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Preface: Evolution of molecules in space: From interstellar clouds to protoplanetary nebulae

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Elements among the most abundant in space (H, C, O, and N) have the ability to form various organic molecules and ice in molecular clouds and in protoplanetary systems. The variety of organic molecules, ice, and related components should record the origin and evolution of molecular clouds and planetary systems, and can therefore be a powerful tracer of star and planet formation. This special issue aims at addressing recent progress and challenges for understanding the formation and evolution of ice and organic matter in space.

Comets, interplanetary dust, and carbonaceous chondrites contain various organic materials (e.g., Alexander *et al*., 2017 and references therein), which are broadly classified into solvent soluble organic matter (SOM) and solvent/acid insoluble organic matter (IOM). They record various chemical processes in interstellar medium, molecular clouds, protoplanetary disks, and parent bodies, but their formation and evolution processes are still under debate. In this special issue, four articles discuss the formation and alteration of organic molecules in various environments in the early stage of the Solar System formation through laboratory experiments, analysis of meteorite SOMs with high resolution mass spectroscopy, and comparison between laboratory-synthesized and meteorite organic molecules.

Sugahara *et al*. (2019) focused on photochemical synthesis of nitrogen-bearing molecules in molecular clouds because of their importance as pre-biotic molecules and as a potential career of ^{15}N-enriched signature of extraterrestrial organics. They synthesized organic residues from UV-irradiated H_2O-CH_3OH-NH_3 amorphous ice at ~12 K (Piani *et al*., 2017; Tachibana *et al*., 2017), and found three amines and eleven amino acids in the residues. The compound-specific nitrogen isotope analysis of amino acids showed that negligible isotopic fractionation of nitrogen occurred during UV-irradiation of the amorphous ice in relation to the starting gas (NH_3) composition, implying that the ^{15}N-enrichment in extraterrestrial organic matter was caused by other processes and/or represents the initial nitrogen isotopic composition of gas.

Orthous-Daunay *et al*. (2019) conducted UV-irradiation experiments of chondritic SOMs extracted from Murchison (CM2) chondrite to examine UV irradiation effect on the SOM chemisty. The analysis of photo-irradiated Murchison SOMs with Orbitrap high resolution mass spectrometry showed that UV irradiation causes selective photo-induced alteration of SOMs by removing hydrogen and small carbon bearing volatile species. This results in shifting the mass distribution of remaining molecules to lower masses and increasing the fractions of aromatic cycles and double bonds in molecular structures. This study suggests that the chondritic SOMs never experienced severe photo-irradiation in the Sun's parent molecular cloud and/or the protosolar disk before incorporation into planetesimals.

Solvent soluble organic molecules in different chemical groups of carbonaceous chondrites may represent different chemical environments of parent planetesimals. Naraoka and Hashiguchi (2019) analyzed soluble CHN organic molecules extracted from CM and CR carbonaceous chondrites. They found that hydrogenated alkylpiperidines ($C_nH_{2n+1}N$) are more abundant in the CR chondrite (Yamato 002540) while alkylpyridines ($C_nH_{2n-5}N$) are more abundant in the CM chondrites (Murray and Murchison). This difference in the relative abundance of hydrogenated alkylpiperidines and alkylpyridines within the CHN molecules could be attributed to the difference in redox condition between CR and CM chondrite parent bodies.

Isono *et al*. (2019) investigated the bulk chemical characteristics of soluble polar organic molecules synthesized from formaldehyde and ammonia under hydrothermal

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conditions, where solid organics similar to chondritic IOMs can be formed (Kebukawa *et al*., 2013). The soluble polar organic molecules synthesized at 200°C were richer in hydrogen than those at 90°C, which could be due to an effective cross-disproportionation reaction between organic molecules and formic acid at higher temperatures. The synthesized molecules were found to be less reduced than methanol-soluble organic molecules in Murchison CM chondrite, implying either that Murchison SOMs formed under more reducing conditions or that they formed through other processes than hydrothermal reaction on the parent body.

Aerogel capture of dust particles, which was used in the Stardust mission to collect cometary particles (Brownlee *et al*., 2006), can potentially be one of the best ways to collect intact extraterrestrial organics without terrestrial contamination. Kebukawa *et al*. (2019) performed experiments by impacting Murchison meteorite powder into an ultralow-density silica aerogel with velocities of 4.4 and 5.9 km/s to evaluate damage to organics during hyper velocity impacts. Analysis of the recovered Murchison grains by various techniques showed a large degree of destruction of organic matter in the grains after 5.9 km/s impact, but little or no degradation of organics was observed for the grains after 4.4 km/s. This result will be a useful benchmark to elucidate the nature of organic matter collected by the ultralow-density silica aerogel in the Tanpopo mission, an astrobiology space experiment at the Japanese Experiment Module on the International Space Station (Yamagishi *et al*., 2009).

Understanding molecular processes of volatile species in ice is essential to understanding physicochemical processes occurring in molecular clouds, protoplanetary disks, icy small bodies such as comets and satellites, and cryospheres of planets. For instance, noble gases in ice from comet 67P/Churyumov-Gerasimenko by the Rosetta spacecraft have provided insights into the origin of volatile elements on terrestrial planets (Marty *et al*., 2017). Bekaert *et al*. (2019) observed multiply ionized Xe (up to Xe^{6+}) and O, when Xe was trapped in H_2O ice, with a newly developed resonant two-step laser ablation mass spectrometry technique. In this experiment, Xe multiple ionization cannot be explained by laser ionization. The authors concluded that electrons, which form by ionization of Xe interacting with H_2O molecules in ice, are accelerated back to the ice surface after ablation. Bombardment of the ice surface by several hundreds of eV electrons is probably the cause of Xe subsequent ionization, and Coulomb explosion. Cometary surfaces may experience similar processes during perihelion approach, which should be the focus of future investigations.

Noguchi *et al*. (2019) experimentally determined the diffusivity and solubility of methane in ice Ih. They found that methane molecules diffuse through the ice structure by breaking hydrogen bonds between water molecules, and that methane solubility is lower than that of light noble gases (He and Ne) due to its larger van der Waals radius. Because there has been no direct measurement of the diffusivity and solubility of methane in ice Ih, the newly determined parameters can be used in many geological and cosmochemical applications such as estimating the methane flux from sub-surface Martian ice and reconstructing the Earth's paleoatmosphere from ice core samples.

We hope that the papers in this special issue contribute for better understanding the evolution of molecules in molecular clouds and in protoplanetary systems.

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