ORGANIC MATTER IN THE ASTEROID RYUGU SAMPLES INFERRED FROM ITS INFRARED TRANSMISSION SPECTRA. Y. Kebukawa*[1], E. Quirico[2], E. Dartois[3], L. Bonal[2], C. Engrand[4], J. Duprat[5], J. Mathurin[6], A. Dazzi[6], A. Deniset-Besseau[6], H. Yabuta[7], H. Yurimoto[8], T. Nakamura[9], T. Noguchi[10], R. Okazaki[11], H. Naraoka[11], K. Sakamoto[12], S. Tachibana[12,13], S. Watanabe[14], Y. Tsuda[12], and The Hayabusa2-initial-analysis organic macromolecule team. [1]Yokohama National University, Yokohama, Kanagawa, 240-8501, Japan, [2]IPAG, Université Grenoble Alpes, 38000 Grenoble, France, [3]Institut des Sciences Moléculaires d'Orsay, UMR8214, Université Paris-Saclay/CNRS, 91405 Orsay, France, [4]IJCLab, UMR 9012 Université Paris-Saclay/CNRS, 91405 Orsay, France, [5]Muséum National d'Histoire Naturelle, UMR CNRS 7590, SU, IMPMC, Paris, France, [6]Institut Chimie Physique, UMR 8000, Université Paris-Saclay/CNRS, 91405 Orsay, France, [7]Hiroshima University, Higashi-Hiroshima, Hiroshima, 739-8526, Japan, [8]Hokkaido University, Sapporo 060-0810, Japan, [9]Tohoku University, Sendai 980-8578, Japan, [10]Kyoto University, Kyoto 606-8502, Japan, [11]Kyushu University, Fukuoka 819-0395, Japan, [12]Japan Aerospace Exploration Agency (JAXA), Sagamihara 252-5210, Japan, [13]The University of Tokyo, Bunkyo-ku, Tokyo, 113-0033, Japan, [14]Nagoya University, Chikusa-ku, Nagoya, 464-8601, Japan. *Email: kebukawa@ynu.ac.jp

Introduction: The surface samples from Ryugu, a C-type asteroid were successfully obtained by Hayabusa2 mission, and returned to the Earth on December 6, 2020. The first touchdown samples and second touchdown samples were separately stored in sample container chamber A and chamber C, respectively. The initial analyses began in June 2021, after curation and initial description at JAXA. Immediately after sample allocations, the organic macromolecule subteam started analyses of the Ryugu particles, to decipher the nature of the organic matter and its origin, parent body processing, and interaction with water and minerals [1]. Fourier transform infrared (FTIR) spectroscopy is a nondestructive technique for functional group chemistry and structures which is suitable for both organic and inorganic compounds. To date, IR absorption (transmission) spectra have been obtained from various chondrites and other astromaterials such as interplanetary dust particles (IDPs), micrometeorites and cometary dust particles [e.g., 2-8]. As a part of the initial analysis in the organic macromolecule team, IR absorption spectra from the intact Ryugu particles and extracted insoluble organic matter (IOM) were obtained using FTIR microspectroscopy, to understand the nature of organic matter in Ryugu.

Methods: Several samples were analyzed in parallel in the team, in Japan (Yokohama National Univ., YNU) and in France (IPAG, Grenoble and Orsay-lab teams) to increase the robustness of the analysis. The aggregates in chamber A (A0108) and chamber C (C0109) were analyzed as intact Ryugu particles. IOM was obtained after solvent extraction and HF/HCl demineralization from the aggregates A0106 and C0107 [1]. The samples were pressed between two diamond windows and then FTIR measurements were performed on the diamond windows in transmission mode.

