Chapter 3
Chemical Interactions Among Organics, Water, and Minerals in the Early Solar System

Hikaru Yabuta

Abstract Chondritic meteorites are thought to have originated from primitive small bodies of the Solar System formed 4.5 billion years ago. Investigations on origin and chemical evolution of organic molecules in the early Solar System have been extremely improved through the chemical analyses of carbonaceous chondritic meteorites, which are derived from primitive small bodies. While carbonaceous chondrites have provided a number of significant insights on possible building blocks of life as well as the relationship between the compositions of organics and the parent body aqueous processes, precursors and locations for formation of meteoritic organics are yet to determine. It is because most of the information on the earlier stage of the Solar System history was erased by extensive degrees of aqueous alteration on the meteorite parent bodies. For constraining the origin of organic molecules in the early Solar System, it is necessary to investigate more primitive Solar System materials available to us than the typical carbonaceous chondrites, as well as it is very important to correctly determine the different evolution stages by observation to reveal the relationships between organic chemistry and mineralogy.

Through the coordinated analyses of anhydrous and hydrated Antarctic micrometeorites (AMMs), we depicted a scenario that highly aromatic organic macromolecule (a.k.a. insoluble organic material) in carbonaceous chondrites could be a hydrolysis product of N- and/or O-rich macromolecule in a small icy body, which were formed via photochemistry in interstellar clouds or outer solar nebula. The hydrolysis probably occurred during the early stage of parent body aqueous alteration. An ultracarbonaceous AMM (UCAMM), which is highly C-rich materials and cometary origin, contains amorphous silicate grains (so-called glass with embedded metal and sulfides [GEMS]) depleted in Mg and S. The altered GEMS indicates that the cometary parent body experienced very weak aqueous alteration caused by planetesimal shock.

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3.1 Introduction: Enigma on Origin of Organic Molecules in the Carbonaceous Chondrites

Asteroids and comets, the remnants that did not grow into large bodies during the history of planetary formation, preserve the precursor materials in the early Solar System. These small bodies are thought to have delivered organic molecules and water to the Earth and other planets, which are necessary for planetary habitats (Chyba and Sagan 1992). Both asteroids and comets are originally derived from accretion of interstellar dusts (Fig. 3.1), which are thought to be micron-sized particles consisting of an amorphous silicate core, refractory organic inner mantle, and an outer mantle of ice (Greenberg and Li 1997). The volatile components of the dust mantle were formed by condensation of atoms and molecules in the gas phase and on dust surfaces in interstellar clouds (e.g., Tielen and Hagen 1982; Ehrenfreund and Charnley 2000; Öberg 2016). Through the subsequent photochemical reactions in interstellar dense cloud, a variety of molecules were produced (e.g., Sandford 1996; Bernstein et al. 1999; Nuevo et al. 2011). After interstellar cloud collapsed to form a young Sun, a protoplanetary disk was formed. In a protoplanetary disk, distributions of temperature and UV flux yielded the chemical diversity of the dusts, followed by dust growth to form planetesimals (Nomura et al. 2007; Ciesla and Sandford, 2012). As a result, rocky planetesimals, so-called asteroids, were formed in inner Solar System, whereas icy planetesimals, so-called comets, were formed in outer Solar System, such as Kuiper Belt and Oort cloud (Fig. 3.1). Subsequently, asteroids experienced internal heating due to the decay of short-lived radiogenic nuclides (e.g., ^{26}Al). This event caused aqueous alteration (0–150 °C) (e.g., Brearley 2006, and references therein) and thermal metamorphism (200–700 °C) (e.g., Huss et al. 2006, and references therein) in the asteroid parent bodies, which lasted for several million years (e.g., Fujiya et al. 2013). Asteroids also experienced shorter duration thermal metamorphism induced by impacts. Both secondary processes and radial distance resulted in chemical compositions of asteroids, which are reflected by the reflectance spectral types of asteroids: stony objects (S-type), dark carbonaceous objects (C-type), very dark objects without spectral feature of phyllosilicates (D-type), metallic objects (M-type), and so on (Tholen and Barucci 1989) (Fig. 3.1). Comets could experience these secondary processes as well, although they were less altered due to the low inner temperature of icy bodies. Conditions, timescales, and durations of the secondary processes depend on the sizes, structure, and heat sources of parent bodies, which increased chemical diversity in asteroids and comets. Thus, the Solar System can be said to be “a chemical factory” of life’s building blocks.

To date, primitive carbonaceous chondrite meteorites have been frequently investigated for understanding origin and evolution of organic molecules in the early Solar System. In general, carbonaceous chondrite contains several weight% total organic carbon, which can be divided into soluble (free) and acid-insoluble

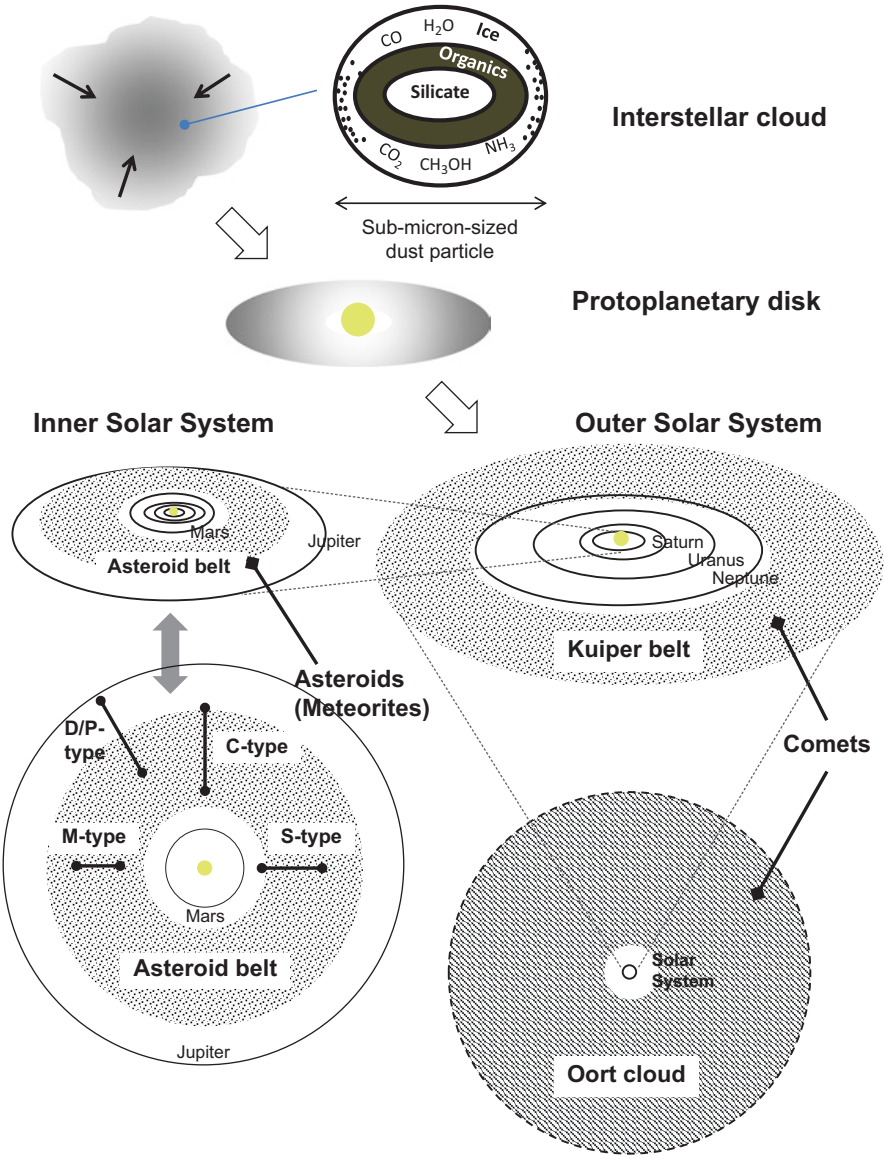


Fig. 3.1 Outline of Solar System evolution from interstellar clouds to asteroids and comets

(refractory) fractions. The insoluble organic matter (IOM) accounts for more than a half of total organic carbon. Although the intact molecular structure of IOM is still unknown due to its complex, macromolecular configuration, IOM is composed of aromatic molecular network crosslinking with short-branched aliphatic chains and various oxygen functional groups (Cody et al. 2002; Glavin et al. 2018) (Fig. 3.2). Soluble organic molecules have been historically very well studied represented by

