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

(Credit: JAXA, University of Tokyo & collaborators)

Hikaru Yabuta
(Dept. Earth and Planetary Systems science, Hiroshima University)
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)
Journey of Hayabusa 2

December 3, 2014
Launch

December, 2018
Arrival

18-month observation &
Collect the surface sample

June, 2018

December, 2019
Leaving

December, 2020
Return to the Earth

Sample analyses

December, 2019
Leaving

Make an artificial crater

Hurl impactor into the asteroid

(Credit: JAXA)
Important roles of organic molecules in the early Solar System

**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

- **Chondrite**
  - Enstatite chondrite
  - Ordinary chondrite
  - Carbonaceous chondrite

- **Achondrite**

- **Martian**
- **Lunar**
- **Iron**
- **Stony-iron**
- **Stony**

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

Organics and water in the early Solar System are preserved

Undifferentiated meteorites
- Enstatite chondrite
- Ordinary 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 systematic investigations of asteroids and comets in different evolution stages.
**Organic compounds in primitive carbonaceous chondrite**

**Soluble organic compounds**
- Carboxylic acids +++
  (mono-, di-, hydroxy-)
- Amino acids ++
- Alcohols ++
- Aldehydes ++
- Ketones ++
- Amides ++
- Amines ++
- PAHs ++
- Aliphatic hydrocarbons ++

**Acid-Insoluble macromolecular organic solid (IOM)**

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

10 – 1000 mg

Solvent / Water extraction

2 – 5 wt% total organic carbon

ca. 1 wt%

**Glavin, Alexander, Aponte, Dworkin, Elsila and Yabuta, 2018**

(C100H75N4O17S3)

Unidentified compounds
(Schmitt-Kopplin et al. 2010)
How to characterize organic molecules..?

“Anatomy” of meteorites

Extraction/Isolation

Interaction of light and materials

Interaction of magnetic field and materials

Measuring weight

Weight scale

X-ray

MRI

Observation

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

**Extraction/Isolation**

**Chromatography**

**Measuring “mass”**

1. **Isotope mass spectrometry**

2. **X-ray (Synchrotron X-ray), Laser, Infrared**

**Interaction of light and materials**

**Interaction of magnetic field and materials**

**Observation**

- **Electron microscopy**
- **Polarized light microscopy**

- **NMR**
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 ($^{13}\text{C}/^{12}\text{C}$), hydrogen (D/H), and nitrogen ($^{15}\text{N}/^{14}\text{N}$)
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).
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,

\[ \text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H} \]  
(Ion-molecule reaction)

\[ \text{H}_3^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2 \]  
(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°C) 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.

<table>
<thead>
<tr>
<th>Classification of chondrite</th>
<th>Petrologic types</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aqueous alteration</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Carbonaceous (C)</td>
<td></td>
</tr>
<tr>
<td>CI</td>
<td></td>
</tr>
<tr>
<td>CM</td>
<td></td>
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<td>CR</td>
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<td>CH</td>
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<td>CV</td>
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<tr>
<td>CO</td>
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<tr>
<td>CK</td>
<td></td>
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<tr>
<td>Ordinary (O)</td>
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<tr>
<td>H</td>
<td></td>
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<tr>
<td>L</td>
<td></td>
</tr>
<tr>
<td>LL</td>
<td></td>
</tr>
<tr>
<td>Enstatite (E)</td>
<td></td>
</tr>
<tr>
<td>EH</td>
<td></td>
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<tr>
<td>EL</td>
<td></td>
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<tr>
<td>R</td>
<td></td>
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<tr>
<td>K</td>
<td></td>
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</tbody>
</table>

- Organics have been studied
- Hayabusa2 (C-type asteroid)
- Hayabusa (S-type asteroid)

