Hayabusa 2021 Symposium Schedule (Online Meeting)

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(*8th ISAS Symposium of the Solar System Materials*)

16th(Tue)-17th(Wed) of November 2021

Oral : Zoom Meeting (10+5 min for Invited and normal talks, 7+3 min for 10 min short talks)

Poster : Zoom Meeting Breakout Rooms

Non-real time discussion : Slack

Day-1 (Nov 16th) : Oral Session

JST	GMT	EST	PST	No.	Title	Author/Presenter	Invited
		(-1day)	(-1day)		Session-0 : Opening session: T. Okada		
09:45	00:45	19:45	16:45	S0-1	Opening and Logistics	Tatsuaki Okada	
09:50	00:50	19:50	16:50	S0-2	Status of JAXA Curation activity and future plan	Tomohiro Usui	
					Session-1: Ryugu sample : S. Tachibana, T. Usui		
10:00	01:00	20:00	17:00	S1-1	An overview of initial descriptions for samples returned from C-type asteroid Ryugu	Toru Yada	Invited
10:15	01:15	20:15	17:15	S1-2	First NIR hyperspectral imaging of Hayabusa2 returned samples by the MicrOmega microscope within the ISAS Curation Facility	Cedric Pilorget	Invited
10:30	01:30	20:30	17:30	S1-3	Initial analysis of Hayabusa2 returned samples from asteroid (162173) Ryugu	Shogo Tachibana	
10:45	01:45	20:45	17:45	S1-4	Progress of chemical characterization of asteroid Ryugu samples	Hisayoshi Yurimoto	Invited
11:00	02:00	21:00	18:00	S1-5	Initial analysis of “stone” size Ryugu samples: current status	Tomoki Nakamura	Invited
11:15	02:15	21:15	18:15	S1-6	Mineralogy and surface modification of small grains recovered from the asteroid 162173 Ryugu	Takaaki Noguchi	Invited
11:30	02:30	21:30	18:30	S1-7	Initial Analysis of Volatile Components in the Hayabusa2 Samples	Ryuji Okazaki	Invited
11:45	02:45	21:45	18:45	S1-8	An initial look at the distributions and compositions of organic macromolecules in the asteroid Ryugu samples	Hikaru Yabuta	Invited
12:00	03:00	22:00	19:00	S1-9	Soluble Organic Matter (SOM) analysis of the Hayabusa2 samples: The first results	Hiroshi Naraoka	Invited
12:15	03:15	22:15	19:15		<Lunch break> [Group Photo-1]	All	
					Sessions-2 : Ryugu Sample (Cont.) : R. Brunetto, A. Nakato		
13:30	04:30	23:30	20:30	S2-1	A first look at the interior and exterior of Ryugu preserved in samples collected by Hayabusa2	Eizo Nakamura	Invited
13:45	04:45	23:45	20:45	S2-2	The C-type asteroid Ryugu: A first detailed look by Phase2 Curation Kochi (Ph2K)	Motoo Ito	Invited
14:00	05:00	00:00	21:00	S2-3	JAXA Detailed Description -Variation of surface characteristics of Ryugu returned samples-	Aiko Nakato	
14:15	05:15	00:15	21:15	S2-4	Overview of the features of returned samples from the C-type asteroid 162173 Ryugu based on optical microscope observations and their weights	Akiko Miyazaki	10 min
14:25	05:25	00:25	21:25	S2-5	Initial description of Ryugu returned samples: characteristics of individual grains by FT-IR analysis	Kentaro Hatakeda	10 min
14:35	05:35	00:35	21:35	S2-6	MicrOmega detections of C-rich phases in Ryugu returned samples within the Hayabusa2 JAXA Extraterrestrial Curation Center	Jean-Pierre Bibring	
14:50	05:50	00:50	21:50	S2-7	MicrOmega detections of carbonates in Ryugu returned samples within the Hayabusa 2 JAXA Extraterrestrial Curation Center	Damien Loizeau	10 min
15:00	06:00	01:00	22:00	S2-8	The 2.7μm OH band in different grains of Ryugu from the two collection sites, as seen by MicrOmega in the Hayabusa2 Curation Facility	Tania Le Pivert-Jolivet	10 min
15:10	06:10	01:10	22:10	S2-9	Microscale diversity of H, C, and N isotopes in asteroid Ryugu	Larry R. Nittler	
15:25	06:25	01:25	22:25	S2-10	Diversity of Insoluble Organic Matter at the Nanoscale in Asteroid Ryugu	Rhonda Stroud	
15:40	06:40	01:40	22:40	S2-11	Infrared transmission spectra of Ryugu particles and their unique adsorption behavior	Yoko Kebukawa	
15:55	06:55	01:55	22:55	S2-12	Thermal history of Ryugu based on Raman characterization of Hayabusa2 samples	Lydie Bonal	
16:10	07:10	02:10	23:10	S2-13	Elemental and isotopic compositions of organic grains from asteroid Ryugu	Laurent Remusat	
16:25	07:25	02:25	23:25		<Coffee Break>		
					Sessions-3 : Ryugu Sample (Cont.) : H. Sugahara, D. Yamamoto		
16:40	07:40	02:40	23:40	S3-1	Exposure Conditions of Samples Collected on Ryugu’s Two Touchdown Sites Determined by Cosmogenic Nuclides	Kunihiko Nishiizumi	
16:55	07:55	02:55	23:55	S3-2	Small grains from Ryugu: handling and analysis pipeline for Infrared Synchrotron Microspectroscopy	Stefano Rubino	
17:10	08:10	03:10	00:10	S3-3	Preliminary results from FTIR hyper-spectral imaging campaign on Ryugu small grains and fragments.	Zelia Dionnet	
17:25	08:25	03:25	00:25	S3-4	Iron valence state and mineralogy in particles from asteroid Ryugu	Mathieu Roskosz	
17:40	08:40	03:40	00:40	S3-5	Three-dimensional analysis of Ryugu sample particles using X-ray nanotomography.	Akira Tsuchiyama	
17:55	08:55	03:55	00:55	S3-6	Surface morphologies and space weathering features of Ryugu samples	Toru Matsumoto	
18:10	09:10	04:10	01:10	S3-7	CNHOS contents with their isotopic compositions and preliminary organic profiles from the Hayabusa2 samples	Yoshinori Takano	
18:25	09:25	04:25	01:25	S3-8	Compound distribution determined by nanoLC-Orbitrap MS	François-Régis Orthous-Daunay	
18:40	09:40	04:40	01:40	S3-9	Highest molecular diversity and structural complexity revealed with ultrahigh resolution mass spectrometry and nuclear magnetic resonance spectroscopy of Ryugu´s samples	Philippe Schmitt-Kopplin	
18:55	09:55	04:55	01:55		Discussion on Ryugu sample	S. Tachibana (Lead)	
					[Group Photo-2]	All	

An overview of initial descriptions for samples returned from C-type asteroid Ryugu.

T. Yada[1], M. Abe[1], A. Nakato[1], K. Yogata[1], A. Miyazaki[1], K. Kumagai[2], K. Hatakeda[2], T. Okada[1], M. Nishimura[1], S. Furuya[1,3], M. Yoshitake[1,4], A. Iwamae[2,5], Y. Hitomi[2], H. Soejima[2], K. Nagashima[1], R. Sawada[2], L. Riu[1,6], L. Lourit[6], C. Pilorget[6], V. Hamm[6], D. Loizeau[6], R. Brunetto[6], J.-P. Bibring[6], Y. Cho[3], K. Yumoto[3], Y. Yabe[3], S. Mori[3], S. Sugita[3], S. Tachibana[1,3], H. Sawada[1], K. Sakamoto[1], T. Hayashi[1], D. Yamamoto[1], R. Fukai[1], H. Sugahara[1], H. Yurimoto[7], T. Usui[1], S. Watanabe[8], Y. Tsuda[1]

[1]Inst. Space Astronaut. Sci., Japan Aerosp. Explor. Agency (JAXA), Kanagawa 252-5210, Japan (yada@planeta.sci.isas.jaxa.jp), [2]Marine Works Japan Ltd., Yokosuka 237-0063, Japan, [3]UTOPS, Grad. Sch. Sci., Univ. Tokyo, Tokyo 113-0033, Japan, [4]Japan Patent Office, Chiyoda-ku, Tokyo 100-8915, Japan, [5]Toyo Univ., Bunkyo-ku, Tokyo 112-8606, Japan, [6]Institut d'Astrophysique Spatiale, Université Paris-Saclay, CNRS, 91400 Orsay, France, [7]Dept. Earth Planet. Sci., Grad. Sch. Sci., Hokkaido Univ., Hokkaido 060-0808, Japan, [8]Dept Earth Planet. Sci., Grad. Sch. Sci., Nagoya Univ., Nagoya 464-8601, Japan.

Introduction: Hayaubsa2 spacecraft operated by JAXA explored a near-Earth asteroid 162173 Ryugu from Jun 2017 to Nov 2019 [1]. During the exploration, the spacecraft accomplished touchdown sampling on the asteroid's surface in Feb and Jul of 2019 [2]. The samples recovered by the first touchdown were stored in the Chamber A of a sample catcher and those by the second one were in the Chamber C [2]. The sample catcher was sealed in a sample container, which was set in a reentry capsule of the spacecraft, and the capsule was returned to the Earth, the Woomera Prohibited Area in South Australia, on 6 Dec 2020 [2, 3].

Extraction Procedures for Ryugu samples: As the container was transported from Australia to Japan by air and arrived at cleanrooms of the Extraterrestrial Sample Curation Center (ESCuC), it was disassembled to remove unnecessary parts and cleaned on its surface in the cleanrooms and introduced into the clean chamber (CC) 3-1 to be evacuated to high vacuum [2, 3]. In the static vacuum condition, the container was opened and the sample catcher was extracted from the container. The catcher was transported to the next chamber, CC3-2, and a lid of the Chamber A of the catcher was removed from the catcher and a few mm-size particles were recovered from the Chamber A to a quartz glass container in vacuo. Then the catcher with rest of samples was transported to the next chamber, CC3-3, then the catcher handling environment have changed from vacuum to purified nitrogen condition. Hereafter, all the extraction works and initial descriptions have been done in this purified nitrogen condition in the clean chambers. The catcher was firstly measured with a balance equipped in the chamber CC4-2 to confirm the bulk samples' weight in it, to be 5.4 grams [3]. Then it was dismantled with catcher handling tools in the chamber CC4-1 to recover samples from each chamber of the catcher to sapphire dishes of 23mm in diameter.

Initial descriptions for bulk and individual Ryugu samples: Each of the bulk samples in the dishes were observed and photographed with a stereomicroscope equipped above the chamber CC4-2. Then they were also measured with the balance for their bulk weights to be 3.2 grams and 2.0 grams from the from the Chamber A and C, respectively [4]. They were then analyzed with a Fourier Transmission Infrared spectrometer (FT-IR) for their near infrared reflectance spectra in wavelength ranging from 2.0 to 4.0 μm [4]. They were also analyzed with a MicrOmega, infrared imager comparable to that onboard instrument of MASCOT lander released from Hayabusa2 spacecraft, for obtaining overall and local infrared spectra in the bulk Ryugu samples [1, 5-7]. Finally, they were analyzed with an optical microscopic imaging through six filters (ul: 0.39 μm, b: 0.48μm, v: 0.55 μm, Na: 0.59 μm, w: 0.70 μm, x: 0.85 μm), compatible with the ONC-T camera of Hayabusa2, onboard instrument of Hayabusa2 [8]. After the series of initial descriptions for bulk Ryugu samples, individual particles have been handpicked from the bulk samples to sapphire dishes for individual samples with a vacuum tweezer, and described in the same manner as the bulk samples experienced [9-11]. The results of initial descriptions for bulk Ryugu samples are presented in [4]. Their small bulk densities and dark visible and infrared spectral features indicates that obtained samples are representative of surface materials of Ryugu. Together with absence of high temperature components like a chondrule and a Calcium-Aluminum rich Inclusion (CAI) and presence of 2.7 μm absorption band in infrared spectra, which corresponds to hydroxyls (-OH) absorption implying abundant phyllosilicate, they are most similar to CI chondrites among known planetary materials.

Data archive and sample distributions: All the obtained data by the initial descriptions have been archived in Hayabusa2 sample data catalog [12]. This catalog will be in public soon as a reference of Announcement of Opportunity (AO) for Ryugu samples, which will start in early 2022. Any researcher can apply for the AO, and Ryugu samples will be distributed to Principle Investigators (PIs) of selected proposals in the middle of 2022.