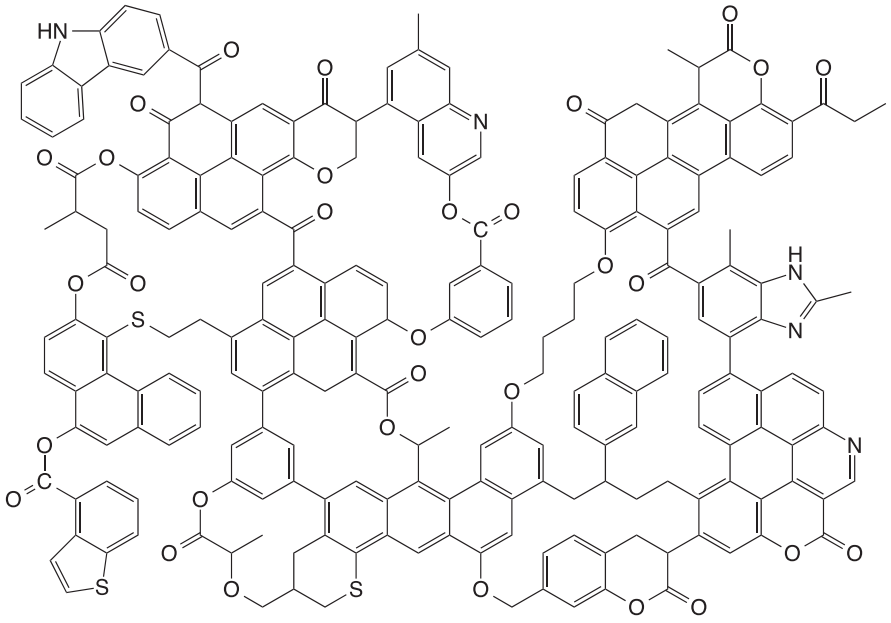


Fig. 3.2 A model of the molecular structure of the IOM in primitive carbonaceous chondrites (i.e., CM group) that is consistent with what is known about its functional group chemistry (Glavin et al. 2018)

amino acids and a variety of compounds of biochemical interests (Pizzarello et al. 2006; Glavin et al. 2018). The total abundances of the individual molecules are very low (from ppb to ppm levels), and the sum abundance of the molecules found does not exceed the half of total organic carbon, implying that there still exist unidentified molecules (Schmitt-Kopplin et al. 2010).

Through 50 years of the studies on meteoritic organics, a number of hypotheses have suggested for origin of refractory organic macromolecules in carbonaceous chondrites. Alexander et al. (2007) suggested that IOM is derived from the refractory organics formed via photochemistry in the extreme cold environments, such as interstellar cloud or outer solar nebula, based on the observed enrichments of deuterium (D) and ^{15}N in IOM in meteorites and interplanetary dust particles (IDPs). On the other hand, the potential roles of Fischer-Tropsch (FT) synthesis (e.g., Hill and Nuth 2003) and irradiation reaction of nebular gas (i.e., CO, N_2, H_2O) (Kuga et al. 2015) for the formation of meteoritic IOM have been argued. It was recently suggested that the first IOM might have been formed via hydrothermal reaction of formaldehyde and ammonia on the meteorite parent body based on the spectroscopic similarity between the experimentally synthesized products and meteoritic IOM (Cody et al. 2011; Kebukawa et al. 2013). Thus, there are multiple possible scenarios proposed, and the consensus has yet to be reached. Since there may be diversity in precursor molecules and locations of organic materials, it is very important to determine the specific sources for specific molecules found in individual meteorites and other extraterrestrial samples.

3.2 A Missing Link in the Early Solar System: Chemical Evolution of Organic Molecules from Solar Nebula to Planetesimals

Most of carbonaceous chondrites experienced extensive aqueous alteration on their parent bodies, and thus it is hard to find characteristics of precursor organic materials from the meteorites. It is therefore necessary to investigate more primitive Solar System materials than the typical carbonaceous chondrites, to constrain the origin of organic molecules in the early Solar System. Those pristine samples include comets and comet-derived materials, such as cometary dusts, stratospheric interplanetary dust particles (IDPs), Antarctic micrometeorites (AMMs), etc., since comet is an icy body formed at very low temperature that preserves the materials in the interstellar cloud and solar nebula under better condition (Yabuta et al. 2018). Comet dust sample return mission, Stardust, detected O- and N-rich refractory organic macromolecules, glycine and amines, from the comet Wild 2 dust particles for the first time (e.g., Sandford et al. 2006; Cody et al. 2008; Glavin et al. 2008). The mission to rendezvous with Jupiter-family comet, Rosetta, for the first time discovered dark refractory organic materials on the surface of 67P/Churyumov-Gerasimenko (e.g., Quirico et al. 2016). These results supported the relationship between comets and IDPs. In particular, chondritic porous (CP)-type IDPs have been regarded as short-period comet origin, based on their fragile structure, higher amounts of carbon and volatiles than those in meteorites, and amorphous silicate so-called glass with embedded metal and sulfides (GEMS) (Keller and Messenger 2011). The IDPs show a wide range of hydrogen and nitrogen isotopic compositions (Messenger 2000).

Another clue is the chemical relationship between organics and minerals. For example, the presence of GEMS is a good indicator of the stage prior to aqueous activities on the parent body, since the amorphous silicate is rapidly changed to hydrated silicate minerals when it is exposed to liquid water (Nakamura-Messenger et al. 2011). Thus, the organic materials associated with GEMS could be the precursor materials in interstellar or solar nebula (Keller and Messenger 2011). In contrast, hydrated silicate mineral is a robust indicator of aqueous process in the parent body, and the organics associated with those minerals could be a secondary alteration product. Those classifications based on mineralogy would enable correct understanding of chemical evolution of organic molecules during the process from solar nebula to planetesimals.

This chapter will address the precursors of organic materials and minerals in planetesimals, through the reviews of our recent investigations using the AMMs collected from the surface snow near the Dome Fuji Station, Antarctica. The AMMs include the samples of cometary origin, as Noguchi et al. (2015) discovered chondritic porous AMMs containing GEMS, enstatite whiskers, and organic nanoglobules, which were characteristic to CP IDPs collected at the stratosphere (Fig. 3.3). We carried out coordinated comprehensive chemical analyses of the AMMs, for maximizing the data of organic chemistry, mineralogy, and isotope cosmochemistry from a single AMM particle.

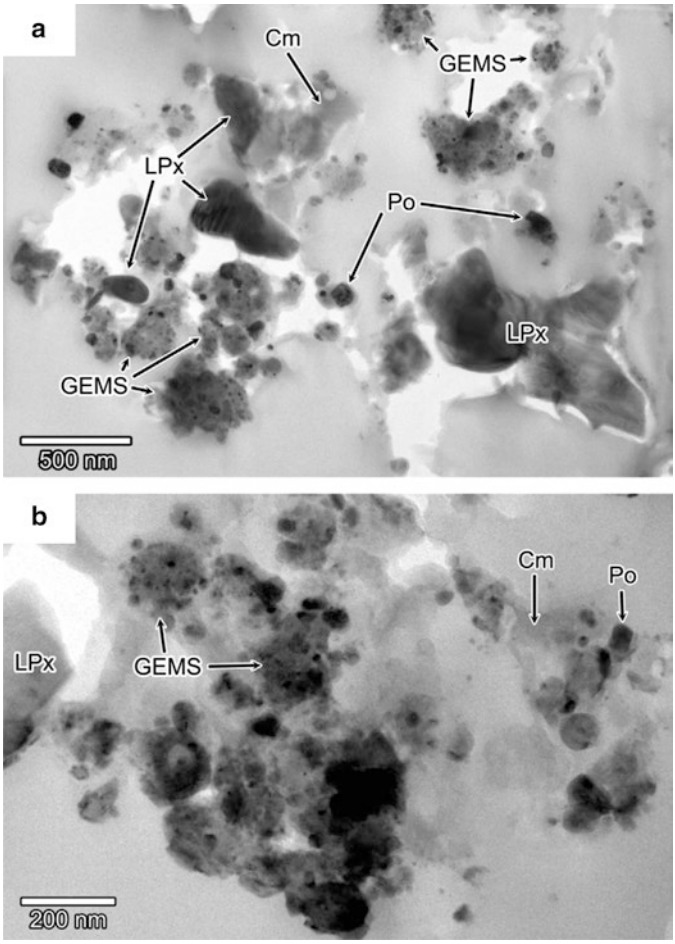


Fig. 3.3 Bright-field image of an ultrathin section of (**a**) a present CP MM D05IB13 and (**b**) a CP IDP L2021. The CP MM contains abundant GEMS. Low-Ca pyroxene (LPx) and pyrrhotite (Po) (Noguchi et al. 2015)

3.3 Different Stages of Parent Body Aqueous Alteration Recorded in Antarctic Micrometeorites

Figure 3.4 shows transmission electron microscopy (TEM) images of the ultrathin sections of two AMMs. AMMs containing GEMS (Fig. 3.4a) were classified as anhydrous micrometeorites (MMs). The organic materials ($\sim 10 \times 3$ μm) account for a major part of the anhydrous MM, and they are associated with olivine and pyrrhotite. On the other hand, AMMs containing phyllosilicate (clay minerals) were classified as hydrous MMs (Fig. 3.4b). The amounts of organic materials are small compared to those in the anhydrous MM, and they are associated with phyllosilicate

