Asteroidal Treasure Hunt: Probing Prebiotic precursors in C-Type Asteroids

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We are investigating two Ryugu fragments with identification numbers of A0542 (0.5mg) and A0552 (0.7 mg), which JAXA curation assigned to our team in the 4th Ryugu sample announcement of opportunity. Our work considers two main objectives, which pay special attention to the search for the chemical cyanide group (-CN), as well as to the primordial mineralogy in which the metal complexes -CN would be present, assessing their detection using flight models (FM) of space mission instruments. More specifically we propose:

1) Unraveling the complexities of prebiotic chemical space and the significance of non-canonical molecules (i.e., those differing from nucleic acid components, such as heterocycles) and prebiotic precursors in the formation of life's fundamental building blocks throughout the Universe. Currently, one of the major questions in origins-of-life research is the origin of nucleotides. Experimental investigations into abiotic non-canonical nucleotide synthesis revealed that many non-canonical pyrimidines and other bases, so as their related glycosides, are formed much more easily than the canonical nucleotides [1, 2, 3, 4]. Subsequently they can serve as monomers for the informational polymers by early life on Earth. These hypothetical ancestral non-canonical bases can be formed in asteroids and preserved up until now.

2) Establishing the compositional link between C- and D-type asteroids and the Martian Moons to contribute to the interpretation of data from forthcoming exploration missions. Yabuta et al. (2023) [5] showed that some organic materials are strongly associated with the mineral matrix. The matrix is mainly composed by phyllosilicates and carbonates, which have been formed by hydrothermal alteration at low temperature on the asteroid parent body. The interaction between the rock and water trigger some reactions (e.g. hydrolysis, oxidation, and aromatization) and diversity of primordial macromolecular species. Recently, some studies on the smectites (a type of layered phyllosilicate) have concluded that N-rich organics, responsible for the near infrared signature detected in Ryugu and likely detected in Ceres samples (proposed as a D-type asteroid related body, [6]), come from molecules located within the interlayer spaces of these phyllosilicates. These organic compounds can then be protected from subsequent alteration and delivered to rocky planets over the course of the Solar System's history [7]. On the other hand, this structural feature affects the Raman measurements [8, 9], and should be considered in the future observations by the RAman spectrometer for the MMX (Martian Moons eXplorer) mission (RAX) to Phobos. Results from this investigation will help to be prepared for the identification by in situ planetary Raman measurements.

We are implementing a comprehensive analytical approach to study the fragments, involving Raman spectroscopy, along with high-resolution mass spectrometry for organic molecule identification, and electron microscopy-based techniques (SEM/TEM-EDX). In addition to standard laboratory microanalysis, we are investigating these samples with flight-like models of various Raman instruments, such as RLS@Rosalind Franklin Flight Spare lab model (Fig. 1) to compare with those that might be detected during a space mission.

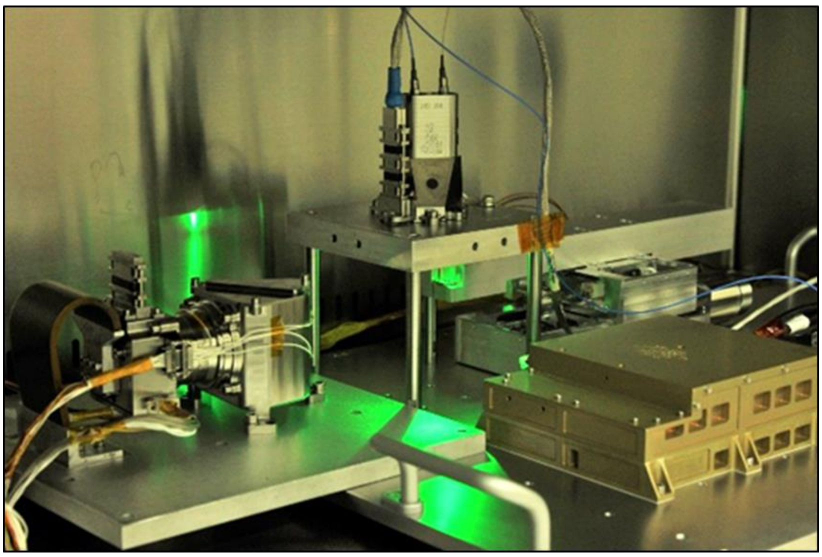

Figure 1. Picture of the Raman Laser Spectrometer for the Rosalind Franklin rover Fight Spare (RLS-FS)

We will present in the conference session the preliminary results of our study. Currently, we have already detected by electron microscopy minerals that have been commonly found in other Ryugu fragments, including fine-grained phyllosilicates (mostly serpentine and saponite-like smectites), carbonates (dolomite, Mg-rich calcite), sulfides (pyrrhotite with characteristic hexagonal platy crystals or sub-spherical aggregates, along with minor pentlandite), oxides (magnetite, commonly appearing as sub-spherical particles and coalescing in framboidal aggregates), and some other minor to accessory minerals such as hydroxyapatite, and carbonaceous fragments of still unknown composition. In agreement with previous studies, we detected neither ferrihydrite nor gypsum, which seems to be a differentiating aspect of Ryugu samples with respect to CI chondrites [11]. Chemical mapping and punctual EDX analyses of different grains and mineral aggregates have already revealed the locally abundant presence of carbon, nitrogen and phosphorus in our Ryugu samples. Further efforts in SEM-EDX and TEM studies will be focused on the detection of organics associated to the phyllosilicates (e.g., saponites) and other minerals.

We also performed some preliminary Raman tests with reference samples to determine measurement protocols to be used with the RLS-FS. We synthetized HCN-polymers and tholins to evaluate the features of disordered graphite and sp2 bonded carbon layers with N defect, which are very sensitive to laser radiation. We are building a library of cyanide complexes using ferrocyanide salts and nitriles that can be used as reference for CN Raman Bands (1900-2500 cm^{-1} area) and laser energy limits (Fig. 2). Considering that olivine and primary phosphate can be modified by cyanide and prebiotic organics in aqueous media [12], we also tested the spectral features of the formation of magnesium, calcium and ammonium ferrocyanides and Prussian blue related complexes. In addition to the synthetic samples, we tested analytical protocols to search for the -CN bands in some meteorites such as Aguas Zarcas, Kolang or NWA 14792.

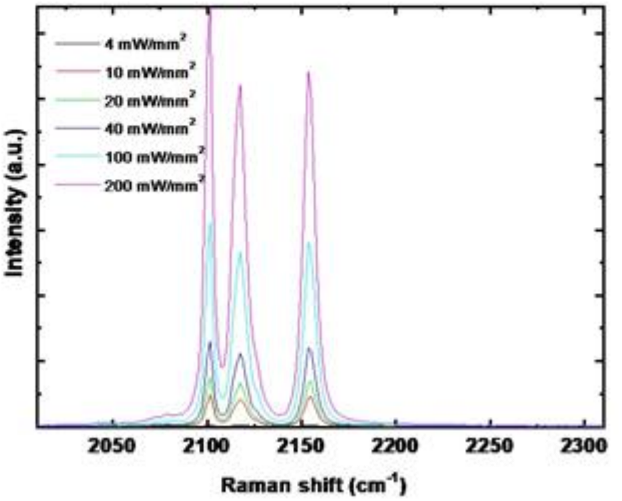

Figure 2. Raman spectra of ferrocyanicde salts and nitriles at different irradiance

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