References: [1] Tsuda Y. et al. (2020) *Acta Astron.* 171, 42-54. [2] Tachibana S. et al. (2021) *LPS, XXXXXII*, Abstract #1289. [3] Yada T. et al. (2021) *LPS, XXXXXII*, Abstract #2008. [4] Yada T. et al., *submitted to Nature Astron.* [5] Pilorget C. et al., *submitted to Nature Astron.* [6] Bibring J.-P. et al., *this meeting.* [7] Yogata K. et al., *this meeting*. [8] Sugita S. et al. (2020) *Science* 364, eaaw0422. [9] Miyazaki A. et al., *this meeting*. [10] Hatakeda K. et al., *this meeting*. [11] Cho Y. et al., *this meeting*. [12] Nishimura M. et al., *this meeting*.

First NIR hyperspectral imaging of Hayabusa2 returned samples by the MicrOmega microscope within the ISAS Curation Facility

[1]Pilorget, C.; [2,3]Okada, T.; [1]Hamm, V.; [1]Brunetto, R.; [2]Yada, T.; [1]Loizeau, D.; [2]Riu, L.; [2,3]Usui, T.; [4]Moussi-Soffys, A.; [2,5]Hatakeda, K; [2]Nakato, A.; [2]Yogata, K.; [2,6]Abe, M.; [1]Aléon-Toppani, A.; [1]Carter, J.; [1]Chaigneau, M.; [1]Crane, B.; [1]Gondet, B.; [2,5]Kumagai, K.; [1]Langevin, Y.; [1]Lantz, C.; [1]Le Pivert-Jolivet, T.; [1]Lequertier, G.; [1]Lourit, L.; [2]Miyazaki, A.; [2]Nishimura, M.; [1]Poulet, F.; [7]Arakawa, M.; [8]Hirata, N.; [8]Kitazato, K.; [2]Nakazawa, S.; [9]Namiki, N.; [2]Saiki, T.; [3]Sugita, S.; [2,3]Tachibana, S.; [2,6,10]Tanaka, S.; [2,6]Yoshikawa, M.; [2,6]Tsuda, Y.; [11]Watanabe, S.; [1]Bibring, J.-P.

[1] Institut d'Astrophysique Spatiale, Université Paris-Saclay, CNRS, 91400 Orsay, France, [2] Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, Sagamihara 252-5210, Japan, [3] University of Tokyo, Bunkyo, Tokyo 113-0033, Japan, [4] Centre National d'Etudes Spatiales, 18 Avenue E. Belin, 31401 Toulouse, France, [5] Marine Works Japan, Ltd., Yokosuka 237-0063, Japan, [6] The Graduate University for Advanced Studies (SOKENDAI), Hayama 240-0193, Japan, [7] Kobe University, Kobe 657-8501, Japan, [8] The University of Aizu, Aizu-Wakamatsu 965-8580, Japan, [9] National Astronomical Observatory of Japan, Mitaka 181-8588, Japan, [10] University of Tokyo, Kashiwa 277-8561, Japan, [11] Nagoya University, Nagoya 464-8601, Japan.

Introduction: On December 6, 2020, the Hayabusa2 mission successfully returned to Earth ~ 5.4 g of samples collected at the surface of the C-type asteroid Ryugu [1,2]. Its surface was first sampled on February 22, 2019, then on July 11, 2019, close to a 15-meter large artificial crater, so as to possibly access sub-surface material [3]. The collected samples are now kept at the Extraterrestrial Samples Curation Center of JAXA at ISAS in Sagamihara, Japan, for a first round of preliminary analyses, with the objective of characterizing in a non-destructive manner both the bulk samples and a few hundreds of grains extracted from them [4]. In particular, the goal is 1) to support their further detailed characterization by the international Initial Analysis Teams, and 2) to build a catalogue of the grains, accessible to the international community through AO selection, starting mid-2022.

Methods: The preliminary characterization of these samples is being conducted with a visible microscope with five color filters, a FTIR spectrometer operating in the 1-4 µm range, and MicrOmega, a hyperspectral NIR microscope developed at Institut d'Astrophysique Spatiale (Université Paris-Saclay/CNRS, Orsay, France), operating in the near-infrared range (0.99-3.65 µm) [5]. This is the first time that preliminary analyses of returned extraterrestrial samples include a characterization by a NIR hyperspectral microscope.

Results: Preliminary outcomes of the analyses performed with MicrOmega will be presented. In particular, the representativity of the samples collected by the Hayabusa2 spacecraft will be addressed through the comparison of the spectra obtained by MicrOmega and of the NIRS3 remote sensing IR spectrometer [6] which performed a spectral characterization (1.8-3.2 µm) of Ryugu's surface, including the sites of the samples' collection [7,8].

At a global scale, all bulks exhibit similar features, with a dominant OH- 2.7 µm component and a 3.3 – 3.5 µm band centered around 3.4 µm. Their variation at different spatial scales and significance will be presented. Specific signatures, detected in grains typically present in <1% of the pixels, but of high relevance regarding the processes determining Ryugu formation and evolution, will also be presented and discussed.

References: [1] Binzel R. P. et al. (2002), *Physical Properties of Near-Earth Objects.* pp. 255-271, [2] Vilas F. (2008) *The Astronomical Journal* 135 (4), 1101-1105, [3] Morota et al. (2020) *Science* 368, Issue 6491, pp. 654-659, [4] Yada T. et al., Nature Astronomy, *submitted*, [5] Bibring J.-P. et al. (2017) *Astrobiology* 17, Issue 6-7, pp.621-626, [6] Iwata T. et al. (2017) *Space Science Reviews* 208 (1-4), 317-337, [7] Kitazato K. et al. (2019) *Science* 364 (6437), 272-275, [8] Kitazato K. et al. (2020) *Nature Astronomy*, Volume 5, p. 246-250.

Initial analysis of Hayabusa2 returned samples from asteroid (162173) Ryugu

Shogo Tachibana[1,2], Hisayoshi Yurimoto[3], Tomoki Nakamura[4], Takaaki Noguchi[5,6], Ryuji Okazaki[6], Hikaru Yabuta[7], Hiroshi Naraoka[6], Kanako Sakamoto[2], Sei-ichiro Watanabe[8], Yuichi Tsuda[2], and the Hayabusa2 Initial Analysis team
[1]*Univ. Tokyo,* [2]*ISAS, JAXA,* [3]*Hokkaido Univ,* [4]*Tohoku Univ.,* [5]*Kyushu Univ.,* [6]*Kyoto Univ.,* [7]*Hiroshima Univ.,* [8]*Nagoya Univ.*

The JAXA's Hayabusa2 spacecraft explored C-type near-Earth asteroid (162173) Ryugu from June 2018 to November 2019, during which two touchdown operations were made to collect surface and subsurface samples. The Hayabusa2 delivered its reentry capsule on December 6, 2020 to Woomera, South Australia [1]. The sample container inside the reentry capsule was opened in the clean chamber system dedicated to Ryugu samples at ISAS, JAXA. Dark particles were found in both chambers A and C, which were used for the storage of the samples collected at the first and second touchdown, respectively. The total amount of the samples exceeds 5 g, which is much larger than the minimum requirement of 0.1 g [2]. Many millimeter-sized particles were present with fine powdery materials, and centimeter-sized grains, close to the maximum obtainable size [3], were found in the chamber C. The color, morphology, and spectroscopic features of the grains indicates that they well represent the surface materials of Ryugu.

The initial analysis of a fraction of returned samples, led by the Hayabusa2 project, has begun in June 2021 after the 6-month sample description at the ISAS curation facility without exposure to the air. The initial analysis aims at maximizing the scientific achievement of the project with answering important fundamental questions such as what materials Ryugu consists of, how Ryugu evolved from its formation to the present, and how similar or different Ryugu samples are to the known meteorites. The findings from Ryugu samples are expected to invoke cosmochemical discussion on the origin and evolution of the Solar System architecture such as the isotopic dichotomy in the early Solar System, the delivery of water and organics to the inner Solar System, and the asteroid-comet continuum. The initial analysis also aims at providing the ground truth for the remote sensing data obtained by the Hayabusa2 spacecraft.

The initial analysis team consists of six sub-teams for 1) chemistry (elements and isotopes) (Lead: Hisayoshi Yurimoto, Hokkaido University), 2) petrology and mineralogy of coarse grains (mm-sized grains [stone]) (Lead: Tomoki Nakamura, Tohoku University), 3) petrology and mineralogy of fine grains (<100 μm-sized grains [sand]) (Lead: Takaaki Noguchi, Kyoto University/Kyushu University), 4) volatiles (Lead: Ryuji Okazaki, Kyushu University), 5) insoluble organic matter (macromolecular organics) (Lead: Hikaru Yabuta, Hiroshima University), and 6) soluble organic matter (organic molecules) (Lead: Hiroshi Naraoka, Kyushu University). The total number of teams members is nearly 300 from fourteen countries. The initial analysis will continue for 12 months. The data obtained during the initial analysis will be archived in the JAXA curatorial sample database to prove the potential of the samples to the community.

Three hundred milligrams of Ryugu samples (6 % of the total samples by mass) have been allocated from JAXA to the initial analysis team; Twenty two grains, which were individually photographed, weighed, and spectroscopically examined in the clean chamber system, and ten aggregate samples that mainly consist of particles smaller than 1 mm in diameter (Table 1).

Table 1. Samples allocated to the Hayabusa2 initial analysis team.

Individual grains (Chamber A)	Individual grains (Chamber C)	Aggregates (Chamber A)	Aggregates (Chamber C)
A0026 3.9 mg	C0002 93.5 mg	A0104 0.3 mg	C0105 0.4 mg
A0040 3.0 mg	C0023 5.0 mg	A0105 4.0 mg	C0106 4.0 mg
A0055 5.9 mg	C0025 5.6 mg	A0106 38.4 mg	C0107 38.8 mg
A0058 3.3 mg	C0033 2.4 mg	A0107 31.0 mg	C0108 33.0 mg
A0063 3.8 mg	C0040 4.9 mg	A0108 3.5 mg	C0109 3.7 mg
A0064 6.7 mg	C0046 2.6 mg		
A0067 3.6 mg	C0055 0.8 mg		
A0080 1.4 mg	C0057 0.9 mg		
A0086 0.9 mg	C0061 1.3 mg		
A0089 1.0 mg	C0076 4.7 mg		
A0094 1.8 mg	C0103 1.5 mg		

The allocated samples have been individually investigated by each sub-team or by collaboration of multiple sub-teams. The C0002 grain from the chamber C is the third largest particle (~9 x 5 x 4 mm) among all the returned particles (Table 1). This grain has been analyzed by all six sub-teams.

In this presentation we discuss the goals and overall activities of the initial analysis of Ryugu samples. Preliminary results of elemental and isotopic analyses, mineralogical and petrological observation, and analyses of volatiles and organic components will be presented from each sub team at the meeting [e.g., 4–22].

References

[1] Tachibana S. et al. (2021) *51st LPSC,* Abstract #1289. [2] Tachibana S. et al. (2014) *Geochem. J.* **48,** 571–587. [3] Sawada H. et al. (2017) *Space Sci. Rev.* **208,** 81–106. [4] The Hayabusa2-initial-analysis chemistry team et al. (2021) *this meeting*. [5] Nakamura T. et al. (2021) *this meeting*. [6] Noguchi T. et al. (2021) *this meeting*. [7] Okazaki R. et al. (2021) *this meeting*. [8] Yabuta H. et al. (2021) *this meeting*. [9] Naraoka H. et al. (2021) *this meeting*. [10] Tsuchiyama A. et al. (2021) *this meeting*. [11] Dionnet Z. et al. (2021) *this meeting*. [12] Rubino S. et al. (2021) *this meeting*. [13] Viennet J.-C. et al. (2021) *this meeting*. [14] Matsumoto T. et al. (2021) *this meeting*. [15] Nishiizumi K. et al. (2021) *this meeting*. [16] Kebukawa Y. et al. (2021) *this meeting*. [17] Bonal L. et al. (2021) *this meeting*. [18] Stroud R. M. et al. (2021) *this meeting*. [19] Nittler L. R. et al. (2021) *this meeting*. [20] Takano Y. et al. (2021) *this meeting*. [21] Orthous-Daunay F.-R. et al. (2021) *this meeting*. [22] Schmitt-Kopplin P. et al. (2021) *this meeting*.

