SEARCH FOR PRIMORDIAL NITROGEN-HETEROCYCLES OF ASTROCHEMICAL INTEREST IN THE AQUEOUS EXTRACTS FROM THE ASTEROID (162173) RYUGU AND ORGUEIL CI-METEORITE.

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Introduction: Sample from the near-Earth carbonaceous asteroid (162173) Ryugu collected by the Hayabusa2 spacecraft enabled us to analyze pristine extraterrestrial materials without exposure to the Earth's atmosphere [e.g., 1,2]. The initial analysis team for the soluble organic matter (SOM) reported the detection of wide variety of organic molecules including racemic amino acids, alkylamines, carboxylic acids, and polycyclic aromatic hydrocarbons (PAHs) in the Ryugu samples [3].

Since asteroid Ryugu has common features with CI carbonaceous chondrites, as has been demonstrated in geochemical and mineralogical studies [4,5], we further expect the presence of other classes of organic molecules in the Ryugu samples. One of the important targets would be nucleobases (i.e., pyrimidine and purine rings), which are the informational component of DNA and RNA biology and have been identified in CI-type Orgueil meteorites [6]. Nucleobases in carbonaceous meteorites [6-8] have been a subject of significant interests due to their potential relationship to the prebiotic molecular evolution on the early Earth. We have recently developed an analytical method for the small-scale detection and identification of nucleobases at parts per billion (ppb; ng/g) to parts per trillion (ppt; pg/g) levels using high-performance liquid chromatography coupled with electrospray ionization high-resolution mass spectrometry (HPLC/ESI-HRMS) [8,9]. In aqueous extracts from the CM-type Murchison meteorite, we successfully detected all five canonical nucleobases (adenine, guanine, cytosine, thymine, uracil) at the concentrations ranging from 4 to 72 ppb [8]. Such highly sensitive methods are well suited for Ryugu analyses where the available sample mass is limited. Here, we searched for nucleobases and other classes of nitrogen (N)-heterocyclic molecules indigenous to the Ryugu samples A0106 and C0107, which were collected at the first and second Ryugu touchdown sites, respectively. In addition, we analyzed the Orgueil meteorite under the same analytical conditions to compare the molecular distribution within Ryugu, Murchison, and Orgueil.

Analytical Methods: The detailed procedure for the extraction of organic molecules from the Ryugu samples has been described elsewhere [3,8]. In brief, we extracted organic molecules from the A0106 (13.08 mg) and C0107 (10.73 mg) Ryugu samples with hot water at 105 ºC for 20 hr in a N_2-purged and flame-sealed glass ampoule. The water extract from the Ryugu samples was further hydrolyzed using ultrapure 6 M HCl at 105 ºC for 20 hrs. About 20% of the hydrolysate was available for this study. The majority of the Ryugu extract was acid-hydrolyzed for the detection of amino acids [3]. We similarly analyzed hot water extracts from the Orgueil meteorite (10.86 mg, Denmark National Museum) both before and after acid hydrolysis. The same procedure was repeated using baked (at 500°C in air for 3 hr) serpentine powder (17.58 mg) as a procedural blank. The extracts from the Ryugu samples and the Orgueil meteorite were introduced into an HPLC/ESI-HRMS with the mass resolution of 140,000 at a mass-to-charge ratio (m/z) of 200.

Results and Discussion: Figure 1 shows mass chromatograms for the extracts from the Ryugu samples and Orgueil meteorite at the m/z = 113.0346, which corresponds to the protonated ion of uracil ($C_4H_4N_2O_2$). We identified a couple of peaks above the background level in each sample chromatogram. By comparing the peak retention time with the authentic standard reagents of uracil and its structural isomers (2-imidazole carboxylic acid: 2-ICA, and 4-imidazole carboxylic acid: 4-ICA), a peak observed at ~16 min can be reasonably assigned to uracil. The concentration of uracil in the Ryugu samples was ~20 ppb, which is comparable to that observed in carbonaceous meteorites such as the CM-type Murchison [8]. In addition to uracil, nicotinic acid (niacin, a B_3 vitamer) and its structural isomer (isonicotinic acid) were also identified in the same extracts (Figure 2).