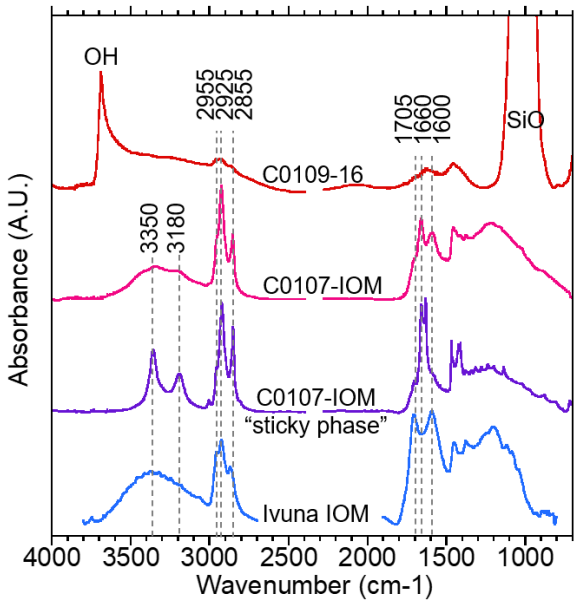

Fig. 1: Typical micro-FTIR spectra of the intact Ryugu grains and IOM (normalized to the highest peak except SiO). An IR spectrum of IOM from the Ivuna CI chondrite [12] is shown for comparison.

Results and Discussion: The IR absorption spectra of both A0108 and C0109 particles were almost identical, and typically consistent with CI chondrites, but some local heterogeneity exists [9-11]. The organic features shown in the FTIR spectra of the Ryugu intact particles were aliphatic C-H stretching at 2960 cm^{-1} (CH_3 asymmetric), 2930-2925 cm^{-1} (CH_2 asymmetric), 2855-2850 cm^{-1} (CH_3 and CH_2 symmetric) and aromatic C=C stretching (~1600 cm^{-1}) (Fig. 1). Carbonyl C=O stretching modes (~1700 cm^{-1}) were not always visible. Extracted IOM displayed these peaks more clearly. In addition, C=O at 1660 cm^{-1} newly appeared, which may be assigned to unsaturated ketones/aldehydes or amides. There was no significant

difference between IR spectra of IOM from A0106 and C0107.

Fig. 2 shows the peak intensity ratios of CH_2/CH_3 vs. aliphatic C-H (CH_2 + CH_3)/aromatic C=C (Ali-CH /C=C) of Ryugu IOM plotted with various chondritic IOM [12,13]. The Ryugu IOM had the highest CH_2/CH_3 with the highest Ali-CH/C=C ratios, indicating that it is rich in long chain aliphatic moieties. The Ryugu IOM in Fig. 2 does not follow the trends of alteration of chondritic IOM — CH_2/CH_3 ratios increase and Ali-CH/C=C ratios decrease with thermal processes. Since the Raman spectroscopic analysis excluded the possibility of long-duration thermal metamorphism as well as short-duration heating [14,15], the high CH_2/CH_3 and Ali-CH/C=C ratios might indicate primitiveness of Ryugu IOM.

The weak absorption at 3350 cm^{-1} and 3180 cm^{-1} overlapped on the broad O-H band at ~3300 cm^{-1} in the IR spectra of Ryugu IOM may be due to N-H stretching (Fig. 1). In addition, Ryugu IOM from both A0106 and C0107 contained minor "sticky phase" which showed intense bands in these regions, as well as an intense C=O peak at 1660 cm^{-1}. It should be noted that the "sticky phase" did not appear in the serpentine blank either during HF/HCl treatment or IR measurements, and thus the contamination during these processes was unlikely. The N-H absorption was also detected from reflectance IR measurements of intact Ryugu particles by JAXA curation. Two individual instruments showed peaks at 3.1 µm (3226 cm^{-1}) [17], and at 3.06 µm (3268 cm^{-1}) with a weaker peak at 3.24 µm (3086 cm^{-1}) [18]. The differences in peak positions between Ryugu IOM in this study and intact particles by the curation might be attributed to alteration of N-H bearing phases by the acid treatment, since the N-H containing functional groups are likely susceptible to acids. The high CH_2/CH_3 ratio of Ryugu IOM is also consistent with the reflectance spectra from curation [18].