Progress of chemical characterization of asteroid Ryugu samples

The Hayabusa2-initial-analysis chemistry team[1],
T. Nakamura[2], T. Noguchi[2], R. Okazaki[2], H. Yabuta[2], H. Naraoka[2], K. Sakamoto[2], S. Tachibana[2], S. Watanabe[2] and Y. Tsuda[2]

[1]*See end of this abstract*
[2]*Tohoku Univ., Kyoto Univ., Kyushu Univ., Hiroshima Univ., Kyushu Univ., JAXA, Tokyo Univ., Nagoya Univ. and JAXA*

It is believed that meteorites come from asteroids. Samples of asteroid (25143) Itokawa returned by the JAXA Hayabusa mission revealed that S-type asteroids are composed of materials consistent with the ordinary chondrite class [1, 2]. The JAXA Hayabusa2 [3] spacecraft launched on December 3rd, 2014 towards an asteroid (162173) Ryugu to clarify relationships between C-type asteroids and the carbonaceous chondrite class. Remote sensing observations from Hayabusa2 show that (1) the albedo of Ryugu is darker than those of every known meteorite class [4, 5], (2) an absorption band at 2.72 µm indicates that phyllosilicates are ubiquitous on Ryugu [5], (3) the strength and shape of the absorption band feature suggests that Ryugu materials experienced heating above 300 °C [6], and (4) thermal inertia suggests that Ryugu materials are more porous than every known carbonaceous chondrite [7]. These results suggest that carbonaceous chondrite class materials are plausible for Ryugu materials, but no known carbonaceous chondrite completely matches the results obtained from Ryugu.

The Hayabusa2 spacecraft made two successful landings operations onto Ryugu to collect asteroidal materials in 2019 and delivered the collected samples to the Earth on December 6th, 2020. The returned samples are detritus from pebbles to clay, exceeding 5 grams in total. Their colors, shapes and macro-structures are consistent with those of the remote sensing observations, indicating that the returned samples are representative of the asteroid Ryugu [8]. The initial analysis of the Ryugu samples began in June 2021. At that time, samples totaling ~125 mg, containing powder and particles from the 1st and 2nd touchdown sites, were allocated to the Initial Analysis Chemistry Team.

The goals of the Initial Analysis Chemistry Team analyses are to provide fundamental answers to questions relating to the provenance of Ryugu samples for in-depth research by international scientists in the future: (i) What are the elemental abundances of Ryugu? (ii) What are the isotopic compositions of Ryugu? (iii) Does Ryugu consist of primary materials formed in the protosolar disk or secondary materials altered on the parent body? (iv) When were Ryugu materials formed? and (v) What are the relations to known meteoritic samples?

Hydrogen, C and S are analyzed by combination of thermogravimetric analysis coupled with mass spectrometry (TG-MS) and by pyrolysis and combustion analyses (EMIA-Step). Major and minor elements are analyzed by X-ray fluorescence analysis (XRF) using laboratory X-rays and synchrotron radiation. Trace elements are analyzed by inductively coupled plasma mass spectrometry (ICP-MS) using calibration curve and isotope dilution methods after acid digestion. We quantify the abundance of 66 elements in Ryugu samples: H, Li, Be, C, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Tl, Pb, Bi, Th, and U. Inorganic and organic element concentrations are also analyzed for H and C.

For isotope analyses, the Ryugu samples are digested with acids, and the target elements are successively separated by ion-exchange column chromatography. We use thermal ionization mass spectrometry (TIMS) and ICP-MS with multi-collectors to measure isotope ratios. We determine isotope ratios for chronological systems of Rb-Sr, Sm-Nd, U-Th-Pb, Lu-Hf, Hf-W, Re-Os, Al-Mg, and Mn-Cr. We also determine stable isotope systematics of Ca, Ti, Cr, Fe, Ni, Sr, Ba, Zr, Mo, Ce, Gd, Ru and Nd to test isotopic dichotomy in the solar system. Oxygen isotope systematics of Ryugu are measured by laser-fluorination isotope-ratio mass-spectrometry (LF-IRMS) for bulk samples and by secondary ion mass spectrometry (SIMS) for individual components in the samples. The SIMS technique is also applied to the Mn-Cr chronological systematics to determine ages of aqueous alteration. Surveying for circumstellar and molecular cloud matter is conducted by isotope microscope and NanoSIMS.

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The Hayabusa2-initial-analysis chemistry team:
H. Yurimoto[1], T. Yokoyama[2], K. Nagashima[3], I. Nakai[4], Y. Abe[5], Y. Terada[6], S. Komatani[7], M. Morita[7], K. Ichida[7], H. Homma[8], K. Motomura[8], K. Yui[4], T. Usui[9], M. K. Haba[2], T. Iizuka[10], S. Yoneda[11], H. Hidaka[12], K. Yamashita[13], M. Bizzarro[14], F. Moynier[15], M. Schöenbächler[16], T. Kleine[17], N. Dauphas[18], Q-Z. Yin[19], M. Wadhwa[20], R. J. Walker[21], R. W. Carlson[22], A. Bouvier[23], Y. Amelin[24], L. Qin[25], I. Gautam[2], R. Fukai[9], Y. Masuda[2], Y. Hibiya[10], A. Ishikawa[2], A. Pack[26], E. D. Young[27], C. Park[28], N. Sakamoto[1], W. Fujiya[29], N. Kawasaki[1], S. Itoh[30], K. Terada[31], M. Ito[32], M. Chaussidon[15], J. Aleon[33], L. Piani[34], S. Russell[35], P. Hoppe[36], S. Amari[37], K. D. McKeegan[27], M-C. Liu[27], G. R. Huss[3], A. N. Krot[3], C. M. O'D. Alexander[22], L. R. Nittler[22], A. M. Davis[18], A. Nguyen[38], N. Kita[39], K. Kitajima[39], T. R. Ireland[40], B-G. Choi[41], A-C. Zhang[42], K. Bajo[1]

[1]Hokkaodo Univ., [2]Tokyo Tech., [3]Univ. Hawai'i, [4]Tokyo Univ. Sci. [5]Tokyo Denki Univ., [6]SPring-8, [7]HORIBA TECHINO SERVICE Co., Ltd., [8]Rigaku Co., [9]JAXA, [10]Univ. Tokyo, [11]National Museum Nature Sci. Tokyo, [12]Nagoya Univ. [13]Okayama Univ., [14]Natural History Museum Denmark, [15]Inst. Phys. Globe Paris, [16]ETH, [17]Univ. Münster, [18]Univ. Chicago, [19]UC Davis, [20]ASU, [21]Univ. Maryland, [22]Carnegie Inst. Sci., [23]Univ. Bayreuth, [24]ANU, [25]China Univ. Geosci., [26]Univ. Göttingen, [27]UCLA, [28]KOPRI, [29]Ibaraki Univ., [30]Kyoto Univ., [31]Osaka Univ., [32]JAMSTEC, [33]MNHN, [34]CRPG, [35]NHM, [36]MPI Chemistry, [37]Washington Univ. St. Louis, [38]NASA, [39]Univ. Wisconsin, [40]Univ. Queensland, [41]SNU, [42]Nanjing Univ.

Initial analysis of “stone” size Ryugu samples: current status

Tomoki Nakamura[1], Megumi Matsumoto[1], Kana Amano[1], Yuma Enokido[1], Mike Zolensky[2], Takashi Mikouchi[3], Yuri Fujioka[1], Mizuha Kikuiri[1], Eiichi Kagawa[1], Daisuke Nakashima[1], Adrian Brearley[4], Mikhail Zolotov[5], Akira Tsuchiyama[6], Masayuki Uesugi[7], Yoshio Takahashi[3], Moe Matsuoka[8], Ralph Milliken[9], Donald Brownlee[10], David Joswiak[10], Miki Takahashi[1], Kazuhiko Ninomiya[11], Tadayuki Takahashi[3], Takahito Osawa[12], Kentaro Terada[11], Frank E. Brenker[13], Beverley Tkalcec[13], Yuki Kimura[14], Satoshi Tanaka[8], Housei Nagano[15], Rosario Brunetto[16], Alice Aléon-Toppani[16], Queenie Chan[17], Mathieu Roskosz[18], Esen Ercan Alp[19], Pierre Beck[20], Aiko Nakato[8], Takaaki Noguchi[21], Masahiko Tanaka[22], Takahiro Hiroi[9], Eri Tatsumi[23], Faith Vilas[24], Amanda R. Hendrix[24], Camilo Jaramillo[25], Gerardo Dominguez[26], Cecile Engrand[16], Jean Duprat[16], Hidenori Genda[27], Kousuke Kurosawa[28], Sara Russell[29], Ashley King[29], Enrica Bonato[30], Chi Ma[31], Kentaro Uesugi[7], Akihisa Takeuchi[7], Jyunya Matsuno[21], Akira Miyake[21], Satomi Enju[32], Masahiro Yasutake[7], Toru Matsumoto[33], Shota Okumura[21], Aki Takigawa[3], Shohei Yamashita[34], Takahiro Kawai[3], Jean-Christophe Viennet[18], Barbara Lavina[19], Toshiaki Tanigaki[35], Kazuo Yamamoto[36], Deborah Domingue Lorin[24], Ferenc Borondics[37], Zélia Dionnet[16], Donia Baklouti[16], Zahia Djouadi[16], Cateline Lantz[16], Stefano Rubino[16], Laszlo Vincze[38], Bart Vekemans[38], Gerald Falkenberg[39], Pieter Tack[38], Ella De Pauw[38], Miles Lindner[13], Benjamin Bazi[38], Shinya Yamada[40], Kenya Kubo[41], Shunsaku Nagasawa[3], Taiga Wada[1], Satoshi Takeshita[34], Akihiro Taniguchi[21], Shin Watanabe[3, 8], Izumi Umegaki[34], Chiu I-Huan[11], Yasuhiro Miyake[34], Kosuke Inoue[42], Seiji Sugita[3], Kohei Kitasato[43], Hisayoshi Yurimoto[14], Ryuji Okazaki[33], Hikaru Yabuta[44], Hiroshi Naraoka[33], Kanako Sakamoto[8], Shogo Tachibana[3,8], Seiichiro Watanabe[15], Yuichi Tsuda[8] and the Hayabusa2-initial-analysis Stone team.

[1]*Tohoku University, Japan, 2NASA/JSC, USA, 3The University of Tokyo, Japan, 4University of New Mexico, USA, 5Arizona State University, USA, 6Ritsumeikan University, Japan and CAS, GIG, China, 7JASRI/SPring-8, Japan, 8ISAS/JAXA, Japan, 9Brown University, USA, 10University of Washington, USA, 11Osaka University, Japan, 12Japan Atomic Energy Agency, Japan, 13Goethe University Frankfurt, Germany, 14Hokkaido University, Japan, 15Nagoya University, Japan, 16University of Paris-Saclay, France, 17University of London, UK, 18Muséum National d'Histoire Naturelle, France, 19Argonne National Laboratory, USA, 20Université Grenoble Alpes, France, 21Kyoto University, Japan, 22National Institute for Materials Science, Japan. 23 Instituto de Astrofísica de Canarias, Spain,, 24Planetary Science Institute, USA, 25Pensylvania State University, 26Callfornia State University, USA, 27Tokyo tech, Japan, 28Chiba tech, Japan, 29Natural History Museum, UK, 30Deutsches Zentrum für Luft- und Raumfahrt, Germany, 31Caltech, USA, 32Ehime University, Japan, 33Kyusyu University, Japan, 34High Energy Accelerator Research Organization (KEK), Japan, 35Hitachi, Ltd., Japan, 36Japan Fine Ceramics Center, Japan, 37SOLEIL Synchrotron, France, 38Ghent University, Belgium, 39DESY, Germany, 40Rikkyo University, Japan, 41International Christian University, Japan, 42Kanazawa University 43University of Aizu, Japan, 44Hiroshima University, Japan.*

As a part of the initial analysis of the Ryugu samples, we perform a variety of analyses of millimeter-sized "stones". Our goals are to elucidate the entire formation process of Cb-type asteroid Ryugu from the viewpoint of petrology and mineralogy and obtain necessary information by sample analysis, and then simulate the formation of Ryugu based on the evidence obtained from sample analysis. Eighteen stones (8 from the chamber A and 10 from the chamber C) were received from the ISAS curation facility on June 1, 2021, and placed into a fully nitrogen-displaced glove box at Tohoku University. At the same time, we also received the powder samples from the chamber A and the chamber C. All the allocated samples were put in the sample transport containers prepared by ISAS in the nitrogen atmosphere inside the clean chamber system dedicated to Ryugu samples. The containers were then transferred to the nitrogen glovebox at ISAS, where all the containers were completely sealed in plastic bags with moisture and oxygen absorbers. No moisture or oxygen was detected when the bags were opened in the glove box at Tohoku University, so it was confirmed that there was no exposure to the atmosphere during transport.