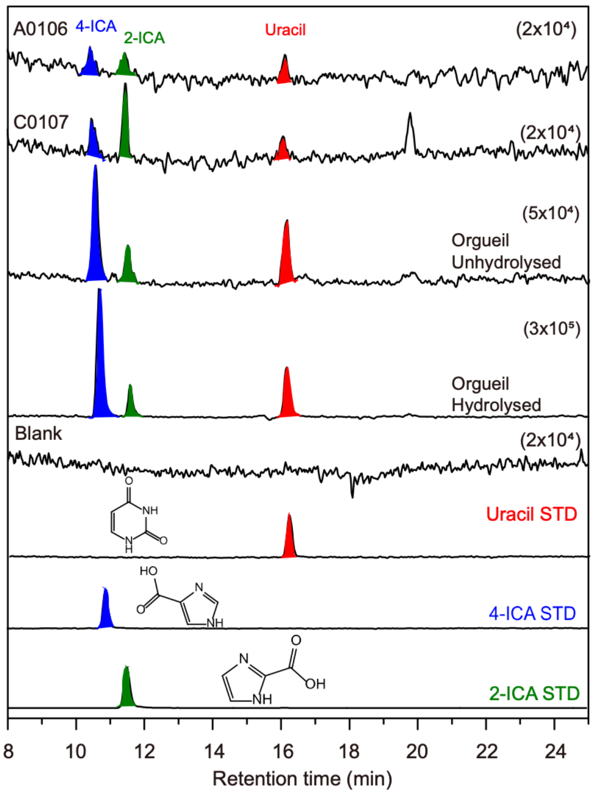

Figure 1: Mass chromatograms for the extracts from Ryugu samples, Orgueil meteorites, blank, and the standard reagents of uracil (red) and its structural isomers 2-ICA (green) and 4-ICA (blue) at the *m/z* = 113.0346.

In overview points, the concentration of nicotinic acid from the Ryugu samples was several times higher than uracil in the same sample. The concentration of the detected N-hetercycles was higher in the sample C0107 (subsurface materials) than in A0106 (surface materials), which could be attributable to different degree of energetic processes with regolith depth where Ryugu samples have experienced in the history.

These N-heterocycles were also detected in the extracts from the Orgueil meteorite. The concentration of uracil was 90 ppb in the hot water extract, and after acid hydrolysis, it increased to 140 ppb. This means the formation of uracil upon the acid hydrolysis of its precursor(s) present in the hot water extract. We expect that uracil and its precursor(s) were potentially present in the hot water extract of the Ryugu samples. In addition to uracil and nicotinic acid, nicotinamide ($C_6H_6N_2O$), another B_3 vitamer, was identified in the Orgueil extract before acid hydrolysis. We discuss further chemical characteristics of a group of N- heterocyclic molecules detected in Ryugu.

The present study strongly suggests that such prebiotic building blocks commonly formed in carbonaceous asteroids including Ryugu, could have been widely distributed across the Solar system and might have played a role in primordial chemistry.

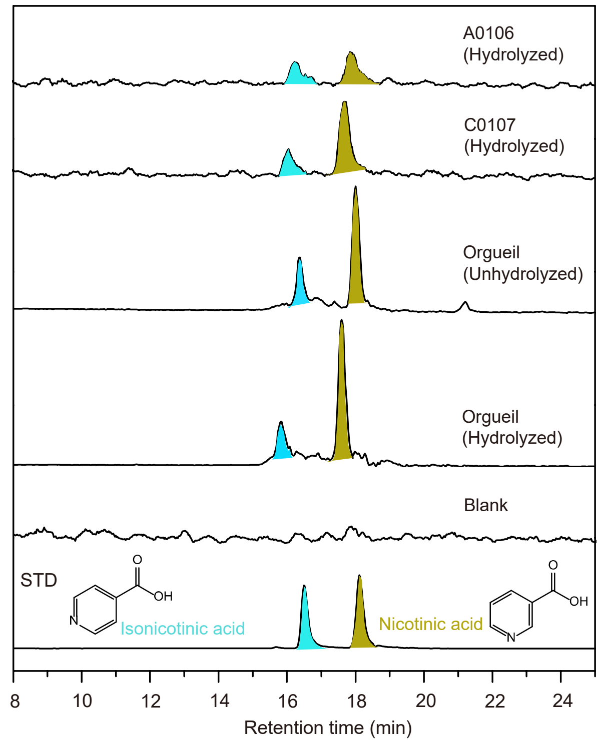

Figure 2: Mass chromatograms for the extracts from Ryugu samples, Orgueil meteorites, blank, and the standard reagents of nicotinic acid (cyan) and isonicotinic acid (olive) at the *m/z* = 124.0393.

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