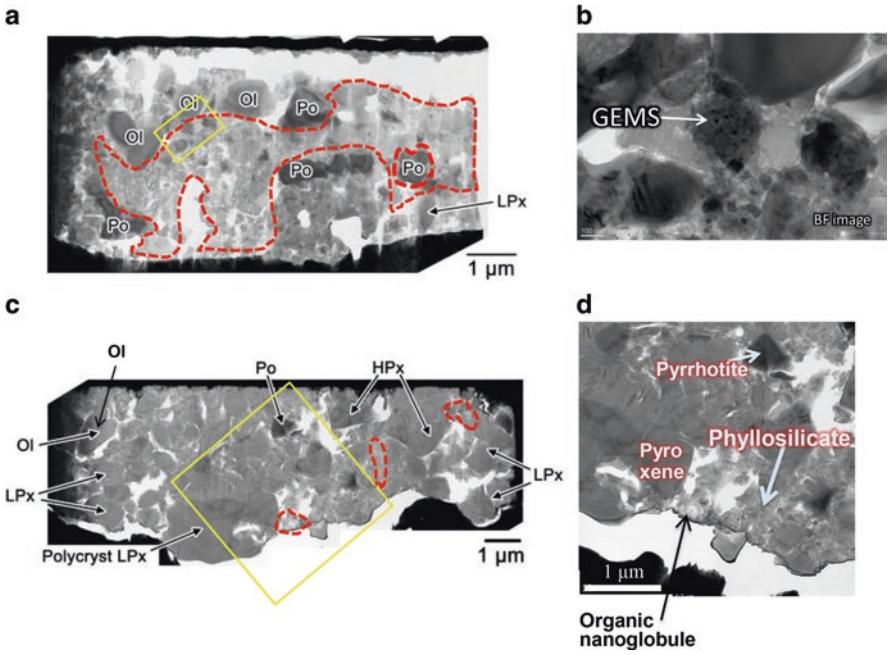


Fig. 3.4 TEM images of ultrathin sections of the AMMs obtained by focused ion beam (FIB). Coarse-grained minerals and aggregates of minerals are labeled. (**a**) D10IB009, (**b**) an enlarged image of yellow square region of (**a**, **c**) D10IB163, (**d**) an enlarged image of yellow square region of (**c**) (Noguchi et al. 2017). *Abbreviations*: *Ol* olivine, *LPx* low-Ca pyroxene, *HPx* high-Ca pyroxene, *GEMS* glass embedded metal and sulfide, *Po* pyrrhotite. The organic materials are surrounded by red broken lines

and pyroxene. This difference probably indicates that the precursor organic materials, which were present before planetesimal formation, were depleted and modified by parent body aqueous alteration.

X-ray absorption near-edge structure (XANES) is a method to assess the types of the organic functional groups constituting a macromolecular sample (Cody et al. 2008). XANES spectra are obtained by scanning x-ray energy and measuring the absorbed x-ray intensity specific to the electronic structures (chemical bonds) of the atom that absorbed the x-ray (Stöhr 1991). The absorbed x-ray intensity corresponds to photoexcitation of carbon 1 s electrons to unoccupied electronic state. Combination with a scanning transmission x-ray microscope (STXM) with high spatial resolution (<30 nm) enables the measurement of XANES spectra of submicron-sized regions of organic macromolecules. Application of STXM-XANES to AMMs revealed that organic material in the anhydrous MM is enriched in N- and O-bearing functional groups, such as nitrile (−C≡N) or purine-pyrimidine, carboxyl groups (-COOH), and aliphatic carbon (-CH_x) (Fig. 3.5). This composition was prominent particularly in the regions indicated with white arrows. According to TEM observation, some of the regions were organic nanoglobules.

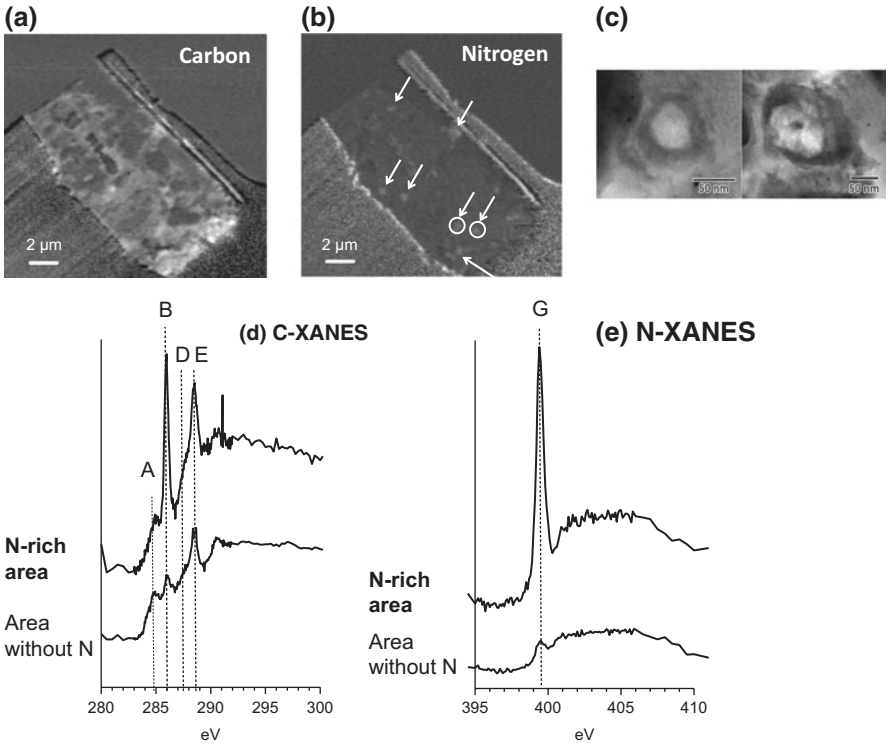


Fig. 3.5 (**a**) Carbon- and (**b**) nitrogen-elemental maps of anhydrous AMM (D10IB009) acquired by a scanning transmission x-ray microscope (STXM) (optical density images). Nitrogen-enriched areas are indicated by white arrows. Circle regions correspond to (**c**) bright-field images of organic nanoglobules. (**d**) Carbon- and (**e**) nitrogen-K edge XANES spectra of a nitrogen-enriched area and an area without enrichment of nitrogen in D10IB009 (Noguchi et al. 2017). Peak A, 1sπ* transition of aromatic carbon (C=C*) at 285 eV; peak B, 1sπ* transition of N-heterocycles (C-N*=C) and/or nitrile (C≡N*) at 286 eV; peak D, 1s3p/s* transition of aliphatic carbon at CHx-C at ~287.5 eV; peak E, 1sπ* transition of carbonyl carbon in carboxyl or ester (OR(C*=O)C) at ~288.4 eV; peak G, 1sπ* transition of N-heterocycles (C-N*=C) and/or nitrile (C≡N*) at 399.4 eV

From this anhydrous MM, enrichments of D ($\delta D = +8000 \sim +10{,}000‰$) and ^{15}N ($\delta^{15}N = +600 \sim +1000‰$) were detected by secondary ion mass spectrometry (SIMS) (Fig. 3.6). These values were comparable with the pristine IDPs (e.g., Messenger 2000; Busemann et al. 2009) and comet Wild 2 dust particles (e.g., Mckeegan et al. 2006; De Gregorio et al. 2010). It has been suggested that the isotopic anomalies of H in the small body organic materials are derived from molecular deuterium enrichment caused by ion-molecule reactions under very low temperature (10–50 K) in interstellar molecular clouds (e.g., Millar et al. 1989) and in protoplanetary disks (e.g., Aikawa and Herbst, 1999). Although the sources of ^{15}N enrichment in the small body organic materials are clearly determined, contribution of interstellar chemistry is indicated (e.g., Charnley and Rodgers 2002; Aleon and Robert 2004). Thus, it is very likely that organic material from the anhydrous MM

