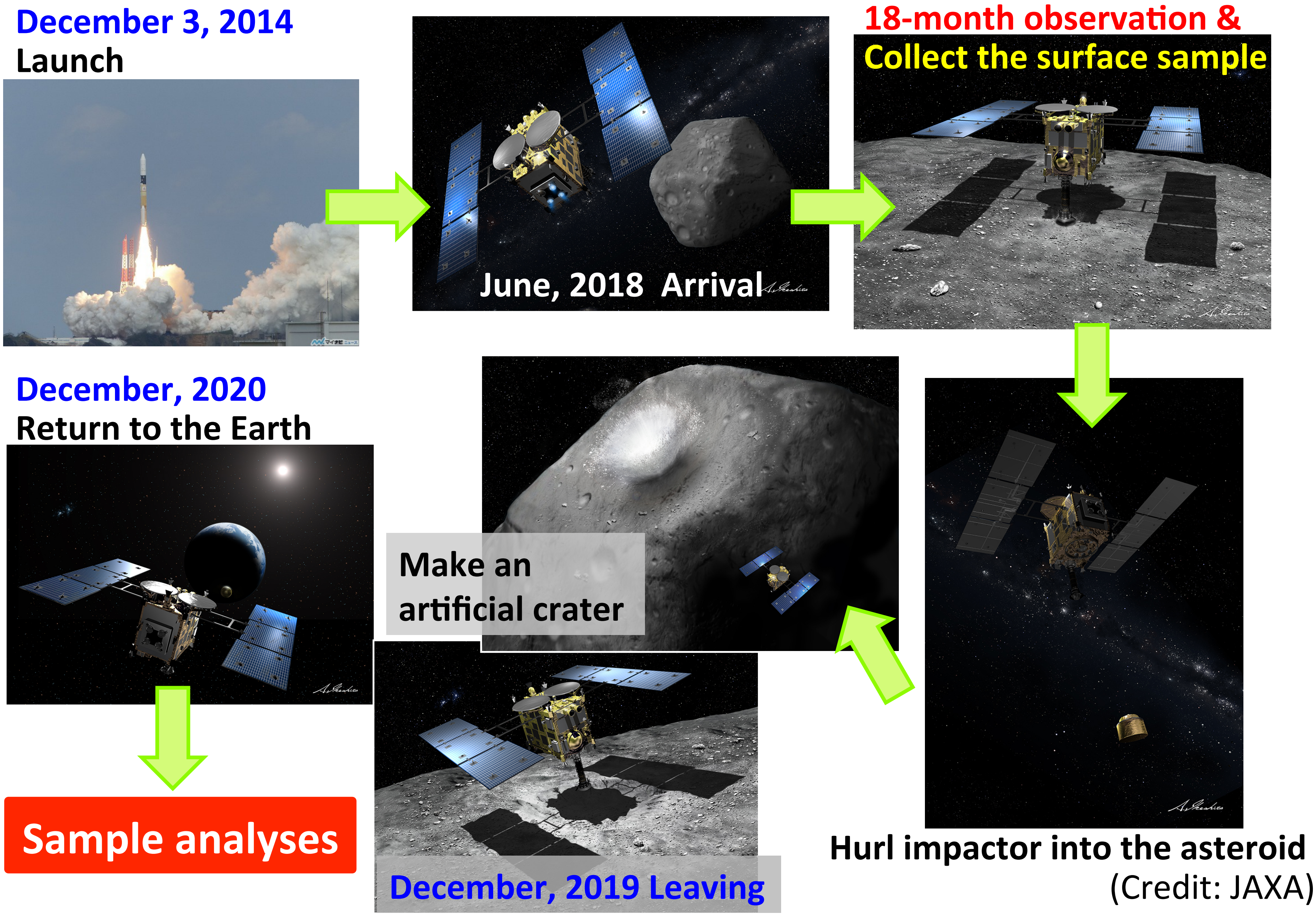


Collection of the asteroid samples containing Organic molecules and Water for the laboratory sample analyses

for understanding the origin and chemical evolution of the building blocks of the Solar System, Life (organics, water) and ocean (water)

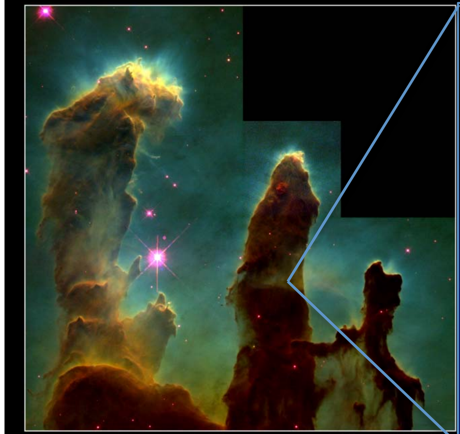
Target is <u>a near-Earth asteroid Ryugu (1999JU3)</u>

Journey of Hayabusa 2

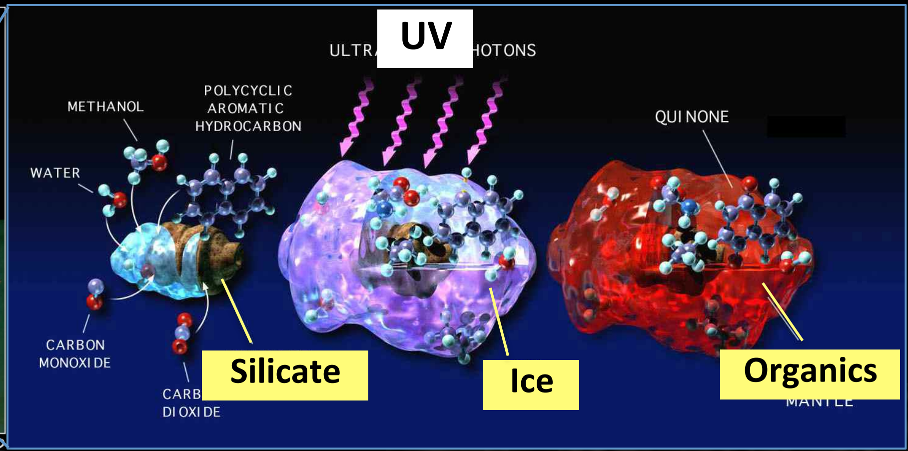


(Credit: JAXA)

Important roles of organic molecules in the early Solar System



Gaseous Pillars · M16 HST · WFPC2
PRC95-44a · ST ScI OPO · November 2, 1995
J. Hester and P. Scowen (AZ State Univ.), NASA

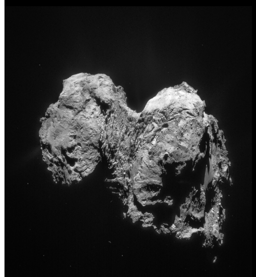


Origin

Interstellar/ Nebula/ Parent body

Evolution

Aqueous alteration, Dehydration, Space weathering (T, duration etc)



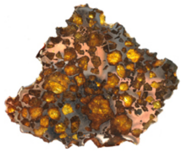
Exogenous delivery of life's building blocks

What kind of organic compounds were delivered to the Earth?

Classification of meteorites

Meteorite

- Martian
- Lunar
- Iron
- Stony-iron
- Stony
  - Achondrite
  - **Chondrite**
    - Enstatite chondrite
    - Ordinary chondrite
    - **Carbonaceous chondrite**

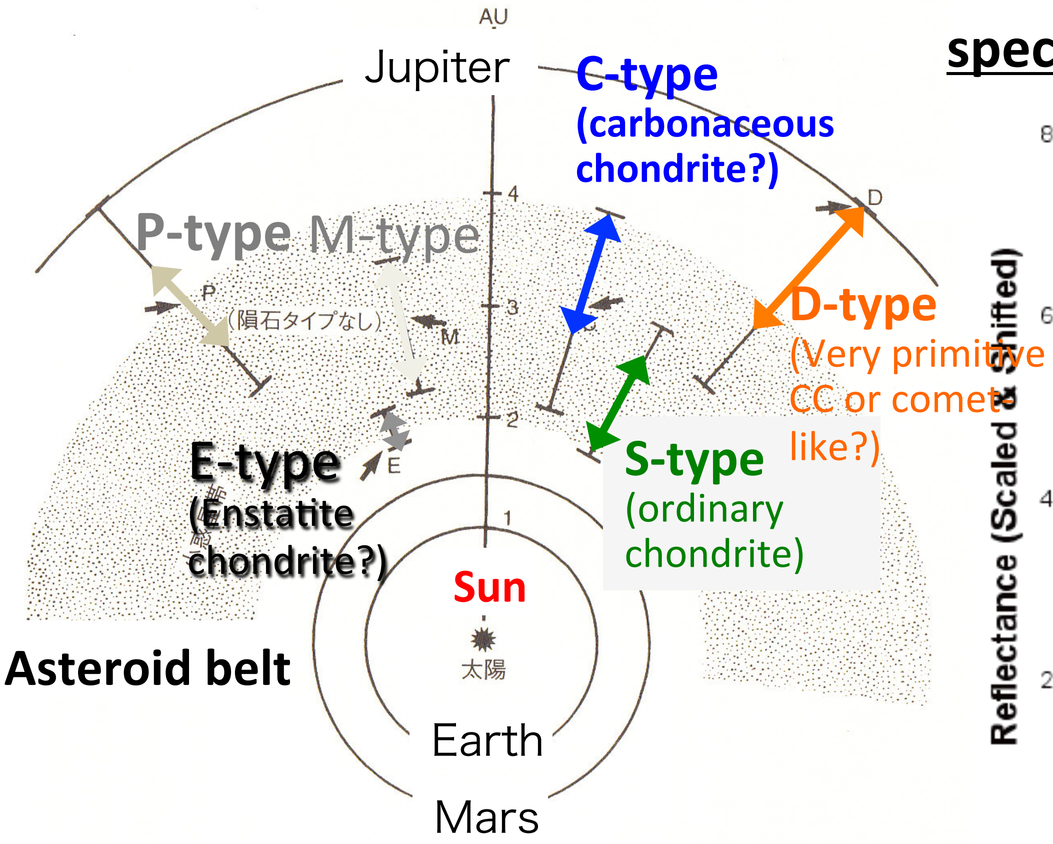


Differentiated meteorites
(their original components were lost due to molten state)