To date, a number of analyses have been carried out successfully and within schedule margins. The analysis started with the measurement of reflectance spectra, which are sensitive to atmospheric oxidation, hydroxylation, and adsorbed water. The ultraviolet, visible, near-infrared, and mid-infrared reflectance spectra were measured while the samples were kept airtight. The spectra of powder samples and stone samples (as aggregates and as a single stone) were successfully obtained. Concurrent with the analyses described below were ultra-violet spectral observations on stone samples, also transported and performed in an inert environment, conducted at the University of Illinois Urbana-Champaign (USA).

A major feature of the stone team's analysis is the use of synchrotron radiation facilities around the world. Since this analysis is non-destructive, stone samples whose reflectance spectra were measured were sent to KEK, SPring-8, ESRF (France), SOLEIL (France), DESY (Germany), and APS (USA). Using these synchrotron radiation facilities, high spatial resolution and sensitivity XRD, STXM, XANES, CT [1], IR-CT, FT-IR [2, 3], XRF, and Mössbauer [4] analyses were performed. Most of the analyses were carried out under airtight conditions on the stone samples and the particulates separated from the stone samples. These analyses allowed us to determine the three-dimensional distribution of solid phases and elements, redox state, density, and porosity of the stone samples.

Furthermore, as a characteristic analysis of the stone team, light elemental analysis using negative Muon was performed at the MLF facility of J-PARC with an exceptionally long allocation of machine time. This is the non-destructive method to measure the concentration of light elements in the whole (not the surface) of stone samples. Because the characteristic X-rays produced by muon irradiation are much higher in energy than the fluorescent X-rays produced by X-ray irradiation, there is little effect of self-absorption by the sample, and therefore, the concentration of light elements such as carbon, oxygen, and sodium in the entire "stone" sample can be determined.

Some stone samples are currently being measured for thermal conductivity and strengths in order to understand the physical properties of asteroid Ryugu. The data obtained from these measurements are useful for interpreting the remote-sensing data data taken from the surface layer of the asteroid Ryugu [5-8]. It is also important for understanding the behavior of the Ryugu material during impact events.

The surfaces of many stone samples were observed by electron microscopy and other techniques, especially on natural “flat” surfaces formed on 5 stones. As a result, characteristric mineral aggregates formed by the reactions with water and characteristic impact features were observed on some samples. Based on the observations of surfaces and the synchrotron measurements of the whole stones, important objects such as characteristic structures and specific crystal aggregates for understanding the formation history of the asteroid were identified, and these parts were separated from the stone samples using a Xe beam (pFIB) and analyzed by various methods including transmission electron microscopy and synchrotron radiation analysis. Many stone samples, from which important objects have been separated, are embedded in epoxy resin and cut to produce many polished sections. Electron microscopy and spectroscopic measurements of the polished surfaces are being carried out to reveal the detailed mineralogical properties and elemental distribution inside the stone samples. In this fall, the allocate beam time for synchrotron radiation will begin, and we plan to analyze single crystals and characteristic objects separated from the stone samples. Photometric measurements in the ultra-violet and visible to near-infrared will also be made this fall on the powders produced in the structural experiments to facilitate comparisons with the ONC-T and NIRS3 remote sensing observations.

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Mineralogy and surface modification of small grains recovered from the asteroid 162173 Ryugu

T. Noguchi[1], T. Matsumoto[1], A. Miyake[1], Y. Igami[1], M. Haruta[1], H. Saito[2], S. Hata[2], Y. Seto[3], M. Miyahara[4], N. Tomioka[5], H. A. Ishii[6], J. P. Bradley[6], K. Ohtaki[6], E. Dobrică[6], T. Nakamura[7], M. Matsumoto[7], A. Tsuchiyama[8, 9]; M. Yasutake[10], J. Matsuno[8], S. Okumura[1], K. Uesugi[10], M. Uesugi[10], A. Takeuchi[10], M. Sun[9], S. Enju[11], A. Takigawa[12], H. Leroux[13], C. Le Guillou[13], D. Jacob[13], M. Marinova[13], F. de la Peña[13], F. Langenhorst[14], D. Harries[14], P. Beck[15], T. H. V. Phan[15], R. Rebois[15], N. M. Abreu[16], T. Zega[17], P.-M. Zanetta[17], M. Thompson[18], M. Lee[19], L. Daly[19], P. A. Bland[20], R. Stroud[21], K. Burgess[21], J. C. Bridges[22], L. Hicks[22], M. E. Zolensky[23], D. R. Frank[6], J. Martinez[24], H. Yurimoto[25], K. Nagashima[6], N. Kawasaki[25], R. Okazaki[2], H. Yabuta[4], H. Naraoka[2], K. Sakamoto[26], S. Tachibana[12], S. Watanabe[27], Y. Tsuda[26], and the Hayabusa2 Initial Analysis Team

[1]*Kyoto Univ., Japan;* [2]*Kyushu Univ., Japan;* [3]*Kobe Univ., Japan;* [4]*Hiroshima Univ., Japan;* [5]*Kochi Core Center, JAMSTEC, Japan;* [6]*Univ. of Hawaii, USA;* [7]*Tohoku Univ., Japan;* [8]*Ritsumeikan Univ., Japan;* [9]*Guangzhou Institute of Geochemistry, China;* [10]*JASRI, Japan;* [11]*Ehime Univ., Japan;* [12]*Univ. of Tokyo, Japan;* [13]*Univ. de Lille, France;* [14]*Univ. of Jena, Germany;* [15]*Univ. Grenoble Alpes, France;* [16]*Penn State, USA;* [17]*Univ. of Arizona, USA;* [18]*Purdue Univ., USA;* [19]*Univ. of Glasgow, UK;* [20]*Curtin Univ., Australia;* [21]*US Naval Research Laboratory, USA;* [22]*Univ. of Leicester, UK;* [23]*JSC/NASA, USA;* [24]*Jacobs Engineering, USA,* [25]*Hokkaido Univ., Japan;* [26]*JAXA/ISAS, Japan;* [27]*Nagoya Univ., Japan*

Introduction: Surface material on airless bodies exposed to the interplanetary space experienced the bombardment by low-energy (~1 keV/nucleon) solar wind particles and micrometeoroid impacts. These processes, alongside the resultant surface modifications, and spectral darkening and reddening are called space weathering [1]. Space weathering of the Moon and the asteroid 25143 Itokawa belonging to S-type asteroids have been investigated intensively [e.g. 1-5]. The *Hayabusa 2* spacecraft returned samples from the asteroid 162173 Ryugu C-type asteroid. The Ryugu samples give us the first opportunity to investigate space weathering of C-type asteroids. The Mineralogy-Petrology Fine (M-P F or Sand) sub-team mainly investigates small grains (typically ~100 µm across). The main purposes of the M-P F sub-team are to understand the variation of mineralogy of the allocated grains and the nature of space weathering of the asteroid Ryugu. The M-P F sub-team is comprised of 51 members belonging to 25 universities and laboratories.

Sample and methods: Numerous small Ryugu grains, ~100 µm across on average, were allocated to the M-P F sub-team. Surface morphology of >350 grains from the chamber A of the sample canister have been observed by JEOL JSM-7001F field emission scanning electron microscope (FE-SEM) at Kyoto Univ. and by Thermo Scios focused ion beam (FIB)-SEM at Kyushu Univ. Elemental mapping analysis was also performed using Energy dispersive spectrometer (EDS) equipped on the FE-SEM. Most of the grains were attached to Au plates with small amounts of epoxy glue in N_2 filled glove box for SEM observation. Some grains were just placed on Pt plates without using any glue to make FIB sections in response to requests from some members. One sample was prepared by Reichelt Ultracut ultramicrotome at Kyoto Univ. In addition to the small grains, the Chemistry sub-team loaned a polished sample of a fragment originating from a large grain A0026 (~3 mm wide) because the sample has a bubble-rich material on its surface. Seven samples were able to be prepared for the detailed analysis. Up to now we have prepared ~80 FIB sections from 40 grains and >30 FIB sections have already been distributed to the members. To understand mineralogy and petrology down to the nanometer of these grains and to clarify the detailed mineralogical analyses of space weathering of the C-type asteroid Ryugu, we are now performing (scanning) transmission electron microscopy ((S)TEM), synchrotron radiation X-ray absorption fine structure (XANES and EXAFS) analysis, nano-tomography, and atom probe analysis at 15 universities and laboratories.

Results: Major minerals of the small Ryugu grains are phyllosilicates (saponite and serpentine), Fe-bearing sulfides, magnetite, dolomite, and a lesser amount of breunnerite. It is obvious that the asteroid Ryugu experienced severe aqueous alteration and did not experience heating enough to make secondary anhydrous minerals such as olivine, pyroxene and Fe metal, which are common in severely heated carbonaceous chondrites. Serpentine in these Ryugu grains may have better crystallinity than that in Orgueil and Ivuna CI chondrites [e.g., 6]. Typical spacing of (001) of saponite is ~1.0-1.3 nm, which suggests partial dehydration of interlayer H_2O molecules. Minor minerals so for observed are hydroxyapatite, ilmenite, magnesiochromite, manganochromite, Cr oxide, Cu-bearing ZnS, $(Fe, Ni)_2P$, $FeCr_2S_4$, cubanite, Na- and Mg-bearing phosphate, forsteritic olivine, and Fe-free low-Ca pigeonite. A moissanite crystal was also identified, which could be a presolar grain.

The surfaces of the most Ryugu grains investigated have highly euhedral pyrrhotite crystals. Their surfaces preserve quite sharp steps, which may reflect growth or dissolution in aqueous solutions. Magnetite crystals that form framboidal aggregates have shapes as rounded as those in Orgueil and Ivuna. In addition, some magnetite crystals have facets as sharp as those in

Tagish Lake C ungrouped meteorite. The presence of these Fe sulfide and oxide suggests that these surfaces did not experience enough exposure to the interplanetary space to degrade the surfaces of these minerals.

After scrutinizing >350 small Ryugu grains by FE-SEM and FIB-SEM, we found 10 small Ryugu grains having obviously different surface morphology. Figure 1 shows an example of such grains with abundant open bubbles. The bubble-rich surfaces form a continuous layer containing abundant bubbles. In Fig. 1(b), the bubble walls are as thick as ~0.5 µm at the thickest places. Most bubble-rich layers have ~50 - ~500 nm thick, but the layer of A0026 has up to ~3 µm thick. The bubble-rich layer in Fig. 1(b) is amorphous and contains abundant tiny Fe sulfide crystals based on selected area electron diffraction (SAED) patterns and electron diffraction mapping. Preliminary analysis of energy-loss near-edge structures of Fe L2, 3 edge of the bubble-rich layer and the subsurface phyllosilicate suggests that the former is much more enriched in Fe^{2+} than the latter. More detailed description of the rugged Fe sulfide and the other phases will be presented in another presentation [7].

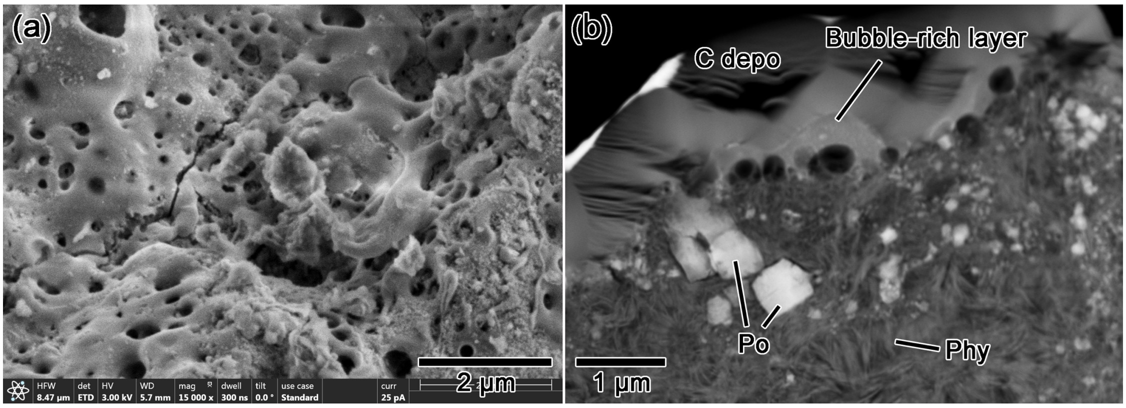

Fig. 1 Secondary electron and annular dark-field images of a small Ryugu grain with a bubble-rich surface. (a) The surface is covered by a gently rolling layer with abundant open bubbles. Abundant bright tiny speckles are on the surface. (b) A cross-section of the bubble-rich layer and the interior. Abbreviations: Po: pyrrhotite; Phy: phyllosilicate; depo: deposition.