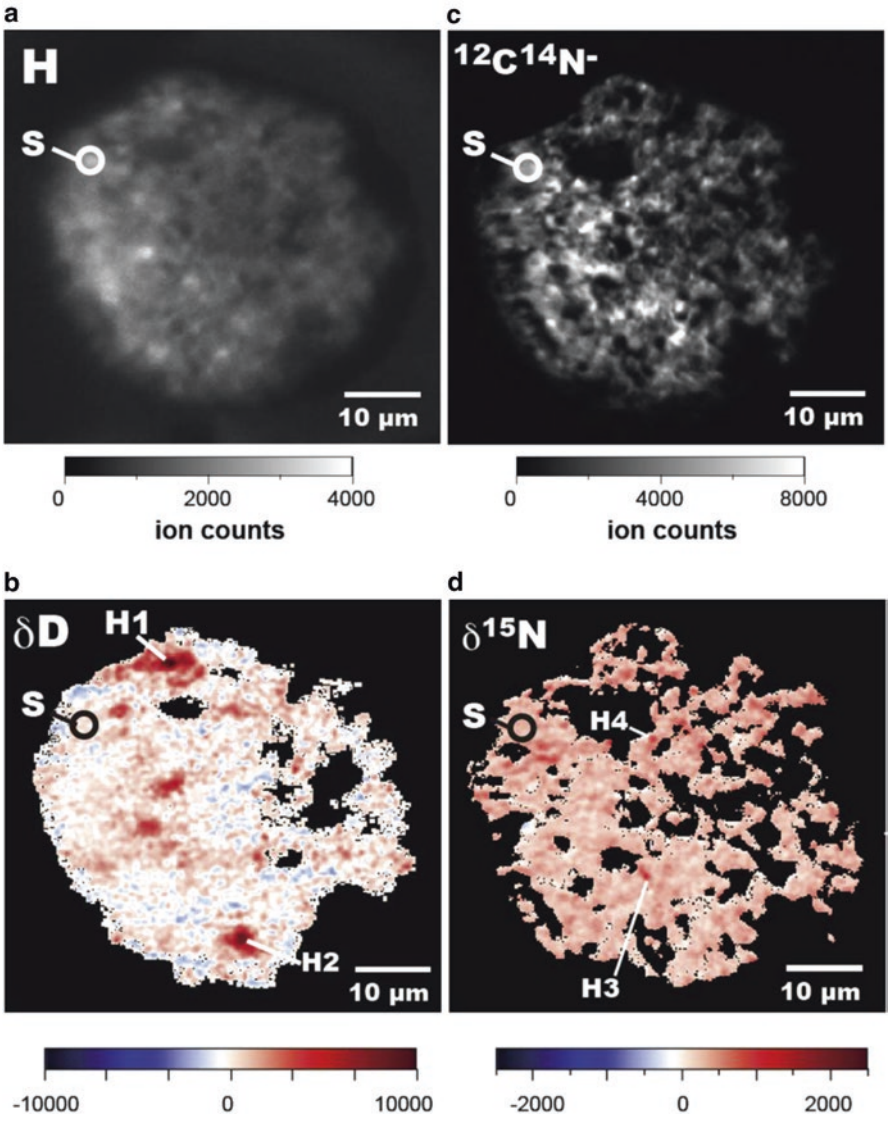


Fig. 3.6 Isotopographs of anhydrous AMM (D10IB009). (**a**) H. (**b**) δD_{SMOW}. H1 and H2 denote δD hotspots (H1, 10,000‰, and H2, 8000‰). (**c**) $^{12}C^{14}N$ and (**d**) $\delta^{15}N_{air}$. H3 and H4 denote $\delta^{15}N$ hotspots (H3, 1000‰, and H4, 600‰). Circles (S) of each image (**a**–**d**) denote the spot analysis area by SIMS to estimate the instrumental mass fractionation (Noguchi et al. 2017)

is originated from interstellar cloud or outer solar nebula. In particular, their isotopic values were comparable with δD of cometary HCN (Meyer et al. 1998) and $\delta^{15}N$ of cometary CN (Schultz et al. 2008), and thus the N- and O-rich functional group chemistry of the anhydrous MM may have been derived from photochemistry of

HCN- or CN-ice. D- and ^{15}N-rich organic nanoglobules may have been also formed during the UV irradiation of ice grains under the cold environment, as suggested by Nakamura-Messenger et al. (2006).

Comparing the C- and N-XANES spectra among the anhydrous and hydrous AMMs and insoluble organic matter (IOM) in Murchison carbonaceous chondritic meteorite, all the samples showed typical three peaks of aromatic carbon, aromatic ketone, and carboxyls with a shoulder of aliphatic carbon (Fig. 3.7). However, the relative peak intensities were slightly different between anhydrous and hydrous MMs, i.e., the peaks of carboxyl groups are higher in the two anhydrous MMs compared to those of hydrous MMs. On the other hand, the spectra of the hydrous MMs were enriched in aromatic carbon, which is similar to those of Murchison IOM. Exceptionally, the spectrum of anhydrous AMM-D10IB004 is rather similar to those of hydrous AMMs.

Characteristic features of organic materials and minerals in the AMMs are summarized in Table 3.1. All the three anhydrous AMMs (D10IB009, D10IB356, D10IB004) characterized by GEMS, Fe-Ni metal, and sulfide are very likely cometary origin having no record of aqueous alteration. Based on the presence of amorphous silicate and minor Fe-rich serpentine, hydrated AMM (D10IB178) is derived from carbonaceous CR3 chondrite-type parent body that experienced weak aqueous

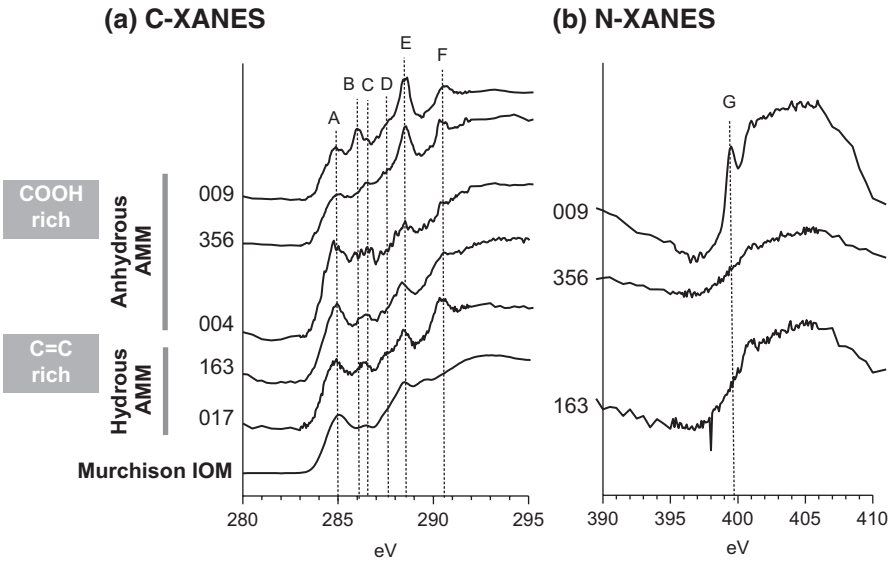
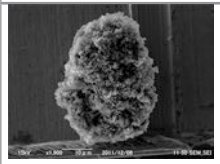
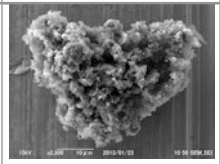
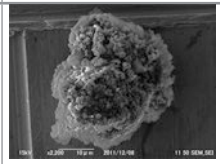
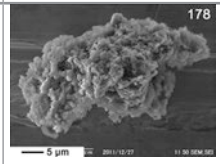
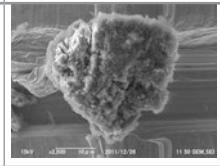
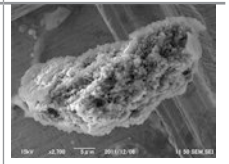


Fig. 3.7 Averaged carbon K edge – XANES spectra of five AMMs (D10IB009, 356, 004, 163, and 017) and Murchison meteorite IOM (Noguchi et al. 2017). Peak A, 1sπ* transition of aromatic carbon (C=C*) at 285 eV; peak B, 1sπ* transition of N-heterocycles (C-N*=C) and/or nitrile (C≡N*) at ~286.6 eV; peak C, 1sπ* transition of vinyl-keto carbon (C=C-C*=O) at ~286.6 eV; peak D, 1s3p/s* transition of aliphatic carbon at CHx-C at ~287.5 eV; peak E, 1sπ* transition of carbonyl carbon in carboxyl or ester (OR(C*=O)C) at ~288.4 eV; peak F, 1sπ* transition of carbonate or carbonic acid (RO(C=O)OR′) at 290.6 eV

Table 3.1 Characteristic features of organic materials and minerals in AMMs investigated in Noguchi et al. (2017)

	CP AMMs (anhydrous)			Fluffy fine grained AMMs (hydrous)		
Sample ID	D10IB009	D10IB356	D10IB004	D10IB178	D10IB163	D10IB017
						
Mineralogy	GEMS, Fe-Ni metal, Sulfide, Olivine, low-Ca pyroxene	GEMS, Fe-Ni metal, Sulfide, Olivine, low-Ca pyroxene	GEMS, Fe-Ni 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**	**COOH, Aliphatic**	**Aromatic, COOH Aromatic ketone, COOH Chondritic IOM-like**	**–**	**Aromatic, COOH, Aromatic ketone, Chondritic IOM-like**	**Aromatic, COOH, Aromatic ketone, Chondritic IOM-like**
	Abundant globules				One globule	
Isotope	δ15N = ~600-1000‰	–	δ15N = ~300‰	–	–	–
	δD = ~8000-10000‰		δD = normal			
Aqueous alteration	No	No	No	Weak	Weak	Moderate

alteration. The other hydrated AMMs (D10IB163 and D10IB017) contain abundant coarse-grained anhydrous minerals with lesser amounts of hydrate silicate minerals which also experienced weak to moderate aqueous alteration. Assuming that those AMMs are reflected by contiguous evolution stages, it is suggested that organic materials containing aliphatic carbon, COOH, and/or N-heterocycles in the anhydrous AMMs reflect the precursor molecule that were formed in interstellar cloud or outer solar nebula. The O- and N-rich molecular compositions could have been hydrolyzed by the subsequent parent body aqueous alteration and converted to highly aromatic, meteoritic organics like compositions as seen in hydrated AMMs. The anhydrous MM (D10IB004) may have experienced a very weak degree of aqueous process which did not affect silicate but sufficiently promoted modification of organic materials. The processes could occur in very primitive icy asteroids that bear comet-like feature, e.g., D-type asteroids.