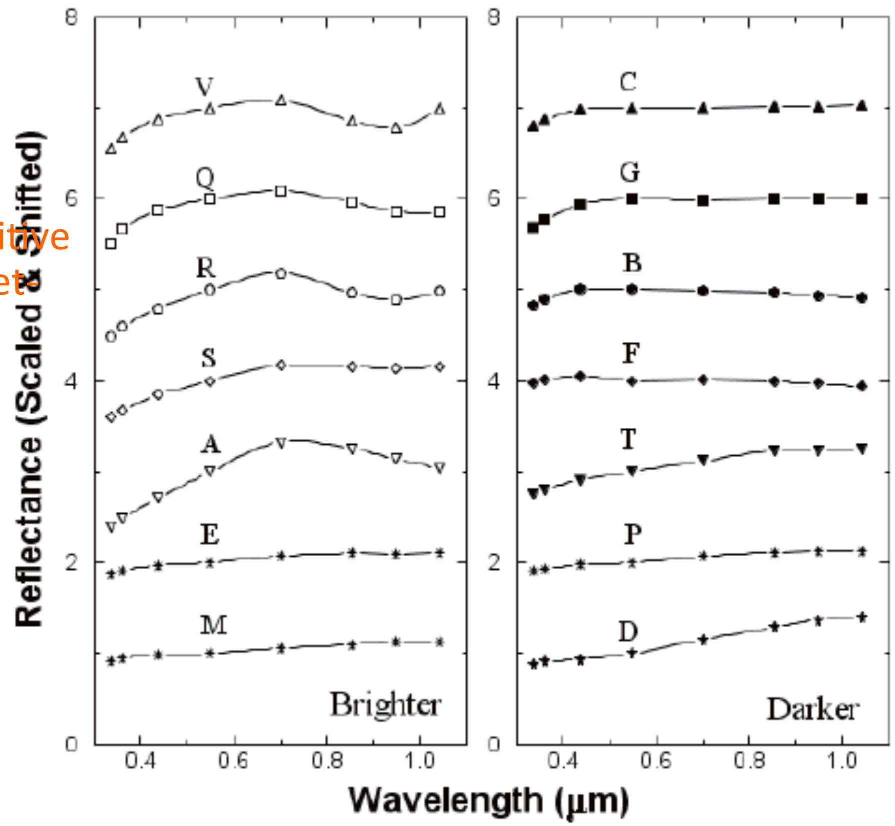
Undifferentiated meteorites

Organics and water in the early Solar System are preserved → **Carbonaceous chondrite**

Asteroids: Parent bodies of meteorites



Classified based on the **reflectance spectra** (Tholen et al. 1984; Hiroi et al. 2010)

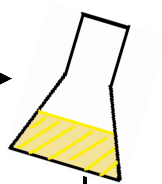


One can comprehensively understand the chemical history of Solar System by <u>systematic investigations of asteroids and comets in different evolution stages</u>

Organic compounds in primitive carbonaceous chondrite

10 – 1000 mg

Solvent / Water extraction →



2 – 5 wt% total organic carbon

Soluble organic compounds	**Acid-Insoluble** macromolecular organic solid (IOM) — ca. **1 wt%**

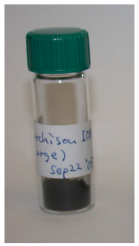
Carboxylic acids +++
(mono-, di-, hydroxy-)

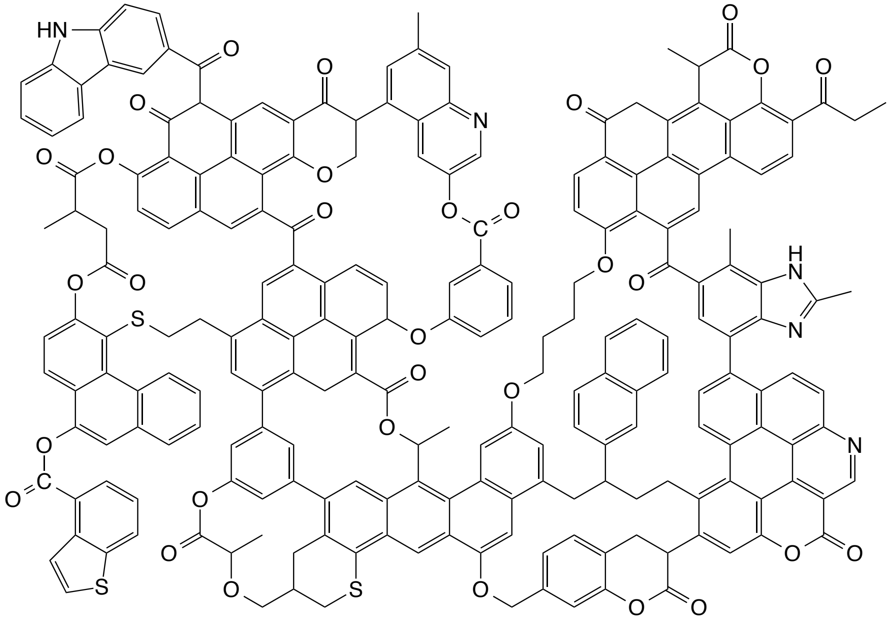
Amino acids ++

- Alcohols ++
- Aldehydes ++
- Ketones ++
- Amides ++
- Amines ++
- PAHs ++
- Aliphatic hydrocarbons ++
- Purines ++
- Pyrimidines ++
- Phosphoric acids ++
- Sulfonic acids ++

Unidentified compounds
(Schmitt-Kopplin et al. 2010)

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





$C_{100}H_{75}N_4O_{17}S_3$

(Glavin, Alexander, Aponte, Dworkin, Elsila and Yabuta, 2018)

How to characterize organic molecules..?
"Anatomy" of meteorites

Extraction/Isolation

Interaction of light and materials

X-ray

Interaction of magnetic field and materials

MRI

Measuring weight

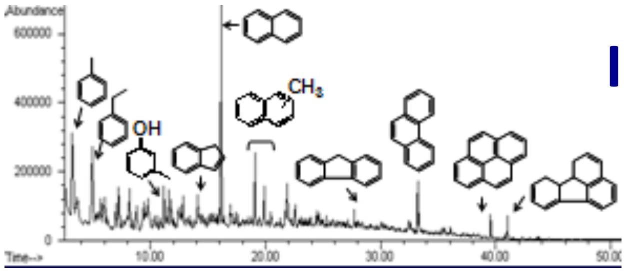
Weight scale

Observation

Endoscope

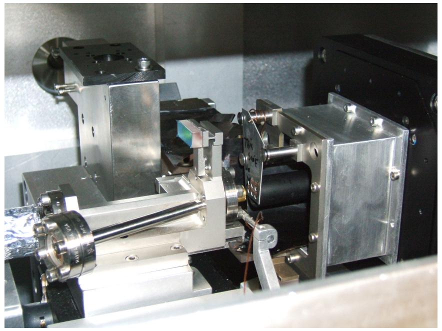
How to characterize organic molecules..?
State-of-art chemical analytical techniques are necessary

Extraction/Isolation



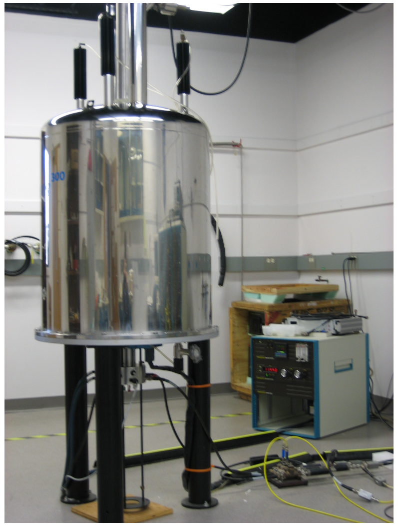
Chromatography

Interaction of light and materials

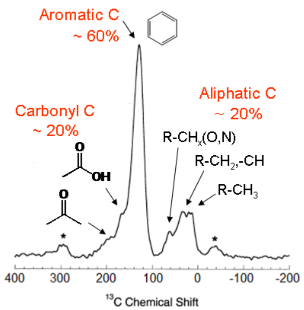


X-ray (Synchrotron X-ray), Laser, Infrared

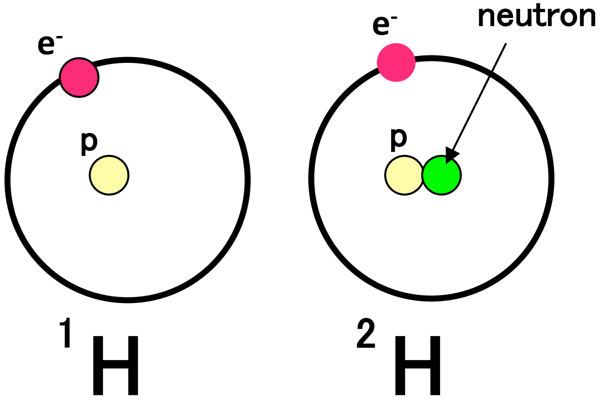
Interaction of magnetic field and materials



NMR



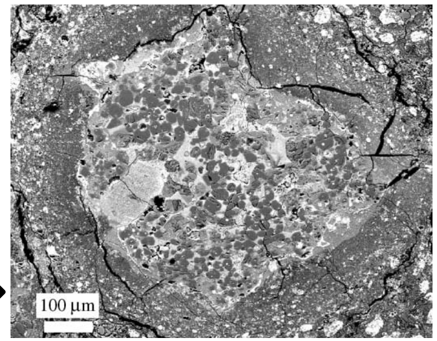
Measuring "mass"