Discussion and conclusion: These major minerals and the petrography of the small Ryugu grains indicate that the asteroid Ryugu experienced severe aqueous alteration that can be classified as C1. The mineralogy and petrology of these grains are similar to CI chondrites but these grains lack ferrihydrite and sulfates, both common among CI chondrites [e.g., 6, 8 and references therein]. The formation of ferrihydrite and sulfates may have occurred by terrestrial weathering. The spacing of (001) of saponite increased to ~1.3 nm on average by using ethylene glycol as the trough liquid during ultramicrotomy, which means that saponite in the Ryugu samples can rehydrate.

Morphology of the bubble-rich layers is apparently similar to melt sheets (Fig. 1a). However, it does not necessarily mean that all the layers were formed through melting by meteoroid impacts. The formation of similar bubble-rich amorphous layers by H^+ or He^+ ion irradiation has already been reported [9-11]. Although the size and number density of bubbles in the amorphous layer are different from the irradiation experiments and the natural samples, the difference can be interpreted by the different fluxes between them. Therefore, we believe that at least thin bubble-rich layers were related to solar wind irradiation. Unlike the irradiation experiments, the bubble-rich layer in Fig. 1(b) is more enriched in Fe, S, and Ca than the subsurface phyllosilicate. Recondensation of elements derived from the surrounding phases may have also played a role in the compositional difference. Because the thickness of the bubble containing layer is quite variable, the relative contribution of irradiation and micrometeoroid impacts that resulted in vaporization and recondensation of elements may be quite different at places. The M-P F sub-team continues to assess the role of recondensation in the space weathering of the Ryugu C-type asteroid. Although small Ryugu grains with the space weathering rims are quite rare among the investigated samples, it does not necessarily mean that such grains are rare on the surface of Ryugu because most of the surfaces are exposed to the interplanetary space may have been destroyed during the sampling sequence using Ta projectiles. If most of the space exposed surface had the bubble-rich amorphous layer on Ryugu, the bubble-rich amorphous surface layers might have affected the reflectance spectra of the asteroid Ryugu.

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Initial Analysis of Volatile Components in the Hayabusa2 Samples

Ryuji Okazaki[1], Bernard Marty[2], Henner Busemann[3], Yayoi N. Miura[4], Keita Yamada[5], Saburo Sakai[6], Ko Hashizume[7], Ken-ichi Bajo[8], Shun Sekimoto[9], Fumio Kitajima[1], Kevin Righter[10], Alex Meshik[11], Jamie Gilmour[12], Naoyoshi Iwata[13], Evelyn Füri[2], Sarah Crowther[12], Naoki Shirai[14], Mitsuru Ebihara[15], Yoshinori Takano[6], Akizumi Ishida[16], Reika Yokochi[17], Olga Pravdivseva[11], Jisun Park[18, 19], Toru Yada[20], Kunihiko Nishiizumi[21], Keisuke Nagao[22], Jong Ik Lee[22], Michael Broadley[2], David Byrne[2], My Riebe[3], Patricia Clay[12], Akihiro Kano[4], Marc Caffee[23], Shinsuke Kawagucci[6], Yohei Matsui[6], Ryu Uemura[24], Makoto Inagaki[9], Daniela Krietsch[3], Colin Maden[3], Mizuki Yamamoto[1], Hisayoshi Yurimoto[8], Tomoki Nakamura[16], Takaaki Noguchi[9], Hiroshi Naraoka[1], Hikaru Yabuta[25], Kanako Sakamoto[20], Shogo Tachibana[4, 20], Sei-ichiro Watanabe[24] and Yuichi Tsuda[20]

[1]*Kyushu Univ.,* [2]*CRPG,* [3]*ETH,* [4]*Univ. of Tokyo.,* [5]*Tokyo Inst. Tech.,* [6]*JAMSTEC,* [7]*Ibaraki Univ.,* [8]*Hokkaido Univ.,* [9]*Kyoto U.,* [10]*NASA JSC,* [11]*Washington Univ.,* [12]*Univ. Manchester,* [13]*Yamagata Univ.,* [14]*Tokyo Metro.,* [15]*Waseda Univ.,* [16]*Tohoku Univ.,* [17]*Chicago Univ.,* [18]*Kingsborough Comm. Coll., ,*[19]*AMNH,* [20]*JAXA,* [21]*UC Berkeley,* [22]*KOPRI,* [23]*Purdue Univ.,* [24]*Nagoya Univ.,* [25]*Hiroshima Univ.*

The major objectives of the Hayabusa2-initial-analysis volatile team are (1) to determine the pristine volatile components in the parental materials of the returned Ryugu samples, and (2) to elucidate the origin and chronological history of the asteroid Ryugu, as well as the evolution of the solar system through determination of volatile carrier phases and abundances of volatile components (e.g., presolar grain abundances). Our analytical data will be linked with remote sensing (NIRS3, ONCs, TIR, and LIDAR) data and theoretical modeling [e.g., 1-5]. For example, the erosion rate and the degree of gardening of the surface layer of the asteroid Ryugu can be estimated based on trapped solar wind (SW) and cosmic ray produced (cosmogenic) nuclides, which will be discussed in conjunction with the results based on the remote sensing data [3-5]. Taken together, these will provide characteristics of the surface materials, such as the degree and duration of the alteration by SW/cosmic ray irradiation and micrometeorite bombardments.

Our analytical plan for the Ryugu samples consists of three approaches (Fig. 1): One is analyses of native volatiles in the Ryugu samples which have been treated WITHOUT air-exposure throughout the whole process, since the collection from the asteroid Ryugu to the gas extraction in the laboratories. The goal of this work is to quantify the indigenous compositions with as minimal terrestrial (atmospheric, biological, and unintentional man-made pollution) contamination as possible. We will obtain

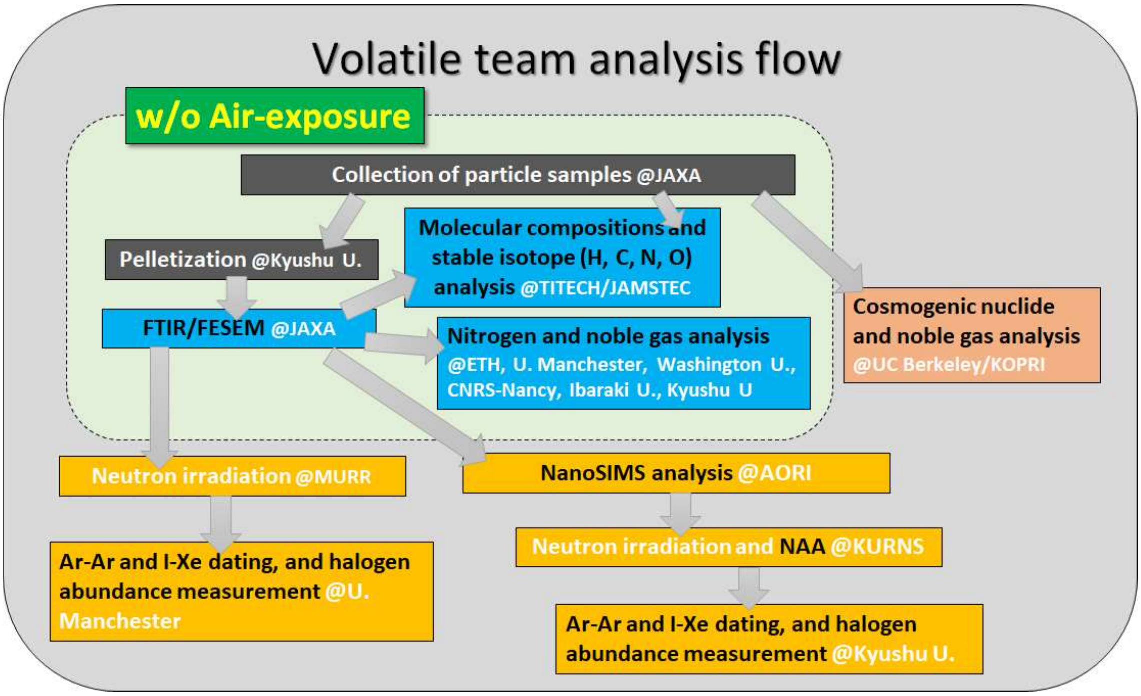

Figure 1. Analytical flow of the volatile team of the Hayabusa2 initial analysis.

the abundances and isotopic compositions of nitrogen, noble gases, and volatile elements (e.g., H and C in H_2, CO, and CO_2, methane, and ethane).

The second approach is analyses of the neutron-irradiated samples to determine the Ar-Ar and I-Xe ages and halogen abundances by noble gas isotope measurements at U. Manchester and Kyushu U., and to obtain abundances of minor/trace elements (e.g., Co, Ni, and Ir) by neutron activation analysis (NAA) at KURNS. Prior to neutron-irradiation, nanoSIMS analysis will be carried out at AORI on the same samples that are used for the Ar-Ar/I-Xe/halogen analysis at Kyushu U. to understand the distribution and isotopic compositions of volatile elements (H, C, N, and O).

The third approach is measurements of cosmogenic long-lived nuclides and noble gas isotopes, which are performed for different samples prepared under an atmospheric environment. The preliminary result of cosmogenic nuclides is reported by [6].

Most of Hayabusa2 samples allocated to the volatile team have been transported to Kyushu Univ. from JAXA, and located in a N_2 glove box installed at Kyushu Univ., and pelletized without air-exposure in June 2021, except for two particles for the volatile element analysis at TITECH/JAMSTEC and five samples for cosmogenic nuclides which were directly allocated to Berkeley U. from JAXA. Twenty four pellets have been prepared (Fig. 2), and sent back to JAXA to perform FTIR and FESEM observations. After these observations, 16 out of 24 samples have been distributed to our team laboratories, ETH, U. Manchester, Washington U., CNRS-Nancy, Ibaraki U., TITECH/JAMSTEC, and Kyushu U. to measure native volatile compositions. Before analysis, we measured the sample weight without air-exposure by using a small weighing container (Fig. 3). These careful operations enable us to obtain the most intact, fresh volatile compositions of the asteroid Ryugu.

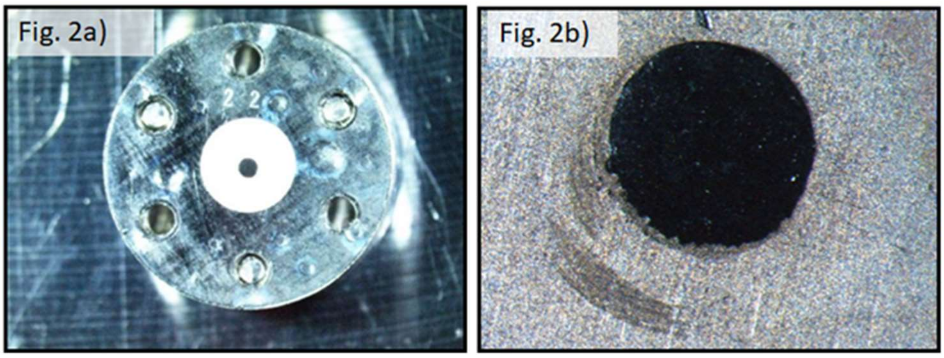

Figure 2. The Hayabusa2 samples pelletized onto a Cu disk without air-exposure (2a). The Cu disk is installed in a metal holder for NanoSIMS analysis and transportation. Enlarged view of the sample is shown in Fig. 2b.

Figure 3. The small weighing container developed for the Hayabusa2 initial analysis.

The remainder of the samples, six pellets have been transported to Tohoku U. and coated with Os and Pt as an antistatic treatment. These samples have now been exposed to the atmosphere. After coating, the 6 samples were shipped to AORI and investigate with NanoSIMS in August 2021. The result of the nanoSIMS analysis will be reported by Drs. Hashizume and Ishida somewhere else.

Following NanoSIMS analysis, the 6 pellet samples were transported to Kyushu U. for installation in diamond container for the NAA. The neutron irradiation and NAA are scheduled to be completed in October. After the NAA, the 6 samples will be analyzed for Ar-Ar age dating. For I-Xe dating and halogen analysis, two other pellet samples, different from the 6 samples that have been analyzed for nanoSIMS and NAA, have been distributed to U. Manchester in July. Now all of these preparatory steps are over and the Ryugu samples are ready for the experiments. We believe that all analyses will proceed successfully.