3.4 Ultracarbonaceous Antarctic Micrometeorites: New Type of Cometary Material?

Ultracarbonaceous Antarctic micrometeorites (UCAMMs) are unique extraterrestrial materials that contain a large amount of carbonaceous materials (Fig. 3.8). These MMs were for the first time discovered by Nakamura et al. (2005). One of the UCAMMs contains light noble gases with a solar wind origin, and two are abundant in presolar grains (Yada et al. 2008; Floss et al. 2012). Other UCAMMs have been independently found from the Concordia Station, Antarctica, by the French-Italian team. It was suggested that organic materials in the UCAMMs could be formed in the outer solar nebula (Duprat et al. 2010), based on the identification of crystalline silicates which were thought to be derived from solar origin and are associated with D-rich organic materials. Dartois et al. (2013) reported D- and ^{15}N-rich UCAMMs

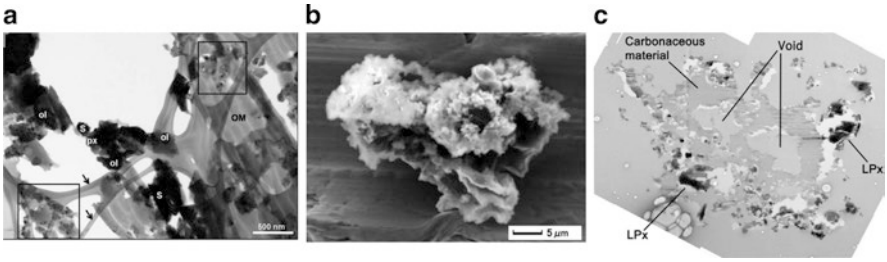


Fig. 3.8 (**a**) Bright-field (BF) TEM image of a UCAMM collected from Concordia Station. The organic materials are indicated as black arrows (Duprat et al. 2010). (**b**) Secondary electron image of the UCAMM (D05IB80) placed on a platinum plate (Yabuta et al. 2017), (**c**) BF-TEM images of ultramicrotomed sections of the UCAMM D05IB80 (Yabuta et al. 2017). *Abbreviations*: *ol* Mg-rich crystalline olivine, *px* Mg-rich crystalline pyroxene, *S* Fe-Ni sulfides, *OM* organic material, *LPx* low-Ca pyroxene. GEMS-like objects are surrounded by black squares

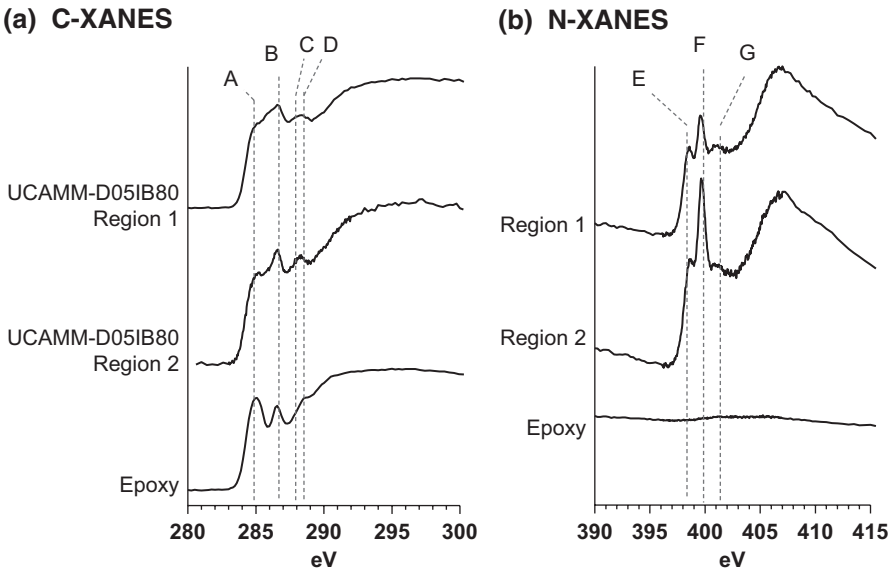


Fig. 3.9 (**a**) C- and (**b**) N-XANES spectra of the regions 1 and 2 of the UCAMM D05IB80 and epoxy. Peak A, 1sπ* transition for aromatic carbon (C=C*) at 285.1 eV; peak B, 1sπ* transition for N-heterocycles (C-N*=C), nitrile (C≡N*), or vinyl-keto carbon (C=C-C*=O) at ~286.6 eV; peak C, 1s3p/s* transition for aliphatic carbon at CHx-C at ~287.5 eV; peak D, 1sπ* transition for carbonyl carbon in amide (NHx(C*=O)C) at ~288.0–288.2 eV and/or 1sπ* transition for carbonyl carbon in carboxyl or ester (OR(C*=O)C) at ~288.4–288.7 eV; peak E, 1sπ* transition for imine (C=N*) at 398.8 eV; peak F, 1sπ* transition for N-heterocycles (C-N*=C) and/or nitrile (C≡N*) at ~399.7 eV; and peak G, 1sπ* transition for amide (N*Hx(C=O)C) or 1s3p/s* transition for amino (C-N*Hx) at 401.5 eV

and suggested organic material in UCAMMs was formed in the Oort cloud by irradiation of ice rich in CH_4 and N_2.

Most of the UCAMMs have common chemical features that are regarded as cometary origin (Duprat et al. 2010; Dartois et al. 2013; Yabuta et al. 2017). High abundances of GEMS and absence of hydrated minerals are the mineralogical characteristics of UCAMMs, which are clearly distinct from most of primitive carbonaceous chondrites. Organic materials in UCAMMs are larger than 100 times those in primitive carbonaceous chondrites, and they contain a variety of nitrogen-bearing functional groups such as nitrile, aromatic N, amide, and imine (Fig. 3.9) (Yabuta et al. 2017). The N/C ratios of organic materials in UCAMMs are five times higher than those in primitive carbonaceous chondrites (Dartois et al., 2013; Yabuta et al. 2017). As is the case of IDPs, UCAMMs show a wide range of H and N isotopic compositions, from values extremely rich in heavy isotopes (Duprat et al. 2010; Dartois et al. 2013) to normal values with terrestrial levels (e.g., Yabuta et al. 2017).