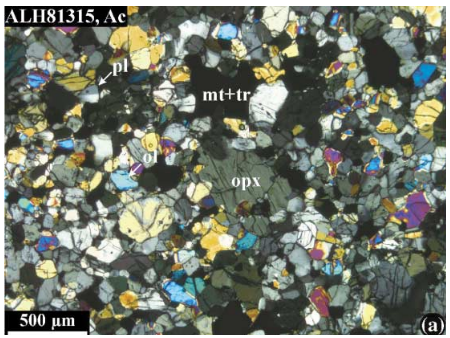


Isotope mass spectrometry

Observation

Electron microscopy →

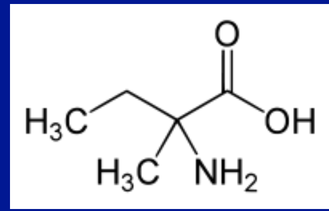




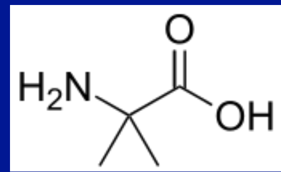
←Polarized light microscopy

Evidences of extraterrestrial organics: Amino acids

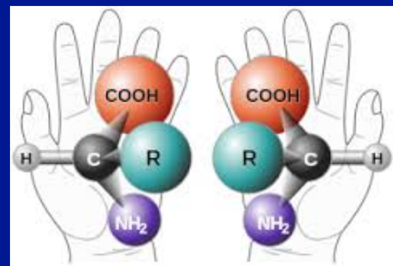
(Cronin and Chang, 1993)



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



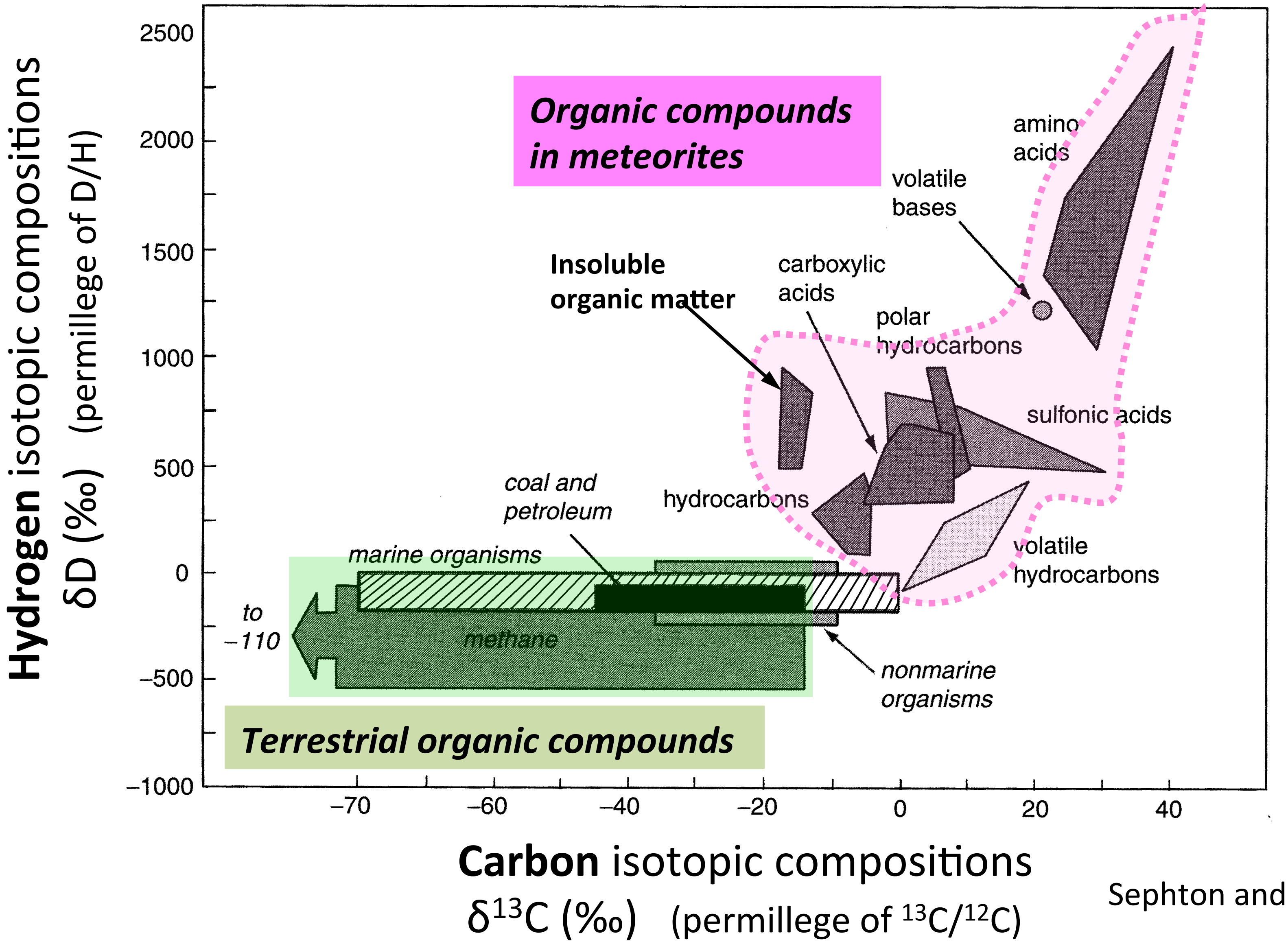
2. **Decrease in abundance with increasing carbon number**
-> The pattern of prebiotic synthesis from smaller molecules to larger molecules



3. **Enantiomer ratios for most of amino acids are racemic (D:L = 1 : 1).** Exceptionally, **slight excess (up to 18%) of L-form of α-methyl amino acids is 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 ($^{15}N/^{14}N$)

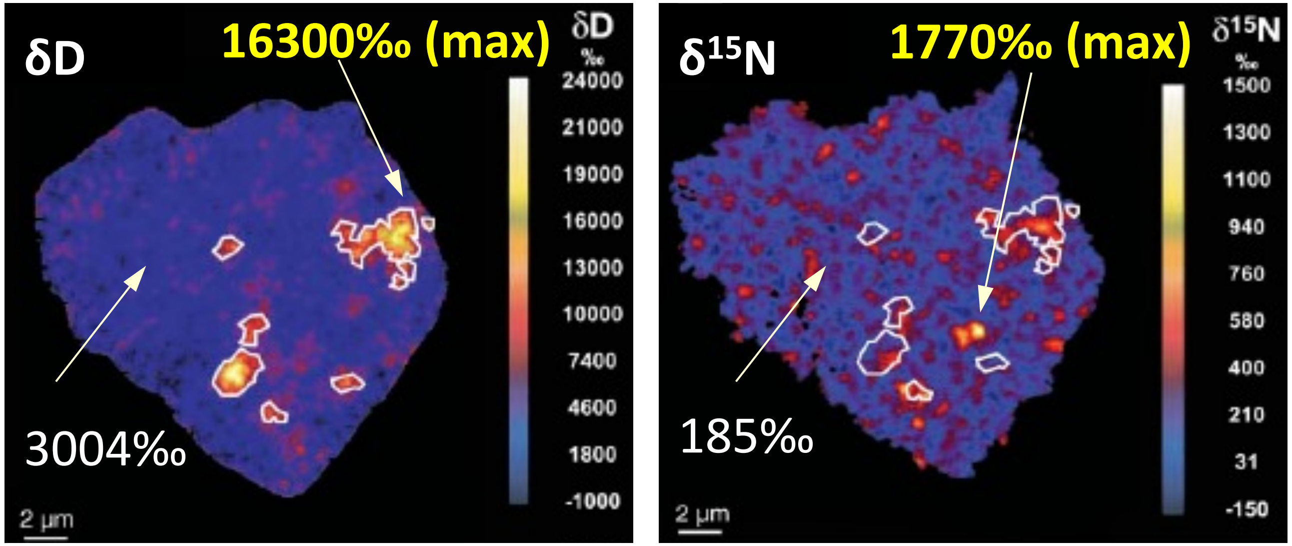
Enrichments of D (and ^{15}N) occur via cosmic ray-induced ion-molecule reaction (under extreme low T) that does not require activation energy (Watanabe, 2005)



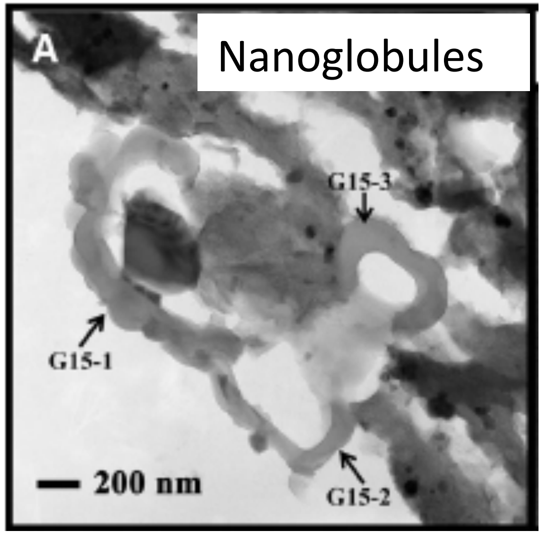
Sephton and Botta (2005) modified

Isotopic anomalies from insoluble organic material in meteorites preserve pristine organics formed by UV irradiation of ice in interstellar molecular cloud or outer regions of protosolar disk

Insoluble Organic Matter from CR chondrite（EET92042）



Busemann et al. (2006)



Nakamura-Messenger et al. (2006)