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lee, %</th>
<th>δx (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orgueil (CI1)</td>
<td>15.2</td>
<td>±4.0 (8)</td>
</tr>
<tr>
<td>Murchison (CM2)</td>
<td>18.5</td>
<td>±2.6 (20)</td>
</tr>
<tr>
<td>LEW 90500 (CM2)</td>
<td>3.3</td>
<td>±1.8 (23)</td>
</tr>
<tr>
<td>LON 94102 (C2)</td>
<td>2.4</td>
<td>±4.1 (8)</td>
</tr>
<tr>
<td>QUE 99177 (CR2)</td>
<td>0.3</td>
<td>±2.1 (8)</td>
</tr>
<tr>
<td>EET 92042 (CR2)</td>
<td>-1.0</td>
<td>±4.3 (8)</td>
</tr>
<tr>
<td>Racemic standard†</td>
<td>-2.3</td>
<td>±1.3 (14)</td>
</tr>
</tbody>
</table>

Glavin and Dworkin (2009)

**Insoluble OM**

Solid state $^{13}$C NMR

**Aqueous alteration (low T Chemical oxidation)**

Cody and Alexander (2005)
Comparative meteorite organic chemistry
- Thermal metamorphosed asteroid parent bodies -

Carbon-XANES of IOM

Graphene

Aromatic C 1s-π*

Graphite

Indarch (EH4) 948°C
Isna (CO3.7) 700°C
Allende (CV3.6) 554°C
Bishunpur (LL3.15) 551°C
ALHA77003 (CO3.5) 425°C
Mokoia (CV3.2) 423°C
Kaba (CV3.1) 371°C
Semarkona (LL3.0) 203°C
ALHA77307 (CO3.0) 203°C

Raman of IOM

X ray absorption feature of highly conjugated sp² carbon (e.g., graphene) can be used as a thermometer of parent bodies (Cody et al. 2008)

Bonal et al. (2007)

Cody, Yabuta, Alexander et al. (2008)
Advantages of small bodies exploration missions

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

Hayabusa1 (2010)
S-type asteroid Itokawa

STARDUST (2006)
Comet 81P/Wild 2 dusts

OSIRIS-REx (2016-)
B-type asteroid Bennu

Rosetta (2004-)
Comet 67P/Churyumov-Gerasimenko

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

S-type near Earth asteroid Itokawa

Release 051101-1 ISAS/JAXA

Ordinary LL5-6 chondrite

Organics and water were not detected

- Thermal metamorphism
- Collision (impact)
- Space weathering
- Rubble-pile
- Formation of Itokawa

Parent body

Surface (heated at 600°C)
Center (heated at 800°C)

Formation of Itokawa parent body (> 20 km)

Separation (ca. 100 m)

Collision (impact)

Rubble-pile

Space weathering

Organics and water 150 year - 300 million years
Scope of Hayabusa2 multi-scale asteroid science

Remote sensing

- Global geology and topography
- Landing site selection
- Both roles of observation and sample analyses

Evolution

MASCOT hopping lander (DLR&CNES)

Sample analyses

- Quantitation of elemental, isotopic, mineralogical, petrological, and molecular compositions

Origin, Age

Heterogeneity

Altitude (km)

Bulk compositions

Origin, Age

km

m

mm

μm

nm
Onboard instruments of Hayabusa2

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

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>CP MMs (anhydrous)</th>
<th>Fluffy fine grained MMs (hydrous)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D10IB009</td>
<td>D10IB178</td>
</tr>
<tr>
<td></td>
<td>D10IB356</td>
<td>D10IB163</td>
</tr>
<tr>
<td></td>
<td>D10IB004</td>
<td>D10IB017</td>
</tr>
</tbody>
</table>

**Mineralogy**
- GEMS, Metal, Sulfdie, Olivine, Low-Ca pyroxene
- GEMS, Metal, Sulfdie, Olivine, Low-Ca pyroxene
- GEMS, Metal, Sulfdie, 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 Mg-rich serpentine
- Olivine, Low-Ca pyroxene, Fe-rich saponite, Minor Mg-rich serpentine

**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

**Isotope**
- $\delta^{15}N = -600\%o$ to $1,000\%o$
- $\delta^2 = -8,000\%o$ to $1,000\%o$
- $\delta^{15}N = -300\%o$
- $\delta^2 = \text{normal}$
- $\delta^{15}N = -300\%o$
- $\delta^2 = \text{normal}$
- $\delta^{15}N = -300\%o$
- $\delta^2 = \text{normal}$

**Aqueous alteration**
- No
- No
- No
- Weak
- Weak
- Moderate

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