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An initial look at the distributions and compositions of organic macromolecules in the asteroid Ryugu samples

Hikaru Yabuta[1], George Cody[2], Cecile Engrand[3], Yoko Kebukawa[4], Bradley De Gregorio[5], Lydie Bonal[6], Laurent Remusat[7], Rhonda Stroud[5], Eric Quirico[6], Larry Nittler[2], Minako Hashiguchi[8], Mutsumi Komatsu[9], Taiga Okumura[10], Yoshio Takahashi[10], Yasuo Takeichi[11], Emmanuel Dartois[3], Jean Duprat[7], Jeremie Mathurin[3], David Kilcoyne[12], Zita Martins[13], Scott Sandford[14], Shohei Yamashita[11], Ariane Deniset[3], Alexandre Dazzi[3], Yusuke Tamenori[15], Takuji Ohigashi[16], Hiroki Suga[15], Daisuke Wakabayashi[11], Maximilien Verdier-Paoletti[7], Smail Mostefaoui[7], Gilles Montagnac[17], Jens Barosch[2], Kanami Kamide[1], Miho Shigenaka[1], Laure Bejach[3], Takaaki Noguchi[18], Hisayoshi Yurimoto[19], Tomoki Nakamura[20], Ryuji Okazaki[21], Hiroshi Naraoka[21], Kanako Sakamoto[22], Shogo Tachibana[10, 22], Sei-ichiro Watanabe[8], and Yuichi Tsuda[22]

[1]*Hiroshima Univ.*, [2]*Carnegie Institution of Washington,* [3]*Université Paris Sud,* [4]*Yokohama National Univ.*, [5]*Naval Research Laboratory*, [6]*Université Grenoble Alpes*, [7]*Muséum national d'Histoire naturelle*, [8]*Nagoya Univ.*, [9]*The Graduate Univ. for Advanced Studies (Sokendai).*, [10]*Univ. of Tokyo*, [11]*High Energy Accelerator Research Organization*, [12]*Advanced Light Source*, [13]*Universidade de Lisboa*, [14]*NASA Ames Research Center*, [15]*SPring8*, [16]*UVSOR, IMS*, [17]*ENS de Lyon*, [18]*Kyoto Univ.*, [19]*Hokkaido Univ.*, [20]*Tohoku Univ.*, [21]*Kyushu Univ.*, [22]*JAXA*

Hayabusa2 is JAXA's asteroid sample return mission that targeted the carbonaceous (C-type) asteroid (162173) Ryugu. The mission aims to unveil the origin and evolution of organic compounds and water in the early Solar System as life's building blocks [1]. Following the arrival of the Hayabusa2 spacecraft at Ryugu on June 27, 2018, observations by onboard remote sensing instruments revealed that Ryugu is a top-shaped asteroid with a very low geometric albedo [2-4] and that its surface is probably partially dehydrated [5]. The Mobile Asteroid Surface Scout (MASCOT) lander observed two types of boulders on the surface of Ryugu: one type was dark and cauliflower-like with a similar morphology to primitive carbonaceous chondrites, and another type was bright and smooth [6]. The lander's radiometer revealed that Ryugu has low thermal conductivity and high porosity unlike any chondritic meteorites, while these thermal properties have similar values to comets [7]. Thanks to the formation of the artificial crater on Ryugu's surface by a small carry-on impactor [8], two successful touchdowns on February 22 and July 11, 2019 have enabled collections of samples from two distinct locations on the asteroid, providing an advantage for investigating the origin and evolution of the Solar System as well as the surface processes of the asteroid. After the sample return on December 6, 2020, the curatorial work on the Ryugu sample has been conducted at JAXA for the first 6 months [9]. With the significant guidance from the observations and curation, the initial sample analysis has a one-year mission from June 2021 to June 2022 to address the question of what kind of asteroid Ryugu is.

Organic compounds are a major component of interstellar dust as along with silicates and water ice due to the high abundances of their elements (C, H, O, N, S, P) in the Galaxy. The initial molecular inventory of the Solar System, inherited from the parental molecular cloud, was modified and new complex molecules formed through a variety of processes in the protoplanetary disk and planetesimals, which resulted in the diverse compositions of asteroids and comets. These small bodies are thought to have contributed to the formation of our habitable planet, through exogenous delivery of organics and water as life's building blocks to the early Earth.

Organic macromolecules from chondritic meteorites have been often characterized as a dark, complex, acid-insoluble organic matter (IOM). IOM accounts for a major portion of total organic carbon in primitive carbonaceous chondrites (CCs). The intact chemical structure of IOM in CCs is still unknown, although a number of previous studies have suggested that it is composed of aromatic network crosslinking with short-branched aliphatic chains and various oxygen-bearing functional groups [10, 11]. Whether IOM was formed in interstellar cloud [12], outer solar nebula [13] or planetesimals [14], is still under debate. Nevertheless, elemental, molecular and isotopic variations of IOM from various types of small body materials, such as chondritic meteorites [15-20], interplanetary dust particles (IDPs) [21], cometary dusts [21-23], and Antarctic micrometeorites (AMMs) [24-27], have enabled our comprehensive understanding of chemical history of the early Solar System.

The Hayabusa2-initial-analysis IOM team consists of 36 members from Japan, USA, France, and Portugal. The scientific goals of IOM team include: i) Decoding the chemical relationship(s) between organics and minerals on a C-type asteroid parent body, ii) Elucidating formation pathways of organic macromolecules in a C-type asteroid, iii) Determining the origin(s) of organics in a C-type asteroid, iv) Investigating the asteroid-comet continuum, v) better understanding Solar System formation and volatile delivery, and vi) Understanding the role of organic macromolecules in the origin of life. In order to accomplish the goals, we aim to unveil the elemental, isotopic, and functional group compositions, structures and textures of organic macromolecules from the Ryugu samples. The analytical procedures are configured by combination of micro-Fourier

Transform Infrared Spectroscopy (FTIR), micro-Raman spectroscopy, synchrotron-based scanning transmission x-ray microscope (STXM), Scanning Transmission Electron Microscopy (STEM) coupled with Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive X-ray Spectroscopy (EDS), Atomic Force Microscope based Infrared Spectroscopy (AFM-IR), and nano-secondary ion mass spectrometry (NanoSIMS). The analytical procedures are applied to the intact Ryugu samples and the IOM isolated by HCl/HF treatment of the Ryugu samples, respectively.

For the first measurements, Chamber A aggregates (A0108) collected upon the first touchdown and Chamber C aggregates (C0109) collected upon the second touchdown have been analyzed. The individual particles from A0108 and C0109 range from 200 to 900 μm in size. Some of the particles were crushed on a diamond window for micro-FTIR, micro-Raman, and NanoSIMS. Slices of other particles were prepared with a focused ion beam workstation (FIB) and/or an ultramicrotome to obtain ultra-thin sections for STXM, STEM-EELS, AFM-IR and NanoSIMS. The water/solvent/HCl extraction residues of other aggregates of Chamber A (A0106) and Chamber C (C0107), which were transferred by SOM team, were treated with 6N HCl and 1N HCl/9N HF to yield IOM for future measurements.

Organic macromolecules have been identified from the Ryugu samples by all the analytical techniques. The organic macromolecules were associated with secondary minerals formed through aqueous alteration [28], and they often exhibited D and/or ^{15}N-rich regions [29, 30]. These results show that the observed organics are of extraterrestrial origin. The FTIR [31] and Raman [32] spectroscopic features as well as the isotopic features [29, 30] of organic macromolecules from the Ryugu samples were comparable with those of the primitive carbonaceous CI/CM chondrites, while the other features were not necessarily consistent with the typical CI/CM, demonstrating that Ryugu samples record heterogeneous chemical history in a pristine state [28, 29].

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Soluble Organic Matter (SOM) analysis of the Hayabusa2 samples: The first results

Hiroshi Naraoka[1], Yoshinori Takano[2], Jason P. Dworkin[3], Kenji Hamase[1], Aogu Furusho[1], Minako Hashiguchi[4], Kazuhiko Fukushima[4], Dan Aoki[4], Yasuhiro Oba[5], Yoshito Chikaraishi[5], Saburo Sakai[2], Nanako O. Ogawa[2], Naohiko Ohkouchi[2], Toshihiro Yoshimura[2], Toshiki Koga[2], Haruna Sugahara[6], Hajime Mita[7], Daniel P. Glavin[3], Jamie E. Elsila[3], Eric T. Parker[3], José C. Aponte[3,8], Hannah L. McLain[3,8], Heather V. Graham[3], John M. Eiler[9], Francois-Regis Orthous-Daunay[10], Cédric Wolters[10], Véronique Vuitton[10], Roland Thissen[10], Junko Isa[11], Philippe Schmitt-Kopplin[12], Norbert Hertkorn[12], Alexander Ruf[13], Hisayoshi Yurimoto[5], Tomoki Nakamura[14], Takaaki Noguchi[15], Ryuji Okazaki[1], Hikaru Yabuta[16], Kanako Sakamoto[6], Shogo Tachibana[6,17], Seiichiro Watanabe[4] and Yuichi Tsuda[6]

[1]Kyushu Univ.,[2]JAMSTEC, [3]NASA Goddard Space Flight Center, [4]Nagoya Univ., [5]Hokkaido Univ., [6]JAXA, [7]Fukuoka Inst. Tech. [8]Catholic Univ/CRESST, [9]California Inst. Tech., [10]Univ. Grenoble Alpes CNRS IPAG, [11]Tokyo Inst. Tech., [12]Helmholtz-Zentrum Muenchen, [13]Aix-Marseille Univ., [14]Tohoku Univ., [15]Kyoto Univ. [16]Hiroshima Univ., [17]Univ. Tokyo

The Hayabusa2 spacecraft successfully collected the surface and possible sub-surface materials of the asteroid 162173 Ryugu. Ryugu is a C-type asteroid characterized by a low-albedo surface probably consisting of hydrous minerals and carbonaceous materials. [1] The direct optical and spectral analysis of the returned samples indicates that Ryugu material is dominated by hydrous carbonaceous chondrite-like matter (similar to CI chondrites) [2]. Since carbonaceous chondrites have generally yielded various types of organic matter, the collected Ryugu grains are expected to contain diverse types of organic compounds including bio-related molecules. The occurrence of organic compounds in the Ryugu surface will provide clues to the evolution of prebiotic molecules and their preservations associated with aqueous alteration of the primitive asteroid. The initial analysis of soluble organic matter (SOM) of the Hayabusa2-returned samples has been performed by an international team consisting of 32 members. Because the sample amount available for comprehensive SOM analyses is limited, and because the SOM is expected to be present as a complex mixture of various types of organic compounds with very small concentrations of each compound, high-sensitivity and high-resolution analytical techniques have been developed using carbonaceous meteorites [e.g. 3].

Two aggregate samples of the Ryugu grains (A106 and C107) were allocated for the solvent extractions and total carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O) measurements. The A106 sample was collected during the 1st sampling in February 2019 and the C107 sample was collected during the 2nd sampling in July 2019 after the Small Carry Impactor (SCI) operation. They consist mainly of particles smaller than 1 mm in diameter, and each sample mass was 38-39 mg. They were firstly investigated spectroscopically in the near infrared wavelength range by the Stone Team prior to the solvent extractions. Other small grains (A0080 and C0057) were also allocated for this study to investigate the spatial distribution of organic compounds on the sample surface. The extraction and analytical measurements implemented by the SOM Team are summarized in Figure 1. Each powder sample was extracted sequentially with non-polar to polar solvents, i.e., hexane, dichloromethane (DCM), methanol (MeOH) and H_2O, for non-targeted analysis to reveal the compound composition. Each solvent extract was analyzed by solution state nuclear magnetic resonance (NMR) spectroscopy [4], Fourier transform-ion cyclotron resonance/mass spectrometry (FT-ICR/MS) with ESI and APPI ionization [5] and by high-resolution mass spectroscopy using Orbitrap MS coupled with nano-liquid chromatography (nanoLC/Orbitrap MS) [6], and using two dimensional gas chromatography/mass spectrometry (GC×GC/MS). The extracted residues were passed to the Chemistry Team for further inorganic element analysis. The other powder sample was subjected to the hot water extraction for amino acid analyses including chiral isomer separation, which was performed by three-dimensional (3D) high-performance liquid chromatography (HPLC) with high-sensitivity fluorescence detection (FD) [7] and by HPLC/FD coupled with quadrupole-time of flight/mass spectrometry (QToF/MS) [8]. After the hot water extraction, the residue was split into two halves. One half was further extracted with hydrochloric acid (HCl) to analyze for amino acids in bound-form. The other half was sequentially extracted with DCM/MeOH (1/1) to analyze semi-polar compounds such as polycyclic aromatic hydrocarbons (PAHs) by GC/MS, followed by further extraction with formic acid to analyze polar heterocyclic compounds, and subsequent extraction with HCl to detect bound-form polar compounds. The extracted residues were passed to the IOM Team for the analysis of insoluble organic matter (IOM). Compound-specific stable isotope analyses will be performed using GC/combustion/isotope ratio mass spectrometry (GC/C/IRMS) if the compound concentration is high enough to enable such an isotopic measurement. All extraction procedures were performed on an ISO 6 (Class 100) clean bench inside an ISO 5 (Class 1000) clean room. Baked serpentine powder was also analyzed as a procedural blank. *In situ* organic compound analysis with the molecular imaging was performed using desorption electrospray ionization (DESI) equipped with Orbitrap MS [9, 10], followed by spatial imaging of organic compounds using ToF/secondary ion mass spectrometry (ToF/SIMS) [11]. The bulk chemical and isotopic compositions of CNS and HO were determined using nano-elemental analysis/isotope ratio mass spectrometry (nanoEA/IRMS) [12] and EA/pyrolysis/IRMS, respectively.