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

For example,

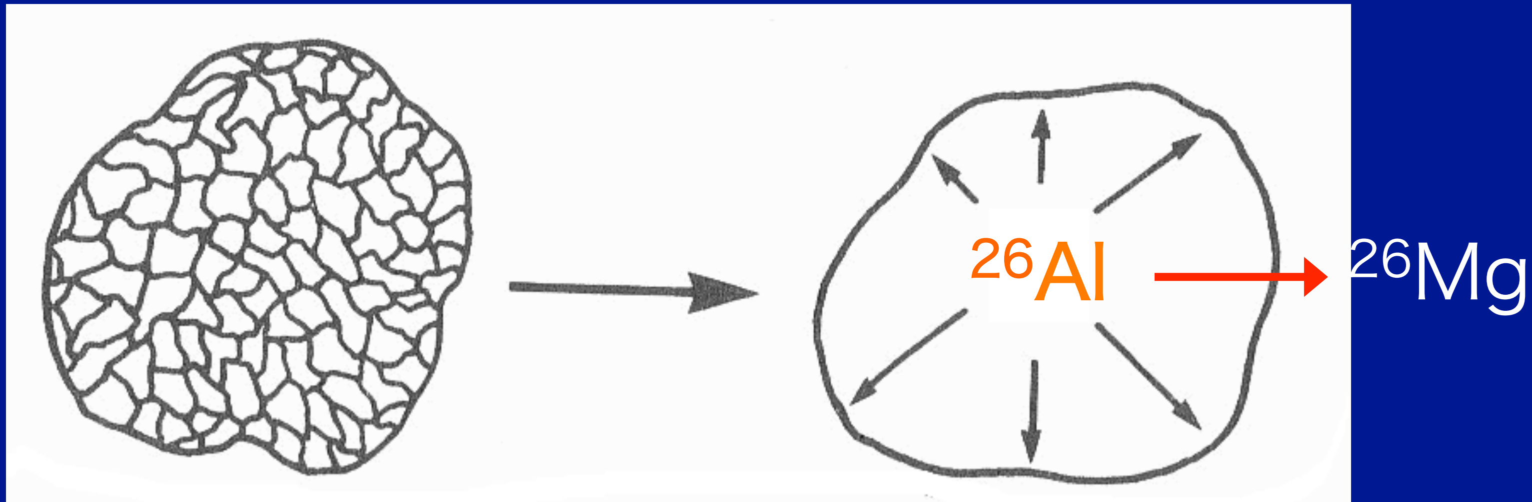
$$H_2 + H_2^+ \rightarrow H_3^+ + H \quad \text{(Ion-molecule reaction)}$$

$$H_3^+ + HD \rightarrow \underline{H_2D^+} + H_2 \quad \text{(exothermic reaction)}$$

Secondary processes on meteorite parent body

Accretion of dusts
-> planetesimals

Heating of parent body due to short-lived radiogenic nuclides (^{26}Al)



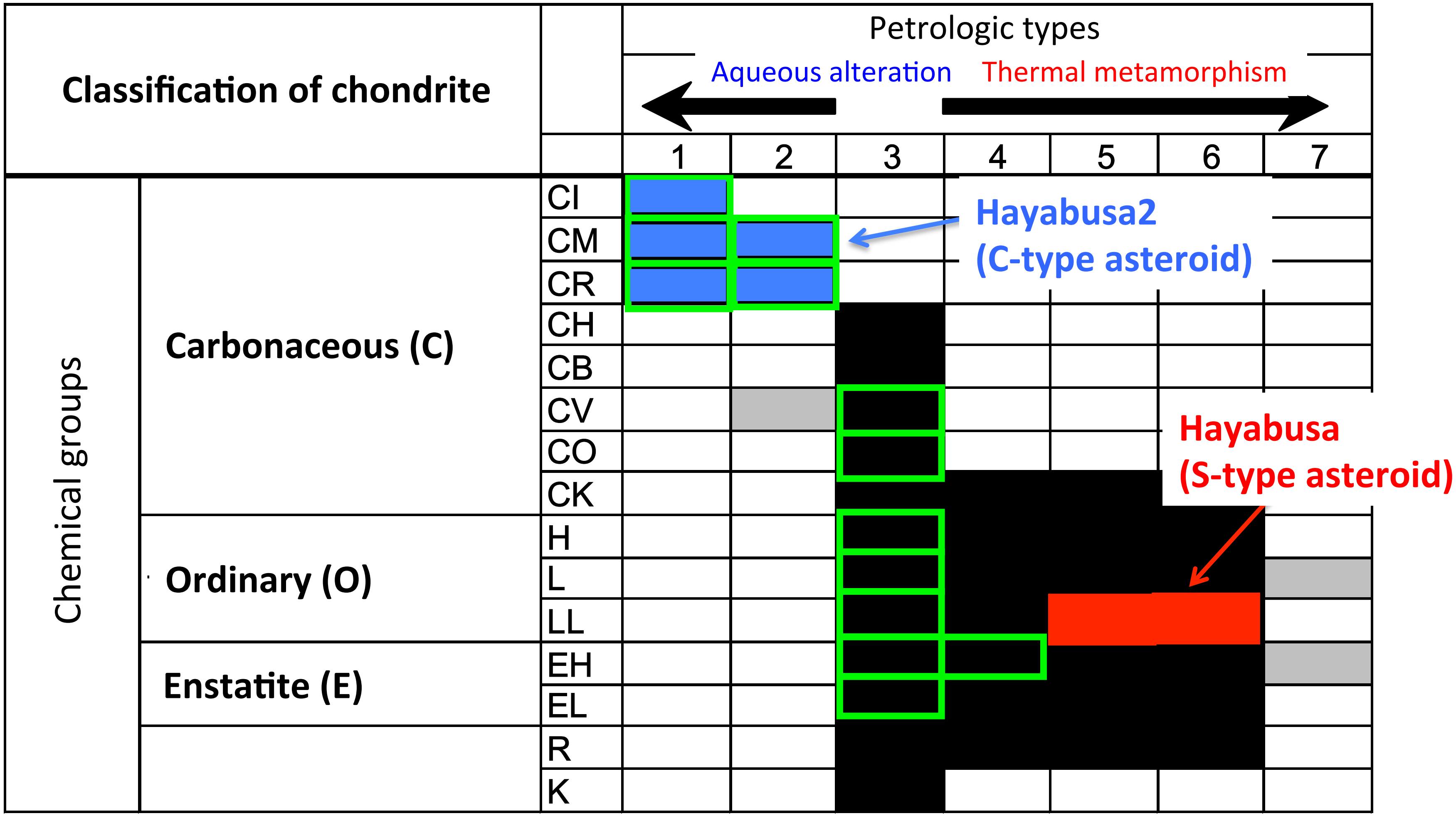
- Internal heating by radiogenic decay or impact-induced short-term heating → **Thermal metamorphism**

- Water-rock-organic reaction (0-150℃) by water ice melted by parent body heating → **Aqueous alteration**

Conditions and timescales of the parent body processes are meteorite to meteorite

Comparative meteorite organic chemistry

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



: organics have been studied

Weisberg et al (2006)

Comparative meteorite organic chemistry

- Water-rich asteroid parent bodies-

Soluble OM (amino acids)

- Amino acids are the most abundant in less altered CR2 (**249 ppm**), while they are depleted in more altered CR1 (**0.9 ppm**)
  (Martins et al. 2007)

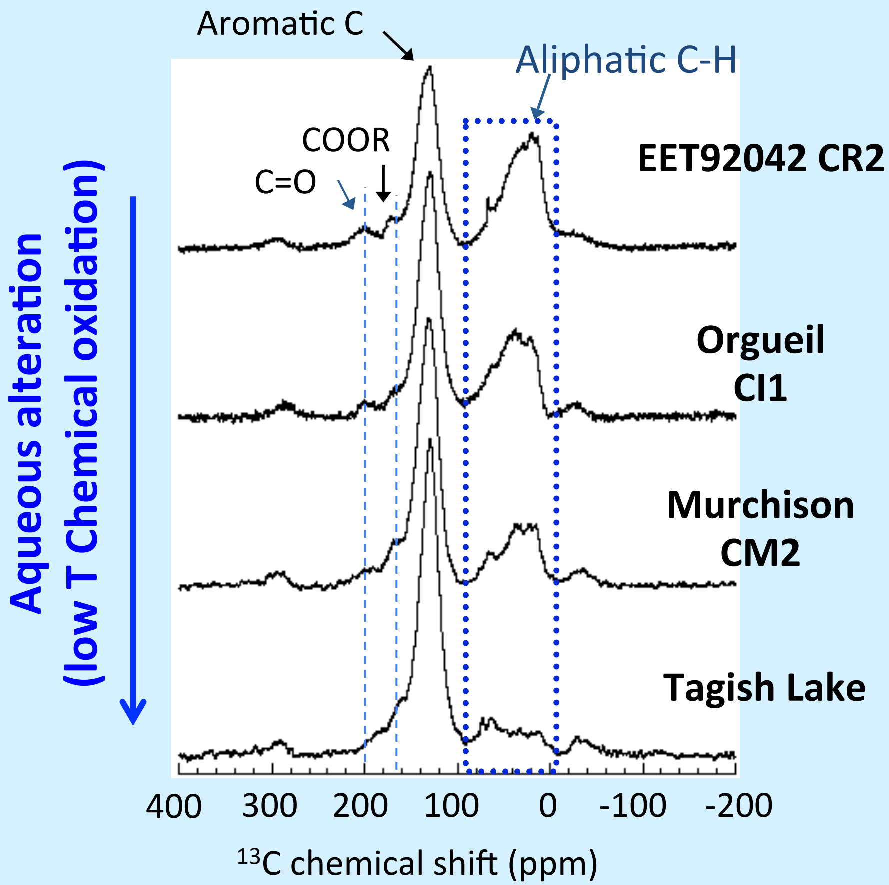
- Large L-enantiomeric excess (Lee) of isovaline was observed for altered CI1 and CM2, but for pristine CR2

	Sample	Isovaline Lee, %	Isovaline δx (n)
more altered	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)
less altered	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