The N/C and O/C ratios of organic material from UCAMM DO05IB80 are very similar to those of comet Wild 2 dust particles (Fig. 3.10) (Yabuta et al. 2017). On the other hand, the values are very different from those of the UV irradiation

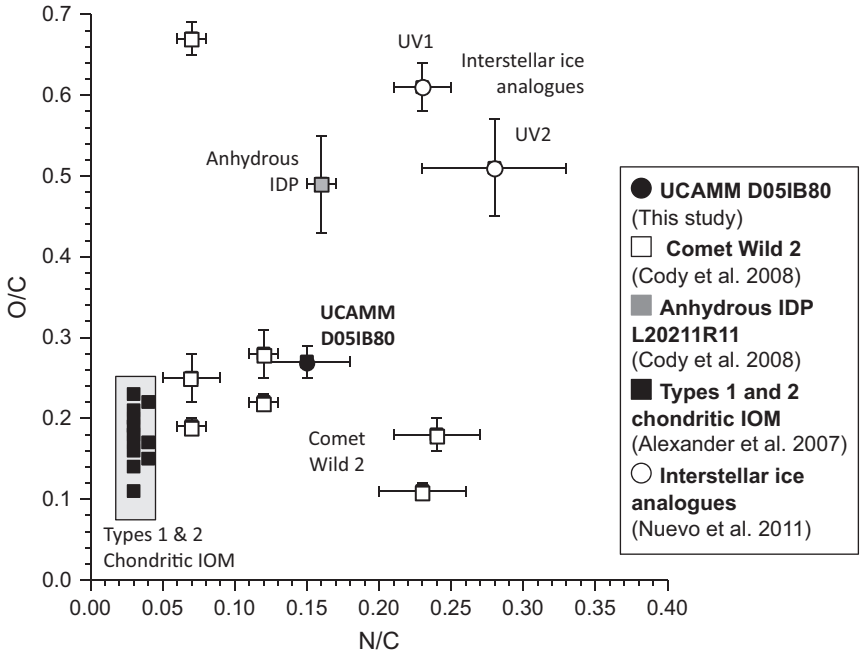


Fig. 3.10 N/C versus O/C ratios of organics in the UCAMM D05IB80 (●, this study), the comet Wild 2 dust particles (□, Cody et al. 2008), the anhydrous IDP L20211R11 (■, Cody et al. 2008), type 1 and 2 chondritic insoluble organic solids (■, Alexander et al. 2007), and the UV irradiation products from interstellar analogues (○, Nuevo et al. 2011) (UV1 H_2O:CH_3OH:CO:NH_3 = 100:50:1:1, UV2 H_2O:CH_3OH:CO:NH_3:C_3H_8 = 100:50:1:1:10). The ratios were estimated from the fitting of C-, N-, and O-XANES spectra (Yabuta et al. 2017)

products from interstellar ice analogues. Thus, interstellar photochemistry alone would not be the process responsible for the formation of the UCAMM. Yabuta et al. (2017) suggested that a very small amount of fluid on a cometary nucleus or icy asteroid must have been necessary for the formation of the UCAMM, based on the following multiple evidences: (i) the presence of sulfur in an entire region of organic materials in UCAMM (organic sulfurization), (ii) deformation and aggregation of organic nanoglobules (change in osmotic pressure) (Fig. 3.10), (iii) inorganic thin layers at the surface of organic materials in UCAMM (precipitation of dissolved ions) (Fig. 3.10), and (iv) depletion of Mg and S from GEMS (Fig. 3.11).

Possible heat sources for the generation of liquid water in icy small bodies include (i) short-lived radioactive nuclides, (ii) perihelion passage (Nakamura-Messenger et al. 2011), (iii) collisions of planetesimals (Cody et al. 2011), and (iv) reduction of the freezing point by the presence of solutes, e.g., ammonia (Pizzarello et al. 2011) or methanol. The condition of aqueous alteration of the UCAMM can be estimated by referring to the hydrothermal experiment of anhydrous IDPs by Nakamura-Messenger et al. (2011). In the experiment, the alteration of amorphous

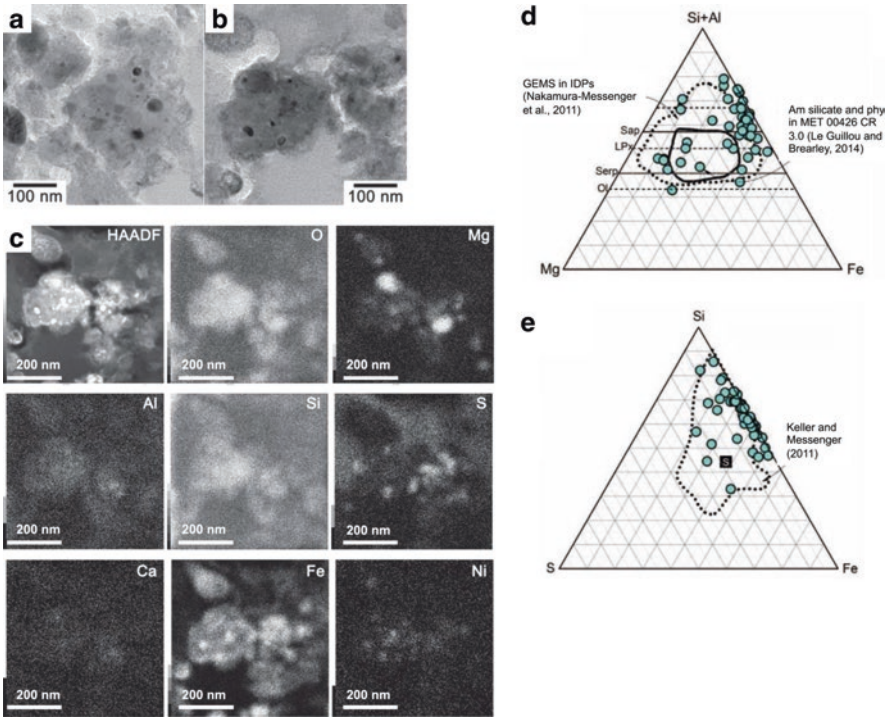


Fig. 3.11 (**a**, **b**) BF-TEM images of GEMS grains in the UCAMM D05IB80. (**c**) HAADF-STEM image and elemental distribution maps of the same GEMS grains in (**b**). In comparison with HAADF-STEM image and O, Si, and Fe maps, depletion of Mg and S are observed. (**d**) [Si + Al]-Mg-Fe ternary diagram and (**e**) Si-S-Fe ternary diagram of GEMS grains in the UCAMM D05IB80 (Yabuta et al. 2017)

silicate into hydrous phyllosilicate proceeded extremely quickly, at 25–160 °C in 12–24 h under basic pH conditions (pH = 12). Since hydrous silicates are not identified in UCAMM DO05IB80, the UCAMM could have experienced a shorter duration reaction at lower temperature, lower pH, and/or slightly oxidizing conditions compared to the experiments. Considering that the degree of alteration would have been much lower than the aqueous alteration on the typical carbonaceous chondritic meteorite parent bodies (i.e., CM and CI groups), which lasted for several million years (e.g., Fujiya et al. 2013), planetesimal collisions are most likely cause to produce a very weak degree of aqueous alteration in a short duration. Weak alteration in short duration was probably caused by planetesimal shock that locally melted cometary ice grains and released water that dissolved the organics; the fluid would have not been mobilized because of the very low thermal conductivity of the porous icy body. This event allowed the formation of the large organic puddle of the UCAMM, as well as organic matter sulfurization, formation of thin membrane-like layers of minerals, and deformation of organic nanoglobules.

3.5 Conclusion

Comprehensive investigations on organic chemistry and mineralogy of Antarctic micrometeorites have enabled determination of the history from solar nebula to planetesimals, including even early stage where phyllosilicates are not affected but organics are sufficiently changed. This submicron-to-nanoscale observation of the organic material-water-mineral interactions in the small body materials would be expected to find an evidence for the transition from comets to asteroids, which may have been caused by Jupiter's migration in the history of Solar System formation (Walsh et al. 2012). Further investigations of greater numbers of primitive meteorites, micrometeorites, and IDPs would be required for understanding the statistical features of comet-asteroid continuum.

In addition, combination of the small body explorations with laboratory experiments would provide clear insights into the origin and evolution of organic molecules in the Solar System. A Japanese asteroid sample return mission, Hayabusa2, aims to reveal the origins and evolution of the Earth-life and ocean, by investigating a C-type asteroid. The spacecraft has arrived at the asteroid (162173) Ryugu on June 27, 2018, will collect the surface of the asteroid during its 18-month stay, and will return the sample to the Earth in the end of 2020 (Tachibana et al. 2014; Yabuta 2018). National Aeronautics and Space Administration (NASA)'s asteroid sample return mission, OSIRIS-REx, will target the B-type asteroid (that is fallen into C-type in a broad sense) (101955) Bennu, which is also thought to be enriched in carbon and water, and return the collected sample to the Earth in 2023 (Lauretta 2017).

Regarding the missions related to cosmic dust science, laboratory analyses of the particles collected at the low Earth orbit by using silica aerogels have been ongoing, as a part of Japanese astrobiology experiment on the International Space Station (Tanpopo mission) (Yano et al. 2017). Demonstration and Experiment of Space Technology for INterplanetary voYage Phaethon fLyby dUSt science, DESTINY+ (DESTINY-plus), is a Japanese mission to flyby of Geminids parent (3200) Phaethon and to conduct in situ dust analyses that is proposed to be launched in 2022 (Arai et al. 2018). The spacecraft will be equipped with Dust Analyzer (impact ionization time-of-flight mass spectrometry (ToF-MS)) as a payload to measure the velocity, orbital, sizes, and masses and chemical composition of interplanetary and interstellar dust particles during deep space cruising phase and the dusts from Phaethon. NASA's Comet Astrobiology Exploration SAmple Return (CAESAR) mission is planned to be launched in 2024, collects surface material from the nucleus of comet 67P/Churyumov-Gerasimenko, and returns the sample to the Earth in 2038 (Squyres et al. 2018). The continuous, systematic explorations of small bodies in different evolution stages will elucidate the substantial role and mechanism of exogenous delivery of organic molecules and water to the early Earth.