We have identified a variety of indigenous organic compounds in the extracts of both A106 and C107 samples. The Ryugu grains host organic molecules under the high-vacuum and cosmic-ray irradiation environment of the asteroid surface. The analysis of extracted molecules is in progress, and the first results will be presented at the symposium.

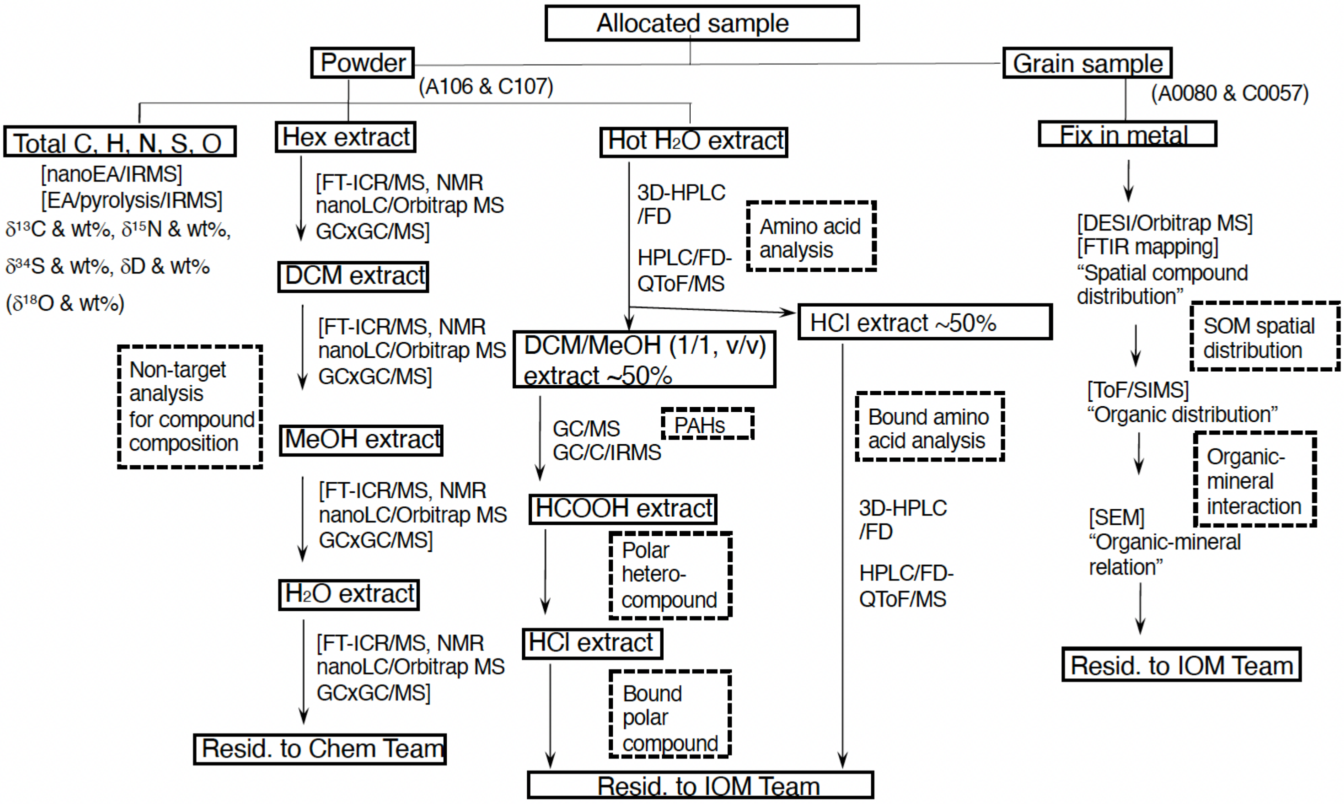

Figure 1. Analytical scheme for the Ryugu samples by the SOM Team.

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A first look at the interior and exterior of Ryugu preserved in samples collected by Hayabusa2

Eizo Nakamura[1], Katsura Kobayashi[1], Ryoji Tanaka[1], Tak Kunihiro[1], Hiroshi Kitagawa[1], Christian Potiszil[1], Tsutomu Ota[1], Chie Sakaguchi[1], Masahiro Yamanaka[1], Yusuke Yati[1],Tomohiro Usui[2], Yuichi Tsuda[2], Seichiro Watanabe[3], Masanao Abe[2], Tatsuaki Okada[2], Toru Yada[2]

[1]*The Pheasant Memorial Laboratory, Inst. for Planetary Materials, Okayama Univ. at Misasa, Tottori 682-0193, Japan.*

[2]*Inst. Space Astronaut. Sci., Japan Aerosp. Explor. Agency (JAXA), Kanagawa 252-5210, Japan*

[3]*Dept Earth Planet. Sci., Grad. Sch. Sci., Nagoya Univ., Nagoya 464-8601, Japan.*

Sample return missions represent great opportunities to study materials from known locations. The Hayabusa mission returned material to Earth from the asteroid Itokawa in 2010 and revealed through geochemistry and micro-petrograpy that it is genetically related to ordinary chondrite meteorites and the surface of the modern-day asteroid is being actively bombarded by hyper-velocity small particles (e.g., Kawaguchi *et al.*, 2003; Nakamura *et al.*, 2012). The Hayabusa2 mission returned material to Earth from Ryugu on 6th of December, 2020 (Tsuda *et al.*, 2020). Based on the very low geometric albedo indicated by remote observations (Sugita *et al.*, 2019; Kitazato *et al.*, 2019), abundant organic matter on Ryugu, compared to those in carbonaceous chondrites, might be expected (Potiszil *et al.*, 2020). The initial uncontaminated and non-destructive observations for the entire set of returned samples in the Phase-1 Curation at JAXA/ISAS (Yada *et al.*, 2021) demonstrated that Hayabusa2 retrieved the representative and unprocessed (albeit slightly fragmented) Ryugu sample. The data further expanded on the indications from the remote sensing observations that Ryugu is dominated by hydrous carbonaceous chondrite-like materials, similar to CI chondrites, but with an optically darker, more porous, and more fragile nature.

In order to analyze both organic and inorganic matter, the pieces of Ryugu were subject to in-depth investigations in the Pheasant Memorial Laboratory (PML), Okayama University at Misasa. The 16 particles of Ryugu sample (A0022, A0033, A0035, A0048, A0073, A0078, and A0085 from the natural surface of the equatorial region of Ryugu, and C0008, C0019, C0027, C0039, C0047, C0053, C0079, C0081, and C0082 from the surrounding site of the artificial impact crater on Ryugu; total ~55 mg) were selected during the Phase-1 Curation. The selected samples were then transferred to the ultimate clean room in the PML for Phase-2 Curation, to catalog the samples via a comprehensive analytical strategy.

The particles were first characterized under digital optical microscope and then their volume and mass were measured to determine their densities. The average density was 1530 ± 250 kg m^{-3}, which was systematically larger than the value reported in Yada et al (2021). To elucidate the systematic differences among the 16 pieces, both plainer surfaces and powder were created from each piece using an ultra-microtome equipped with a diamond knife. The surface was observed using optical microscope and SEM, the major element distribution and mineral phases were determined by EDS installed in SEM, micro-Raman spectroscopy, micro-XRD and TEM, all without coating. Subsequently, major and trace element compositions were determined from a given powder by ICP-MS. Element and isotope compositions of H, C, N and O were determined by gas-source mass-spectrometry, and those of Ne were determined by laser-heating noble-gas-mass-spectrometry using small broken pieces. Solvent soluble organic matter was extracted from sample powders using various solvents, including water, acetonitrile, ethyl acetate and formic acid. Meanwhile, insoluble organic matter was isolated after solvent extraction and demineralization by HCl, HF and boric acid. After the first-round characterization, the microtomed surfaces were surveyed using micro-Raman spectroscopy, SIMS and desorption electrospray ionization-orbitrap-mass spectrometry (DESI-OT-MS).

The 16 pieces were found to consist of magnetite, carbonate, phosphates, sulfides and minor silicate fragments interfiled by matrix (modal abundance of 86-96%) that was dominated by sub-micron-sized phyllosilicates. Average modal abundances of the aforementioned phases (excluding matrix) were 3.7, 2.4, 0.8, 2.5 and 0.4 %, respectively. The phyllosilicates were mainly composed of the serpentine and smectite groups. As noted by the Phase-1 Curation, the existence of high-temperature nebular products, such as refractory inclusions and chondrules were not found. The magnetite was present as micron-sized euhedral to subhedral grains and sub-micron-sized grains with a framboidal and plaquette texture. Non-carbonate carbon-rich phases of several micrometers in size, were discovered embedded in the matrix (modal abundance is ~0.2%). The presence of soluble and insoluble organic matter was confirmed by DESI-OT-MS and FTIR and micro-Raman spectroscopy, respectively. Further characterization of the solvent soluble fraction via HPLC-OT-MS and GC-MS is currently underway. The organic matter is ubiquitous in the matrix according to observations by SIMS and micro-Raman spectroscopy.

The major and trace element compositions and O isotope composition are homogenous, with the major and trace element compositions representing the proto-solar abundance of Lodders (2020). However, a significant variation of H, C, N and Ne isotopic compositions at the sub-mm scale among the particles was found, which suggests that Ryugu has experienced a complex evolutionary history.

In this talk, preliminary results from the Misasa Phase2 Curation team will be presented.

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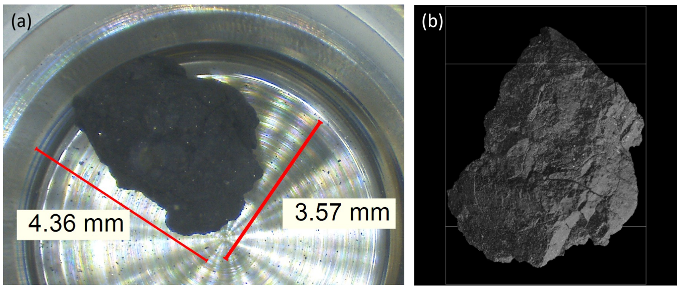
The C-type asteroid Ryugu: A first detailed look by Phase2 Curation Kochi (Ph2K)

M. Ito[1], N. Tomioka[1], M. Uesugi[2], A. Yamaguchi[3], N. Imae[3], N. Shirai[4], T. Ohigashi[5], M. Kimura[3], M-C. Liu[6], R.C Greenwood[7], K. Uesugi[2], A. Nakato[8], K. Yogata[8], H. Yuzawa[5], Y. Kodama[9*], M. Yasutake[2], R. Findlay[7], I.A Franchi[7], J.A. Malley[7], K. Hirahara[10], A. Tsuchiyama[11], A. Takeuchi[2], I. Sakurai[12], I. Okada[12], Y. Karouji[13], T. Yada[8], M. Abe[8], T. Usui[8], S. Watanabe[12], and Y. Tsuda[8].

[1]JAMSTEC Kochi, [2]JASRI/SPring-8, [3]NIPR, [4]Tokyo Met. Univ., [5]UVSOR/IMS, [6]UCLA, [7]Open Univ., [8]JAXA/ISAS, [9]MWJ, [10]Osaka Univ., [11]Ritsumeikan Univ., [12]Nagoya Univ., [13]JAXA/JSEC, [*]Toyo Corp.