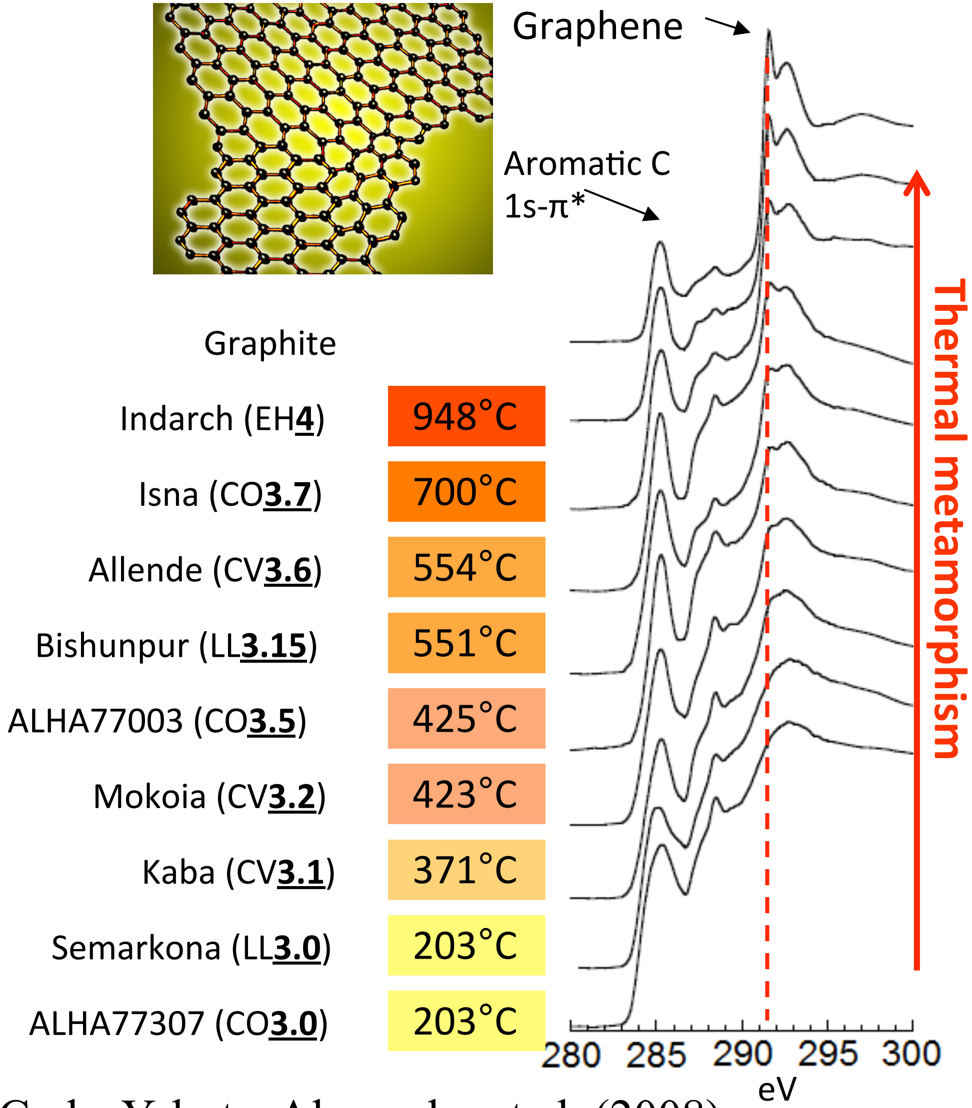


Cody and Alexander (2005)

Comparative meteorite organic chemistry

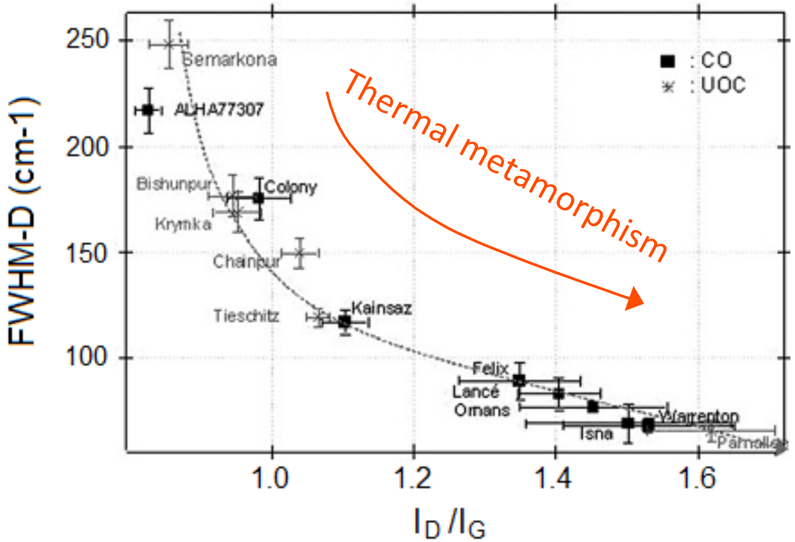
- Thermal metamorphosed asteroid parent bodies -

Carbon-XANES of IOM



Cody, Yabuta, Alexander et al. (2008)

Raman of IOM

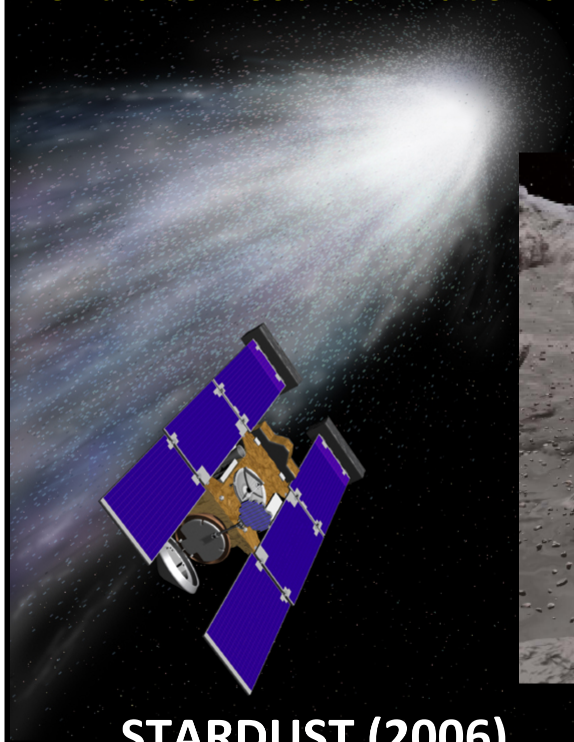


Bonal et al. (2007)

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)

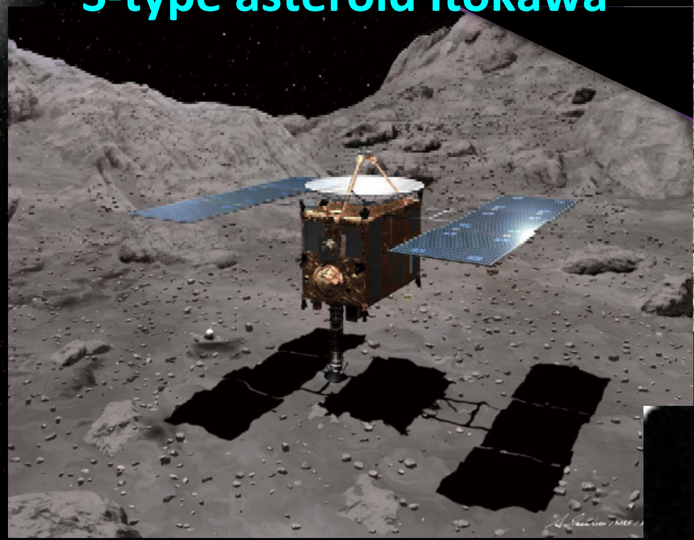
Advantages of small bodies exploration missions

Link between chemical compositions with geology / Contamination-free extraterrestrial materials / Finding of unknown extraterrestrial materials



STARDUST (2006)

Comet 81P/Wild 2 dusts



Hayabusa1 (2010)

S-type asteroid Itokawa

Rosetta (2004 -)

Comet 67P/Churyumov-Gerasimenko

OSIRIS-REx (2016-)