References

Aikawa Y, Herbst E (1999) Deuterium fractionation in protoplanetary disks. Astrophys J 526:314–326

Aléon J, Robert F (2004) Interstellar chemistry recorded by nitrogen isotopes in solar system organic matter. Icarus 167:424–430

Alexander CMO'D, Fogel M, Yabuta H, Cody GD (2007) The origin and evolution of chondrites recorded in the elemental and isotopic compositions of their macromolecular organic matter. Geochim Cosmochim Acta 71:4380–4403

Arai T, Kobayashi M, Ishibashi K, Yoshida F, Kimura H, Wada K, Senshu H, Yamada M, Okudaira O, Okamoto T, Kameda S, Srama R, Krüger H, Ishiguro M, Yabuta H, Nakamura T, Watanabe J, Ito T, Ohtsuka K, Tachibana S, Mikouchi T, Komatsu M, Nakamura-Messenger K, Sasaki S, Hiroi T, Abe S, Urakawa S, Hirata N, Demura H, Komatsu G, Noguchi T, Sekiguchi T, Inamori T, Yano H, Yoshikawa M, Ohtsubo T, Okada T, Iwata T, Nishiyama K, Toyota H, Kawakatsu Y, Takashima T (2018) DESTINY+ mission: Flyby of Geminids parent asteroid (3200) Phaethon and in-situ analyses of dust accreting on the Earth. The 49th Lunar and Planetary Science Conference, Abstract #2570

Bernstein MP, Sandford SA, Allamandola LJ, Gillette JS, Clemett SJ, Zare RN (1999) UV irradiation of polycyclic aromatic hydrocarbons in ices: production of alcohols, quinones, and ethers. Science 283:1135–1138

Brearley A. J. (2006) The action of water. Meteorites and the early solar system II (Lauretta D. S. McSween Jr. H.Y 587–624 Tucson: University of Arizona Press

Busemann H, Nguyen AN, Cody GD, Hoppe P, Kilcoyne ALD, Stroud RM, Zega TJ, Nittler LR (2009) Ultra-primitive interplanetary dust particles from the comet 26P/Grigg-Skjellerup dust stream collection. Earth Planet Sci Lett 288:44–57

Charnley SB, Rodgers SD (2002) The end of interstellar chemistry as the origin of nitrogen in comets and meteorites. Astrophys J 569:L133–L137

Chyba C, Sagan C (1992) Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules: an inventory for the origins of life. Nature 355:125–132

Ciesla F, Sandford SA (2012) Organic synthesis via irradiation and warming of ice grains in the solar nebula. Science 336:452–454

Cody GD, Alexander CMO'D, Tera F (2002) Solid-state (^{1}H and ^{13}C) nuclear magnetic resonance spectroscopy of insoluble organic residue in the Murchison meteorite: a self-consistent quantitative analysis. Geochim Cosmochim Acta 66:1851–1865

Cody GD, Ade H, Alexander CMO'D, Araki T, Butterworth A, Fleckenstein H, Flynn G, Gilles MK, Jacobsen C, Kilcoyne ALD, Messenger K, Sandford SA, Tyliszczak T, Westphal AJ, Wirick S, Yabuta H (2008) Quantitative organic and light-element analysis of comet 81P/Wild 2 particles using C-, N-, and O- XANES. Meteor Planet Sci 43:353–365

Cody GD, Heying E, Alexander CMOD, Nittler LR, Kilcoyne ALD, Sandford SA, Stroud RM (2011) Establishing a molecular relationship between chondritic and cometary organic solids. Proc Natl Acad Sci U S A 108:19171–19176

De Gregorio BT, Stroud RM, Nittler LR, Alexander CMO'D, Kilcoyne ALD, Zega TJ (2010) Isotopic anomalies in organic nanoglobules from comet 81P/wild 2: comparison to Murchison nanoglobules and isotopic anomalies induced in terrestrial organics by electron irradiation. Geochim Cosmochim Acta 74:4454–4470

Dartois E, Engrand C, Brunetto R, Duprat J, Pino T, Quirico E, Remusat L, Bardin N, Briani G, Mostefaoui S, Morinaud G, Crane B, Szwec N, Delauche L, Jamme F, Sandt C, Dumas P (2013) Ultracarbonaceous Antarctic micrometeorites, probing the solar system beyond the nitrogen snow-line. Icarus 224:243–252

Duprat J, Dobrica E, Engrand C, Aléon J, Marrocchi Y, Mostefaoui S, Meibom A, Leroux H, Rouzaud J-N, Gounelle M, Robert F (2010) Extreme deuterium excesses in ultracarbonaceous micrometeorites from central Antarctic snow. Science 328:742–745

Ehrenfreund P, Charnley SB (2000) Organic molecules in the interstellar medium, comets, and meteorites: a voyage from dark clouds to the early Earth. Annu Rev Astron Astrophys 38:427–483

Floss C, Noguchi T, Yada T (2012) Ultracarbonaceous Antarctic micrometeorites: origins and relationships to other primitive extraterrestrial materials. Lunar Planet Sci XLIII. #1217

Fujiya W, Sugiura N, Sano Y, Hiyagon H (2013) Mn–Cr ages of dolomites in CI chondrites and the Tagish Lake ungrouped carbonaceous chondrite. Earth Planet Sci Lett 362:130–142

Glavin DP, Dworkin JP, Sandford SA (2008) Detection of cometary amines in samples returned by stardust. Meteorit Planet Sci 43:399–413

Glavin DP, Alexander CMO'D, Aponte JC, Dworkin JP, Elsila JE, Yabuta H (2018) The origin and evolution of organic matter in carbonaceous chondrites and links to their parent bodies. In: Abreu N (ed) Primitive meteorites and asteroids: physical, chemical, and spectroscopic observations paving the way to exploration. Elsevier, Amsterdam, pp 205–271

Greenberg JM, Li A (1997) Silicate core-organic refractory mantle particles as interstellar dust and as aggregated in comets and stellar disks. Adv Space Res 19:981–990

Hill HGM, Nuth JA (2003) The catalytic potential of cosmic dust: implications for prebiotic chemistry in the solar nebula and other protoplanetary systems. Astrobiology 3:291–304

Huss GR, Rubin AE, Grossman JN (2006) Thermal metamorphism in chondrites. In: Lauretta DS, Mcsween HY Jr (eds) Meteorites and the early solar system II. University of Arizona Press, Tucson, pp 567–586

Kebukawa Y, Kilcoyne ALD, Cody GD (2013) Exploring the potential formation of organic solids in chondrites and comets through polymerization of interstellar formaldehyde. Astrophys J 771:19

Keller LP, Messenger S (2011) On the origins of GEMS grains. Geochim Cosmochim Acta 75:5336–5365

Kuga M, Marty B, Marrocchi Y, Tissandier L (2015) Synthesis of refractory organic matter in the ionized gas phase of the solar nebula. Proc Natl Acad Sci U S A 112:7129–7134

Lauretta DS, Balram-Knutson SS, Boynton BEWV, Drouet d'Aubigny C, Dellagiustina DN, Enos HL, Golish DR, Hergenrother CW, Howell ES, Bennett CA, Morton ET, Nolan MC, Rizk B, Roper HL, Bartels AE, Bos BJ, Dworkin JP, Highsmith DE, Lorenz DA, Lim LF, Mink R, Moreau MC, Nuth JA, Reuter DC, Simon AA, Bierhaus EB, Bryan BH, Ballouz R, Barnouin OS, Binzel RP, Bottke WF, Hamilton VE, Walsh KJ, Chesley SR, Christensen PR, Clark BE, Connolly HC, Crombie MK, Daly MG, Emery JP, McCoy TJ, McMahon JW, Scheeres DJ, Messenger S, Nakamura-Messenger K, Righter K, Sandford SA (2017) OSIRIS-REx sample return from asteroid (101955) Bennu. Space Sci Rev. https://doi.org/10.1007/s11214-017-0405-1

McKeegan KD, Aléon J, Bradley J, Brownlee D, Busemann H, Butterworth A, Chaussidon M, Fallon S, Floss C, Gilmour J, Gounelle M, Graham G, Guan Y, Heck PR, Hoppe P, Hutcheon ID, Huth J, Ishii H, Ito M, Jacobsen SB, Kearsley A, Leshin LA, Liu M-C, Lyon I, Marhas K, Marty B, Matrajt G, Meibom A, Messenger S, Mostefaoui S, Mukhopadhyay S, Nakamura-Messenger K, Nittler L, Palma R, Pepin RO, Papanastassiou DA, Robert F, Schlutter D, Snead CJ, Stadermann FJ, Stroud R, Tsou P, Westphal A, Young ED, Ziegler K, Zimmermann L, Zinner E (2006) Isotopic compositions of cometary matter returned by stardust. Science 314:1724–1728