Overall, the FTIR organic signatures of the Ryugu samples generally agree with other initial analysis results showing that Ryugu is CI-like and escaped significant thermal events, as well as the recent publications from JAXA curation detecting NH-rich compounds [17, 18]. The difference between Ryugu and carbonaceous chondrites may indicate freshness of the Ryugu samples that escape modification of organic matter due to long preservation on the Earth.

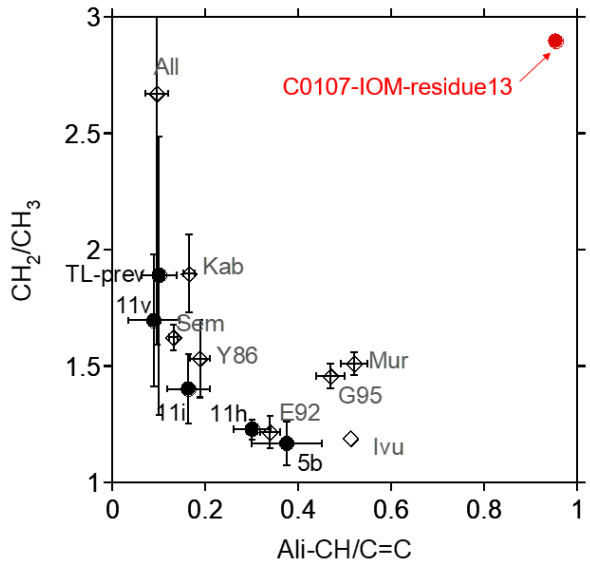

Fig. 2: The CH_2/CH_3 intensity ratio versus the aliphatic-CH/C=C intensity ratio determined by FTIR for IOM from Ryugu and various chondrites indicating trends in the relative concentrations of organic functional groups [12, 13]. All: Allende (CV3.2/>3.6), Kab: Kaba (CV3.0/3.1), Sem: Semarkona (LL3.00), Y86: Y-86720 (CM-heated), E92: EET 92042 (CR2), G95: GRO 95577 (CR1), Mur: Murchison (CM2), G95: GRO 95577 (CR1), Ivu: Ivuna (CI1), Tag (prev, 11v, 11i, 11h, 5b): Tagish Lake (C2-ung)

Acknowledgments: We thank S. Mochizuki for providing Python program for spectra data analysis. Y.K. was supported by Japan Society for the Promotion of Science KAKENHI (JP17H06458).

References: [1] Yabuta H. et al. Submitted to *Science*. [2] Keller L. P. et al. (2004) *Geochimica et Cosmochimica Acta*, 68, 2577. [3] Osawa T. et al. (2005) *Meteoritics & Planetary Science*, 40, 71-86. [4] Sandford S. A. et al. (2006) *Science*, 314, 1720. [5] Beck P. et al. (2014) *Icarus*, 229, 263. [6] Dartois E. et al. (2018) *Astronomy & Astrophysics*, 609, A65. [7] Battandier M. et al. (2018) *Icarus*, 306, 74. [8] Kebukawa Y. et al. (2019) *Meteoritics & Planetary Science*, 54, 1632. [9] Quirico E. et al. (2022) this conference. [10] Dartois E. et al. (2022) this conference. [11] Mathurin J. et al. (2022) this conference. [12] Kebukawa Y. et al. (2011) *Geochimica et Cosmochimica Acta*, 75, 3530–3541. [13] Alexander C. M. O'D. (2014) *Meteoritics & Planetary Science* 49, 503-525. [14] Bonal L. et al. (2022) this conference. [15] Komatsu M. et al. (2022) this conference. [17] Yada T. et al. (2021) *Nature Astronomy*. [18] Pilorget C. et al. (2021) *Nature Astronomy*.