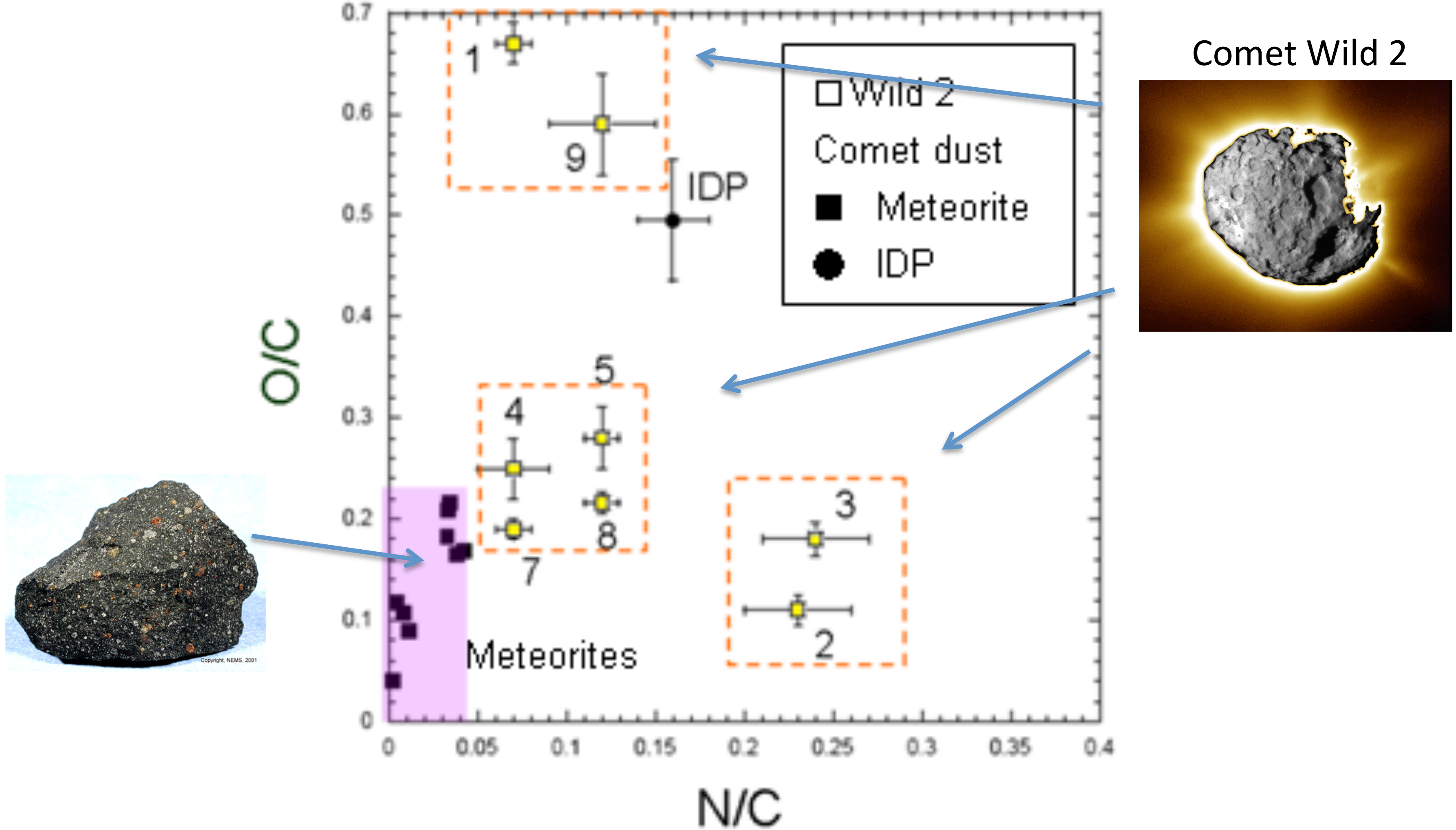
B-type asteroid Bennu

Hayabusa2 (2014 -)

C-type asteroid Ryugu

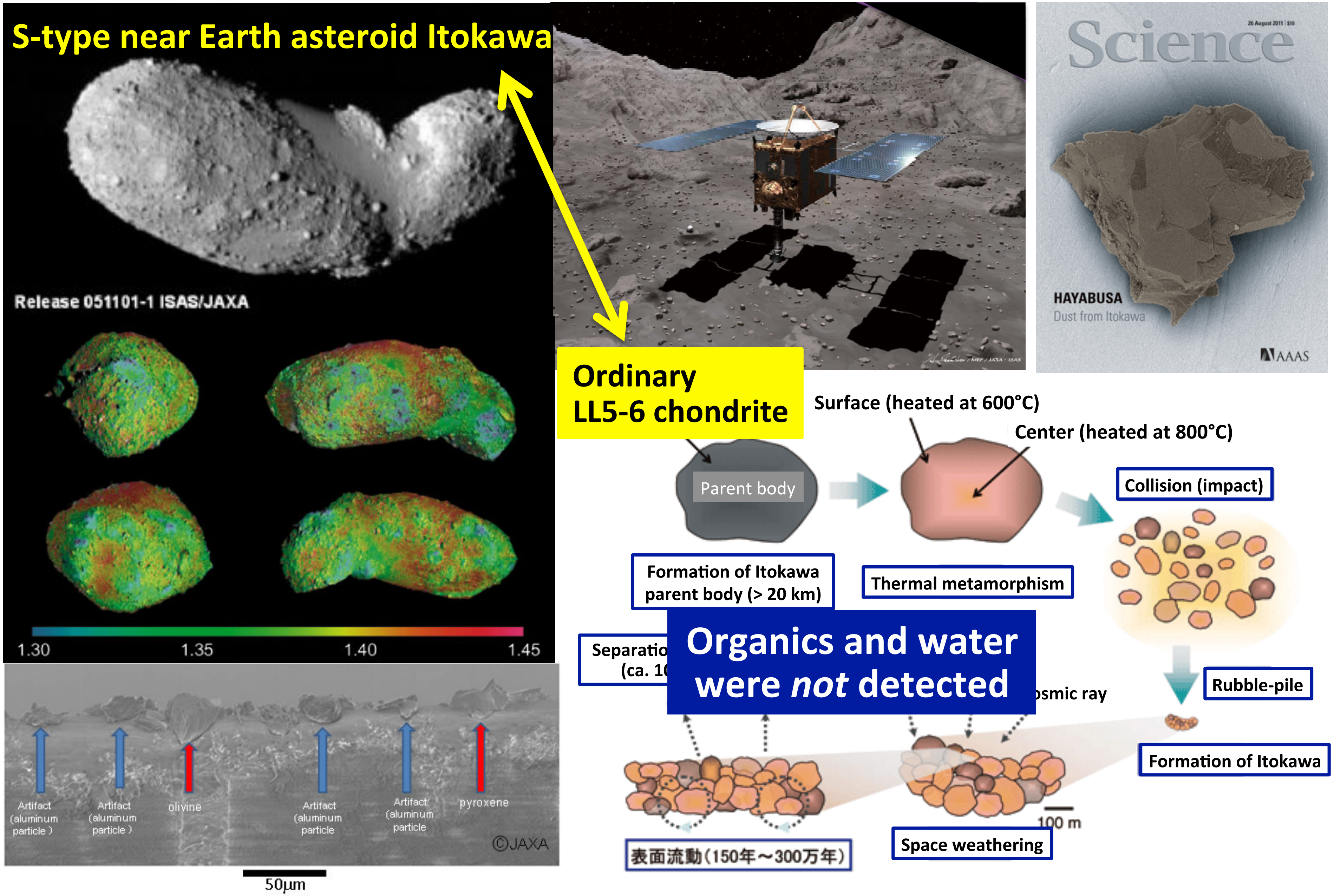
Organic elemental compositions: Comet Wild 2 vs. Meteorites

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

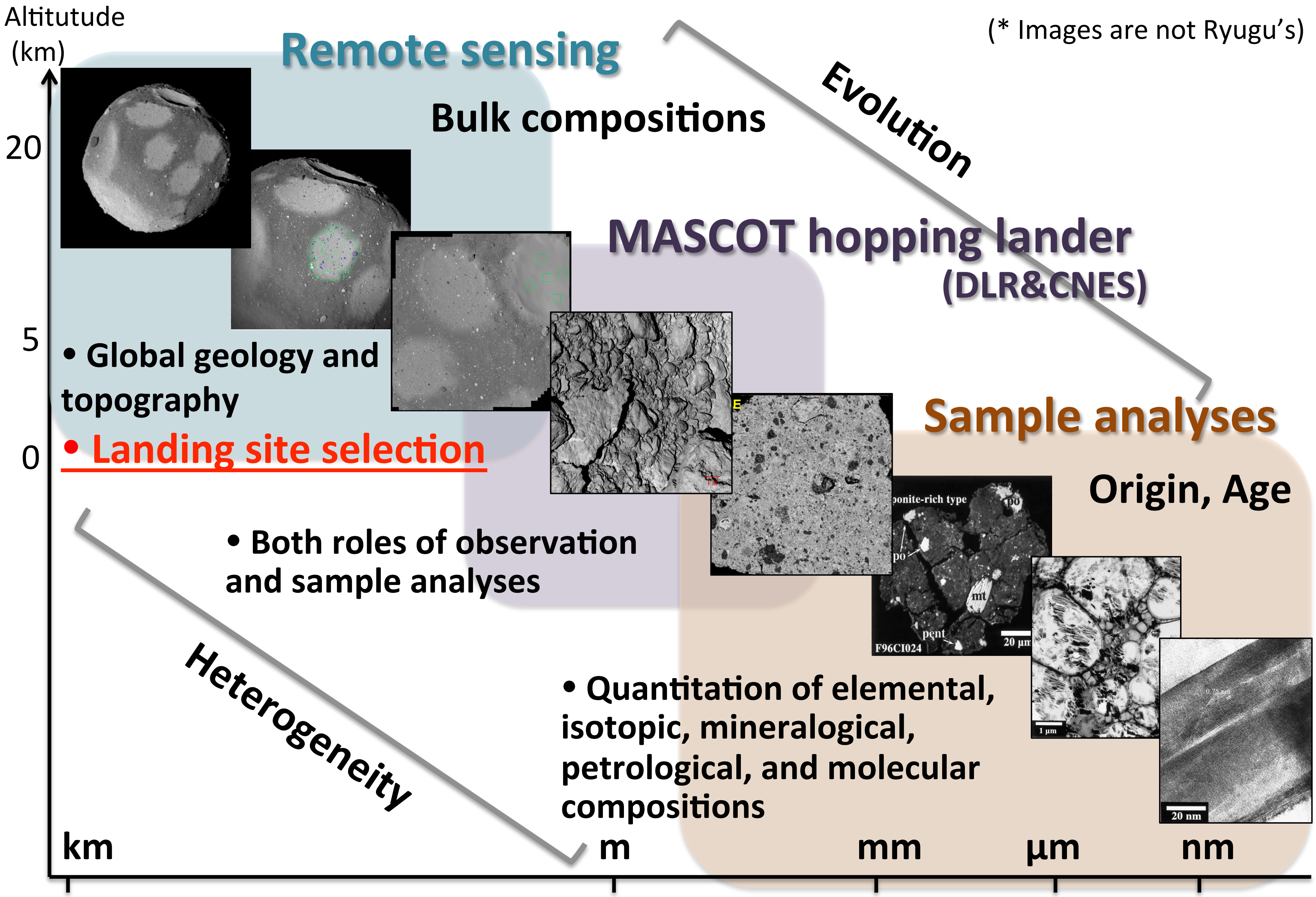


Cody, Alexander, Araki, Kilcoyne, Nakamura-Messenger, Sandford, Yabuta et al. (2008) *MAPS*