Meier R, Owen TC, Jewitt DC, Matthews HM, Senay M, Biver N, Bockelée-Morvan D, Crovisier J, Gautier D (1998) Deuterium in Comet C/1995 O1 (Hale-Bopp). Detection of DCN. Science 279:1707–1710

Messenger S (2000) Identification of molecular-cloud material in interplanetary dust particles. Nature 404:968–971

Millar TJ, Bennett A, Herbst E (1989) Deuterium fractionation in dense interstellar clouds. Astrophys J 340:906–920

Nakamura T, Noguchi T, Ozono Y, Osawa T, Nagao K (2005) Mineralogy of ultracarbonaceous large micrometeorites. Meteor Planet Sci 40:A110

Nakamura-Messenger K, Messenger S, Keller LP, Clemett SJ, Zolensky ME (2006) Organic globules in the Tagish Lake meteorite: remnants of the protosolar disk. Science 314:1439–1442

Nakamura-Messenger K, Clemett SJ, Messenger S, Keller LP (2011) Experimental aqueous alteration of cometary dust. Meteor Planet Sci 46:843–856

Noguchi T, Ohashi N, Tsujimoto S, Mitsunari T, Bradley JP, Nakamura T, Toh S, Stephan T, Iwata N, Imae N (2015) Cometary dust in Antarctic ice and snow: past and present chondritic porous micrometeorites preserved on the Earth's surface. Earth Planet Sci Lett 410:1–11

Noguchi T, Yabuta H, Itoh S, Sakamoto N, Mitsunari T, Okubo A, Okazaki R, Nakamura T, Tachibana S, Terada K, Ebihara M, Imae N, Kimura M, Nagahara H (2017) Variation of mineralogy and organic material during the early stages of aqueous activity recorded in Antarctic micrometeorites. Geochim Cosmochim Acta 208:119–144

Nomura H, Aikawa Y, Tsujimoto M, Nakagawa Y, Millar TJ (2007) Molecular hydrogen emission from protoplanetary disks: effects of X-ray irradiation and dust evolution. Astrophys J 661:334–353

Nuevo M, Milam SN, Sandford SA, De Gregorio BT, Cody GD, Kilcoyne ALD (2011) XANES analysis of organic residues produced from the UV irradiation of astrophysical ice analogs. Adv Space Res 48:1126–1135

Öberg KI (2016) Photochemistry and astrochemistry: photochemical pathways to interstellar complex organic molecules. Chem Rev 116:9631–9663

Pizzarello S, Cooper GW, Flynn GJ (2006) The nature and distribution of the organic material in carbonaceous chondrites and interplanetary dust particles. In: Luretta DS, McSween HY (eds) Meteorites and the early solar system II. The University of Arizona Press, Tucson, pp 625–651

Pizzarello S, Williams LB, Lehman J, Holland GP, Yarger JL (2011) Abundant ammonia in primitive asteroids and the case for a possible exobiology. Proc Natl Acad Sci U S A 108:4303–4306

Quirico E, Moroz LV, Schmitt B, Arnold G, Faure M, Beck P, Bonal L, Ciarniello M, Capaccioni F, Filacchione G, Erard S, Leyrat C, Bockelée-Morvan D, Zinzi A, Palomba E, Drossart P, Tosi F, Capria MT, De Sanctis MC, Raponi A, Fonti S, Mancarella F, Orofino V, Barucci A, Blecka MI, Carlson R, Despan D, Faure A, Fornasier S, Gudipati MS, Longobardo A, Markus K, Mennella V, Merlin F, Piccioni G, Rousseau B, Taylor F, Rosetta VIRTIS team (2016) Refractory and semi-volatile organics at the surface of comet 67P/Churyumov Gerasimenko: insights from the VIRTIS/Rosetta imaging spectrometer. Icarus 272:32–47

Sandford SA (1996) The inventory of interstellar materials available for the formation of the solar system. Meteorit Planet Sci 31:449–476

Sandford SA, Aléon J, Alexander CMO'D, Araki T, Bajt S, Baratta GA, Borg J, Bradley JP, Brownlee DP, Brucato JR, Burchell MJ, Busemann H, Butterworth A, Clemett SJ, Cody G, Colangeli L, Cooper G, D'Hendecourt L, Djouadi Z, Dworkin JP, Ferrini G, Fleckenstein H, Flynn GJ, Franchi IA, Fries M, Gilles MK, Glavin DP, Gounelle M, Grossemy F, Jacobsen C, Keller LP, Kilcoyne ALD, Leitner J, Matrajt G, Meibom A, Mennella V, Mostefaoui S, Nittler LR, Palumbo ME, Papanastassiou DA, Robert F, Rotundi A, Snead CJ, Spencer MK, Stadermann FJ, Steele A, Stephan T, Tsou P, Tyliszczak T, Westphal AJ, Wirick S, Wopenka B, Yabuta H, Zare RN, Zolensky M (2006) Organics captured from comet 81P/wild 2 by the stardust spacecraft. Science 314:1720–1724

Schmitt-Kopplin P, Gabelica Z, Gougeon RD, Fekete A, Kanawati B, Harir M, Gebefuegi I, Eckel G, Hertkorn N (2010) High molecular diversity of extraterrestrial organic matter in Murchison meteorite revealed 40 years after its fall. Proc Natl Acad Sci U S A 107:2763–2768

Schulz R, Jehin E, Manfroid J, Hutsemékers D, Arpigny C, Cochran A, Zucconi J, Stuwe J (2008) Isotopic abundance in the CN coma of comets: ten years of measurements. Planet Space Sci 56:1713–1718

Squyres SW, Nakamura-Messenger K, Mitchell DF, Moran VE, Houghton MB, Glavin DP, Hayes AG, Lauretta DS, the CAESAR Project Team (2018) The CAESAR new frontiers mission: 1. Overview. The 49th Lunar and Planetary Science conference, Abstract#1332

Stöhr J (1991) NEXAFS spectroscopy. Springer, New York. 291 p

Tachibana S, Abe M, Arakawa M, Fujimoto M, Iijima Y, Ishiguro M, Kitazato K, Kobayashi N, Namiki N, Okada T, Okazaki R, Sawada H, Suguta S, Takano Y, Tanaka S, Watanabe S, Yoshikawa M, Kuninaka H, the Hayabusa2 Project Team (2014) Hayabusa2: scientific importance of samples returned from C-type near-Earth asteroid (162173) 1999 JU(3). Geochem J 48:571–587

Tholen DJ, Barucci MA (1989) Asteroid taxonomy. In: Binzel RP, Gehrels T, Matthews MS (eds) Asteroids II. University of Arizona Press, Tucson, pp 298–315

Tielen AGHM, Hagen W (1982) Model calculations of the molecular composition of interstellar grain mantles. Astron Astrophys 114:245–260

Walsh KJ, Morbidelli A, Raymond SN, O'Brien DP, Mandell AM (2012) Populating the asteroid belt from two parent source regions due to the migration of giant planets—"The Grand Tack". Meteorit Planet Sci 47:1–7

Yabuta H (2018) Solar system exploration: small bodies and their chemical and physical conditions. In: Kolb V (ed) Handbook of astrobiology. CRC Press, Boca Raton

Yabuta H, Noguchi T, Itoh S, Nakamura T, Miyake A, Tsujimoto S, Ohashi N, Sakamoto N, Hashiguchi M, Abe K-I, Okubo A, Kilcoyne ALD, Tachibana S, Okazaki R, Terada K, Ebihara M, Nagahara H (2017) Formation of an ultracarbonaceous Antarctic micrometeorite through minimal aqueous alteration in a small porous icy body. Geochim Cosmochim Acta 214:172–190

Yabuta H, Sandford SA, Meech KJ (2018) Organic molecules and volatiles in comets. Elements 14:101–106

Yada T, Floss C, Stadermann FJ, Zinner E, Nakamura T, Noguchi T, Lea S (2008) Stardust in Antarctic micrometeorites. Meteorit Planet Sci 43:1287–1298

Yano H, Sasaki S, Imani J, Horikawa D, Arai K, Fujishima K, Hashimoto H, Higashide M, Imai E, Ishibashi Y, Kawaguchi Y, Kawai H, Kebukawa Y, Kobayashi K, Kobunai K, Kodaira S, Kurosu Y, Mita H, Oda Y, Okudaira K, Ozawa T, Tabata M, Takizawa N, Tomita M, Tsuchiyama A, Uchihori Y, Yabuta H, Yaguchi Y, Yokobori S, Yamagishi A, the Tanpopo Project Team (2017) In-orbit operation and initial sample analysis and curation results for the first year collection samples of the Tanpopo project. The 48th Lunar and Planetary Science conference, Abstract#3040