Hayabusa-1: the first asteroid sample return mission

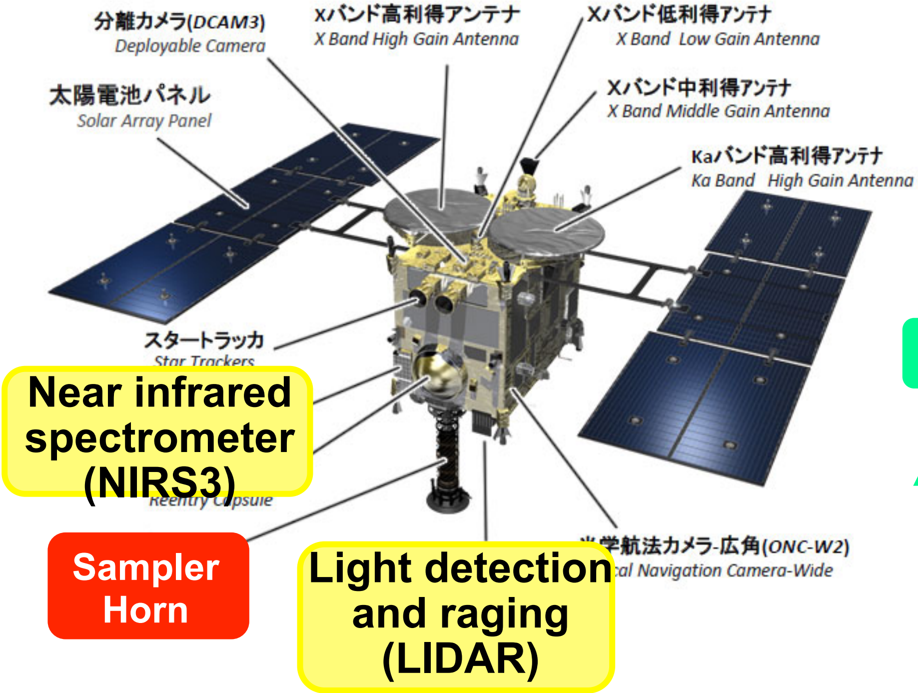


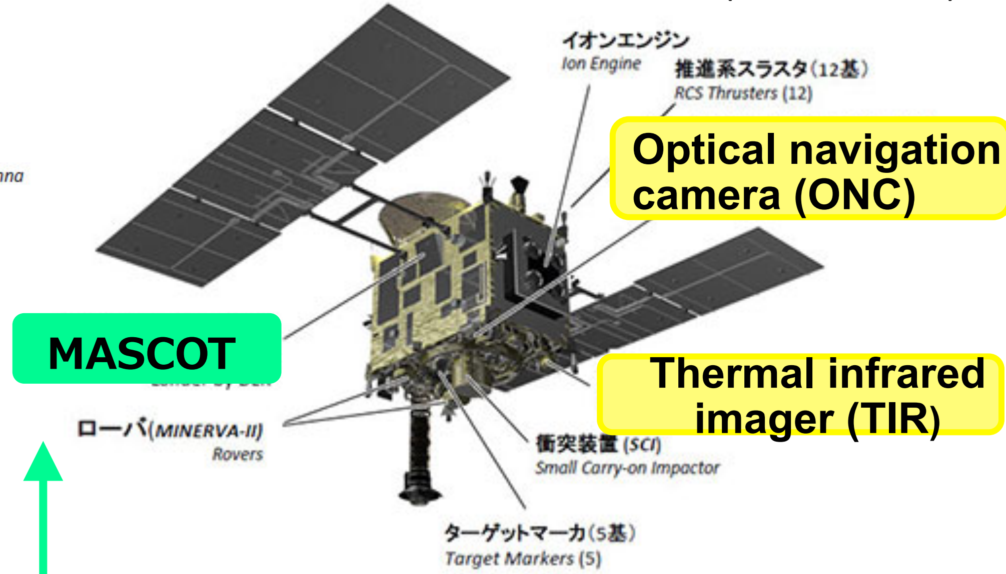
Scope of Hayabusa2 multi-scale asteroid science

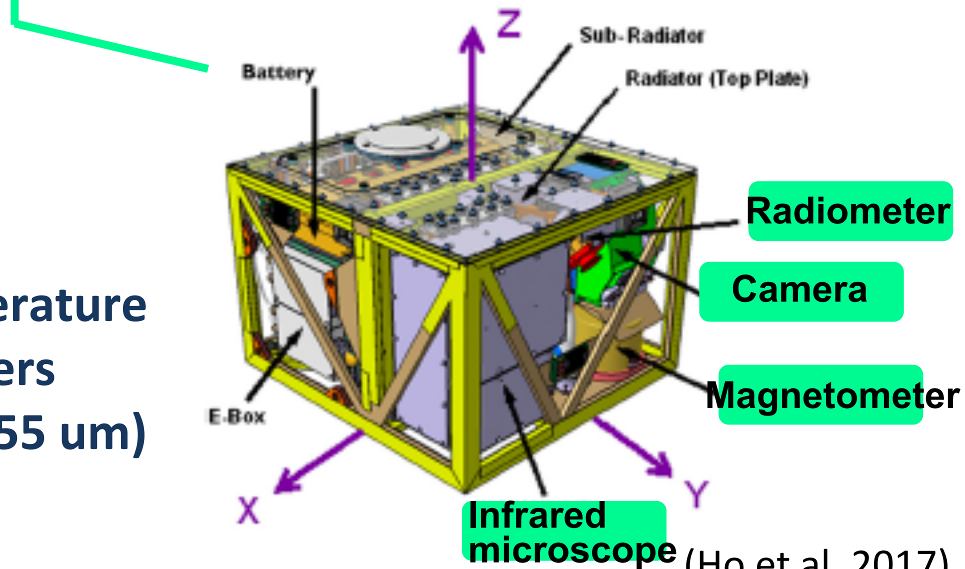


Onboard instruments of Hayabusa2

(Credit: JAXA)







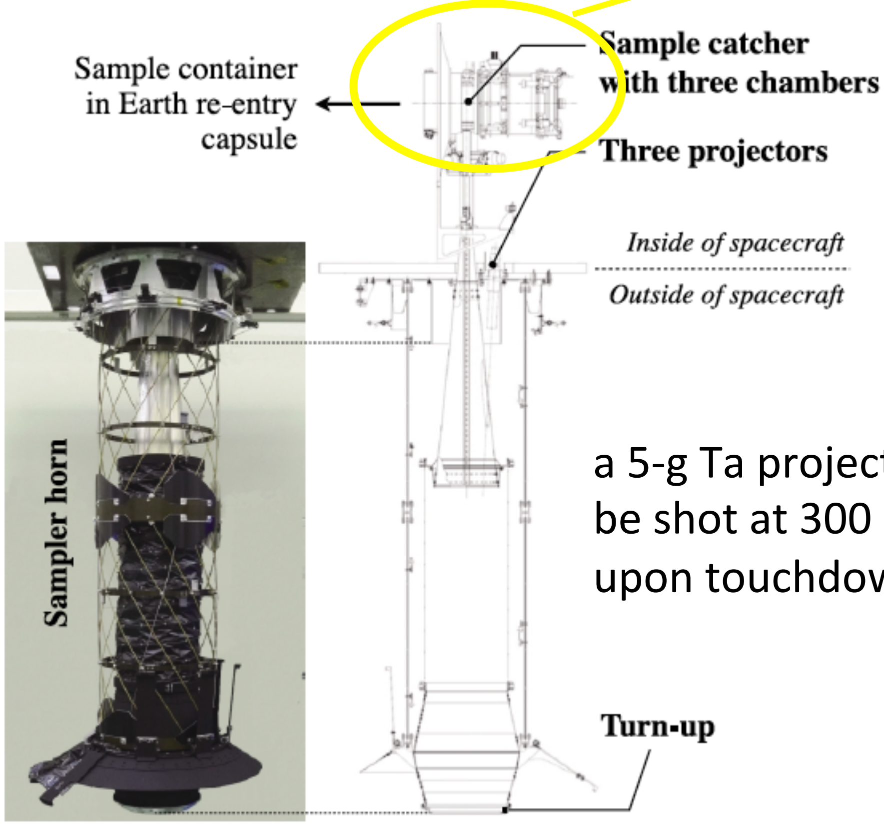
(Ho et al. 2017)

Scientific evaluation criteria:

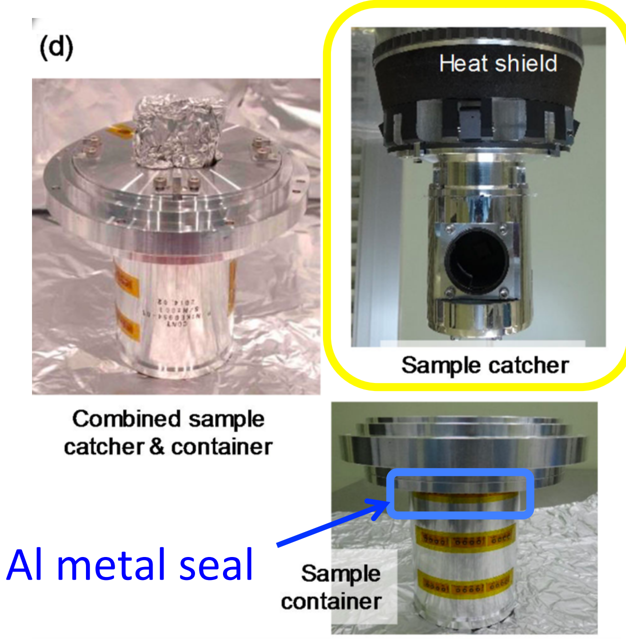
- Shape
- Thermal inertia, grain sizes, temperature
- Distributions of boulders and craters
- Albedo (reflectance at 0.39 and 0.55 um)
- Distributions of hydrous minerals

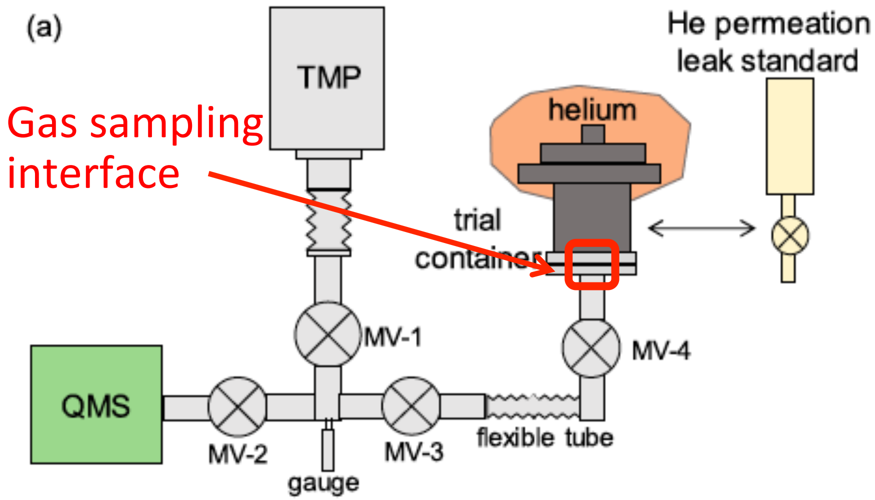
(0.7 um and 3 um absorption bands)

Sampler of Hayabusa 2



a 5-g Ta projectile will be shot at 300 m/s upon touchdown





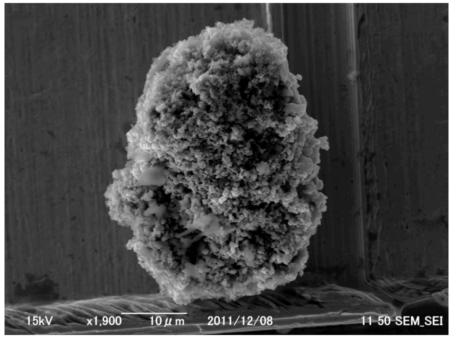
The ejecta will be transferred into a sample catcher through an extendable sampler horn under microgravity (Tachibana et al. 2014)

The collected samples will be **hundreds milligram**

(Okazaki et al. 2016)

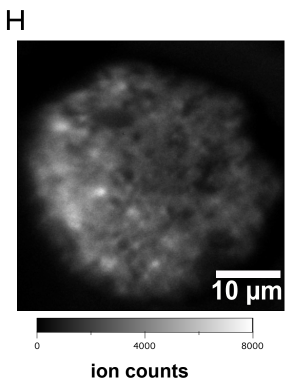
Coordinated sample analyses: Organics, Minerals, Isotopes

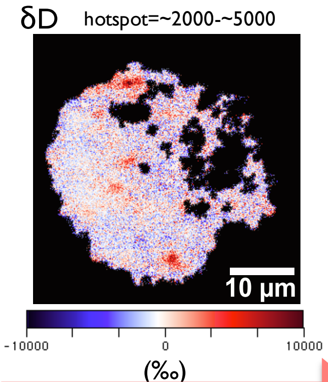
① Electron microscopy
[observation, elemental analysis]



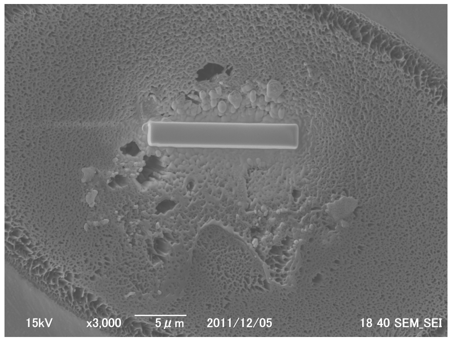
② Embedded in gold plate

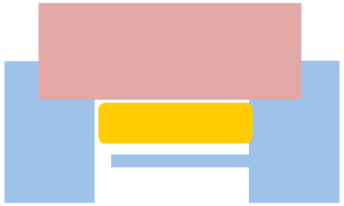
③ Secondary ion mass spectrometry



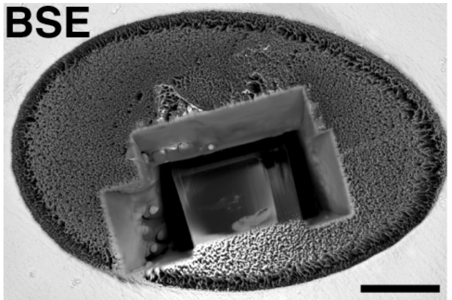


④ Tungsten protection

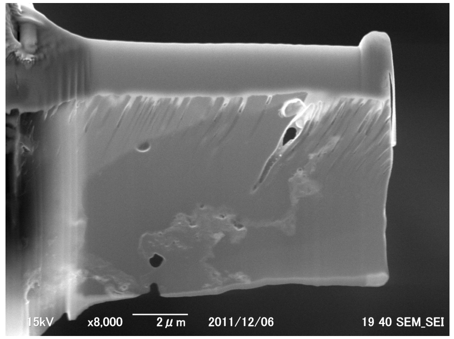


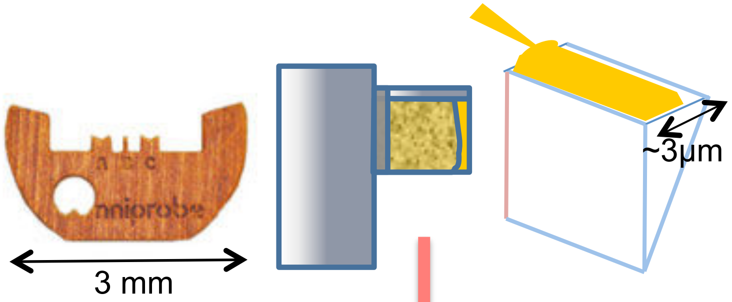


⑤ Focused ion beam extraction



⑥ Ultrathin section
(200 nm thickness)

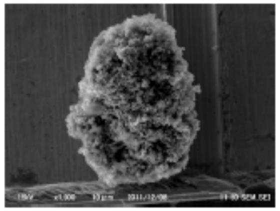
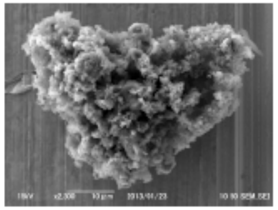
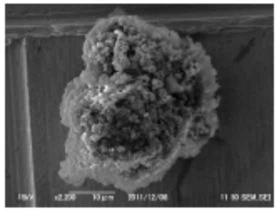
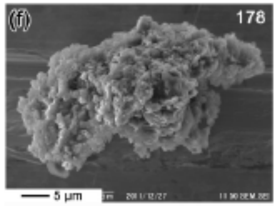
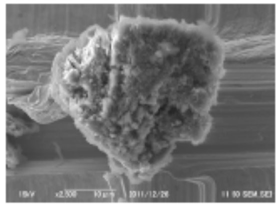
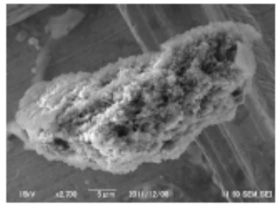




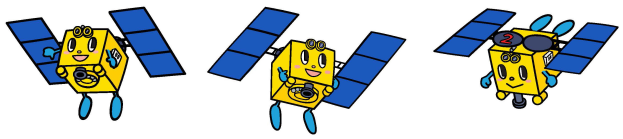
⑦ Synchrotron-based X-ray absorption spectroscopy
[Organic molecular compositions]

⑧ Electron microscopy
[Detailed observations of minerals]

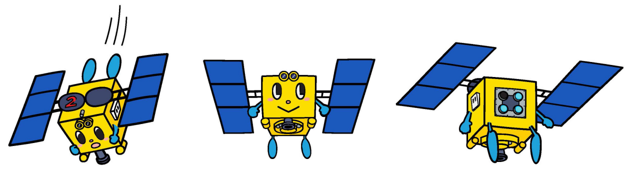
Characteristic features of minerals and organic materials in anhydrous and hydrous Antarctic micrometeorites

	CP MMs (anhydrous)			Fluffy fine grained MMs (hydrous)		
Sample ID	D10IB009	D10IB356	D10IB004	D10IB178	D10IB163	D10IB017
						
Mineralogy	GEMS, Metal, Sulfide, Olivine, Low-Ca pyroxene	GEMS, Metal, Sulfide, Olivine, Low-Ca pyroxene	GEMS, Metal, Sulfide, Olivine, Low-Ca pyroxene	Amorphous silicate, Olivine, Low-Ca pyroxene, Fe-rich saponite, Minor Fe-rich serpentine	Olivine, Low-Ca pyroxene, Fe-rich saponite, Minor Fe-rich serpentine	Olivine, Low-Ca pyroxene, Fe-rich saponite, Minor Mg-rich serpentine, Magnesite
Organic chemistry	Carboxyls (COOH), Aliphatic, Nitrile (CN) or N-heterocycles Abundant globules	COOH, Aliphatic	Aromatic, Aromatic ketone, COOH Chondritic IOM-like	–	Aromatic, Aromatic ketone, COOH Chondritic IOM-like One globule	Aromatic, Aromatic ketone, COOH Chondritic IOM-like
Isotope	δ15N = ~600‰–1,000‰ δD = ~8,000‰–1,0000‰	–	δ15N = ~300‰ δD = normal	–	–	–
Aqueous alteration	No	No	No	Weak	Weak	Moderate

(Noguchi et al. 2017; Yabuta et al. 2018)



Summary



1. Organic molecules in primitive small bodies are important building blocks of Solar System and Life.

2. Comparative study of chemical compositions of organic materials from small bodies in different evolution stages enables comprehensive understanding the chemical history of the early Solar System.

3. The advantages of sample return missions are ;
   i) to collect samples from the known location
   ii) to gain the intact compositions without terrestrial contamitaion/alteration
   iii) to unveil the information of volatiles which meteorites might have lost
   iv) to search for unknown extraterrestrial materials.

3. Hayabusa2 will be the first sample return mission to C-type near Earth asteroid, Ryugu, which aims to understand the co-evolution of organics, water, and minerals.

4. Multi-scale small body science between observation and sample analysis is a new approach for maximizing the achievements from space missions.