The Hayabusa2 spacecraft successfully returned to Earth surface materials from the C-type asteroid 162173 Ryugu on December 6th 2020. The sample capsule contained a large number of small grains (a few to several mm in size), collected from touchdown sites 1 and 2 on Ryugu, with a total mass of ~5.4 g [1, 2]. After initial characterization of the grains by JAXA curation (e.g., size, weight, FTIR and MicrOMEGA spectroscopic survey), we received eight grains (four from Room A and four from Room C) on June 17, 2021 (Figure 1 and Table 1). Detailed study of the materials returned from Ryugu will provide critical information about the origin and early evolution of the Solar System and in particular, the nature of the asteroid-meteorite connection, water-rock interactions on asteroids, the evolution of organics on small bodies, the diversity and history of asteroid families in the main belt.

Figure 1. Largest Ryugu sample (A0002) for the Phase 2 curation Kochi. (a) optical and (b) 3D-reconstruct images



On June 19, 2021, we started initial characterization studies of all our samples using synchrotron radiation-based CT and XRD at the SPring-8. An air-tight sealed carbon nano-tube sample holder was used for CT analysis. In order to avoid degradation and contamination due to interaction with the terrestrial atmosphere (water vapor and oxygen gas) [3], all of the sample preparation (chipping by a chisel, cutting by a counter balanced diamond wire saw, and epoxy mount preparation) was conducted in a glove box in an atmosphere of pure, dry N_2 (Dew point: -80 to -60˚C, O_2 ~50 to 100 ppm). Once we had acquired high-resolution, detailed three-dimensional structural and crystallographic information (0.85 µm/pixel for CT) for each of our samples, we were able to define a priority list for the next phase of the analytical campaign, which involved coordinated micro and bulk analysis.

The micro-analysis plan proposed by Ph2K involves the use of a wide range of multi-beam instruments to acquire detailed micro-textural and chemical information about the samples at a sub-micrometer scale. Ongoing studies have involved the use of FIB, STXM-NEXAFS, NanoSIMS and TEM [4]. In parallel, we are conducting bulk analysis of the samples using SEM-EDS, EPMA, Raman spectroscopy, XRD, large geometry type SIMS, high precision O isotopic analysis by laser fluorination and INAA. We have used air-tight containers (a facility-to-facility transfer container, FFTC [4]) for sample transportation to nation-wide institutes by hand carry. With the assistance UK embassy in Tokyo, a few representative grains were delivered to the Open University without any potentially invasive inspection (i.e., X-ray).

In this talk, we will present the preliminary results of the Ph2K coordinated micro-analysis and systematic bulk chemical analysis campaign, which is focused on providing a detailed understanding of these precious Ryugu returned samples.

References: [1] Morota T. et al. 2020. Science 368, 654–659. [2] Yada et al. 2021. Abstract#2008, 52nd LPSC. [3] Uesugi M. et al. 2020. Rev. Sci. Instrum. 91, 035107. [4] Ito M. et al., 2020. Earth, Planets and Space 72, 133.

Table 1. The Ryugu samples for the Phase2 curation Kochi

Sample No.	mg	µm	SPring-8	Microanalysis (STXM, NanoSIMS, TEM)	Bulk Analysis (SEM-EDS, EPMA, Raman)	High Precision O isotopes	SIMS	INAA	XRD
A0002	19.3	4,092	HR-CT, XRD, XRD-CT	Y				Y	
A0029	9.1	3,069	HR-CT, XRD, XRD-CT	Y	Y			Y	Y
A0037	7.8	3,129	HR-CT, XRD, Phase-contrast CT	Y	Y		Y	Y	Y
A0098	1.9	1,868	HR-CT			Y		Y	
C0009	11.1	3,520	HR-CT, XRD, XRD-CT	Y	Y		Y		
C0014	6.8	3,527	HR-CT		Y	Y			
C0068	1.68	1,980	HR-CT	Y	Y	Y		Y	
C0087	2	3.242	HR-CT			Y			Y

JAXA Detailed Description -Variation of surface characteristics of Ryugu returned samples-

Aiko Nakato[1], Toru Yada[1], Kasumi Yogata[1], Akiko Miyazaki[1], Kentaro Hatakeda[1,2], Kazuya Kumagai[1,2], Masahiro Nishimura[1], Yuya Hitomi[1,2], Hiromichi Soejima[1,2], Kana Nagashima[1], Jean-Pierre Bibring[3], Cedric Pilorget[3], Vincent Hamm[3], Rosario Brunetto[3], Lucie Riu[3], Lionel Lourit[3], Damien Loizeau[3], Tania Le Pivert-Jolivet[3], Guillaume Lequertier[3], Aurelie Moussi-Soffys[4], Masanao Abe[1], Tatsuaki Okada[1] and Tomohiro Usui[1]

[1]*Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency,* [2]*Marine Works Japan, Ltd.,* [3]*Institut d'Astrophysique Spatiale, Université Paris-Saclay, CNRS,* [4]*Centre National d'Etudes Spatiales*

The Ryugu sample brought back by the Hayabusa2 spacecraft in December 2020 weighed ~5.4 g, which is much larger than we expected [1, 2]. After the samples were delivered to JAXA Extraterrestrial Curation Center, individual grains have been picked up and stored into sapphire dish, and analyzed by optical microscope, weighting, FTIR spectroscopy, and MicrOmega hyperspectral imaging [3] for initial description [2]. The obtained data will open in early 2022 for International Announcement of Opportunity (AO) through curatorial Database System for Ryugu Sample [4]. During the ffirst 6 months, we observed 205 individual grains, 100 from chamber A and 105 from chamber C. There are some unique characteristic features on the surface. Here, we propose a morphological classification of these surface features into 4 groups, based on visible characteristics of Ryugu samples. 1/ Dark and fluffy: these features are dominant in Ryugu samples; 2/ Dark and glossy: they are present either on a part or on the entire of grain; 3/ Bright: also present either on a part or on the entire of grain; 4/ White regions: they are observed over 300 µm in size. Those characteristics may be observed alone or in duplicate on a single grain.

In July 2021, 4 grains showing those different features, were allocated as JAXA detailed description (JAXA-DD) (Fig.1). We conduct petrological and mineralogical observation by SEM and XRD to understand the linkage with surface characteristics obtained by the initial description. The purpose of this study is to contribute to the sample selection by researchers at Int'l AO.

FE-SEM/EDS observation was performed using Hitachi SU6600 equipped with slow purge system in order to non-air-exposure transportation from glove box to SEM, on the front surface where the main initial description was made. For two grains A0017 and C0094, where the entire front surface shows unique characteristics, SEM observation was also performed on the back surface. After these observations, we performed a sample chipping under pure N2 atmosphere inside Glove Box. A specially developed tantalum chisel is used for the division. Since tantalum is also used as a bullet when collecting samples on the asteroid, it was selected as materials for the purpose of unifying the potential sources of sample contamination. From the divided sample, we separated small portions showing each of the four characteristics and we performed additional SEM observations. We handled the samples under non-air-exposure environment until the sample division. The small portions are attached to carbon fiber with glue for future XRD analysis using RIGAKU RA-Micro7 HFMR.

In this presentation, we will introduce the variations of Ryugu sample surface characteristics, reflecting variations of their mineralogy and petrography, coordinated with JAXA initial description.

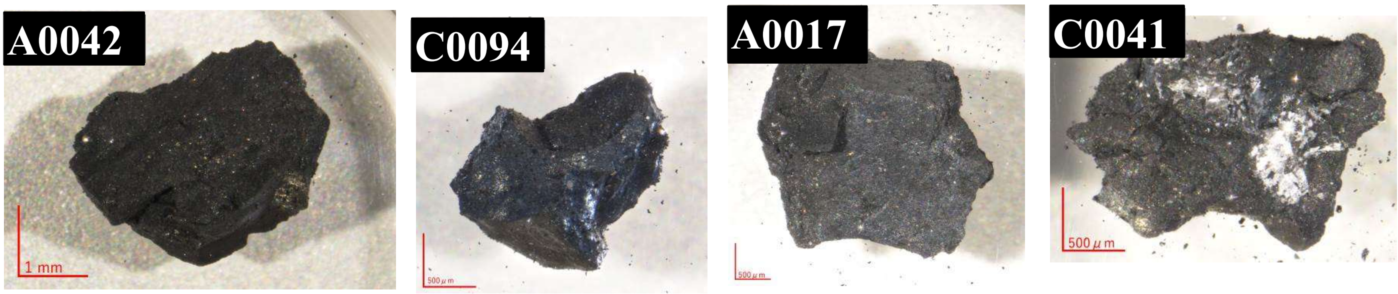


Figure 1. Optical microscopic images of 4 grains allocated to JAXA-DD.

a) A0042 : Dark and fluffy feature is dominant in Ryugu samples. b) C0094: Dark and glossy characteristic is appeared on entire surface. c) A0017: Bright area cover most of the front surface. d) C0041: White region is shown at the right bottom and left top of grain.

References: [1] Tachibana S. et al. (2021) LPS, XXXXXII, Abstract #1289. [2] Yada T. et al. (2021) LPS, XXXXXII, Abstract #2008. [3] Bibring J.-P. et al (2017) Space Sci. Rev. 208, 401-412. [4] Nishimura M. et al. (2021), Astromaterials Data Management in the Era of Sample-Return Missions Community Workshop, Abstract.

Overview of the features of returned samples from the C-type asteroid 162173 Ryugu based on optical microscope observations and their weights

A. Miyazaki[1], T. Yada[1], M. Abe[1,2], A. Nakato[1], K. Yogata[1], K. Nagashima[1],
K Hatakeda[1,4], K. Kumagai[1,4], M. Nishimura[1], Y. Hitomi[1,4], H. Soejima[1,4], M. Yoshitake[1], A. Iwamae[1,4],
S. Furuya[1,3], K. Sakamoto[1], T. Okada[1,3], S. Tachibana[1,3], H. Yurimoto[1,5], T. Usui[1]
[1] Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency,
[2]The Graduate University for Advanced Studies (SOKENDAI) ,[3]University of Tokyo,
[4]Marine Works Japan, Ltd.,[5]Hokkaido University.

Hayabusa2 collected the surface and sub-surface material from the C-type near-Earth asteroid 162173 Ryugu and brought back 5.4 g of samples in total to the Earth [1]. The samples were collected during the two touch-down operations: the samples collected for the first touch-down (TD1) were stored in the Chamber A of the sample catcher, and those collected for the second touch-down (TD2), which was done near the artificial crater made by the SCI [2], were stored in the Chamber C [3]. In the clean chamber dedicated to Hayabusa2 samples [4], the samples in the Chambers A and C were first put in individual sapphire containers for the initial characterization of bulk properties. The samples were first observed with an optical microscope and it was found that the samples from both chambers were aggregation of black-colored mm-sized pebbles and sub-mm sized fine powder, with millimeter-scale particles being the most common [5]. A few centimeter-sized pebbles were also found in the samples recovered from the Chamber C [1]. Then, weight analysis, optical spectroscopy and visual multispectral imaging were performed for the initial characterization. We will present here the features of the individual returned samples based on the microscopic observations and weight analyses.

Pebbles of 1–10 mm in size were removed from the sapphire containers to individual small sapphire dishes. For the first six months after the sample receipt, 100 pebbles from the Chamber A and 105 from the Chamber C were hand-picked one-by-one with vacuum tweezers in the clean chamber under ultra-purified nitrogen atmosphere without exposing to terrestrial atmosphere [6]. The samples in the sapphire dishes are first photographed with an optical stereomicroscope equipped above the clean chamber through a glass window. The size of the individual samples is measured from the microscopic images. Then, the gross weight of the sample and the sapphire dish in the stainless steel capsule was measured with a microbalance equipped in the CC. The weight of an individual sample inside the dish is calculated based on the gross weight of the dish in the stainless steel capsule which was measured in advance.

The preliminary results were reported in [3] and [5]. The observed Ryugu samples have dark spectral features. Many bright and patchy fine inclusions are observed on the surface of some pebbles, but no apparent high temperature components like chondrules nor Calcium-Aluminum-rich-Inclusions (CAI) has been observed with optical microscope analyses [5]. These pebbles show significant morphological variations; grains with rugged surface and with smooth surfaces are observed [3]. These two types of features were also found on the surface textures on Ryugu boulders [7]. Many pebbles are also found to feature curved and straight cracks and some pebbles show elongated block-like morphologies [3]. Densities of individual grains are estimated from the grain weight and the volume of approximated spheroid evaluated from the optical observation, leading to the average density of 1282 ± 231 kg m^{-3}. This density is much lower than the typical grain density of CI chondrites [5]. We will present more detailed features of the returned individual samples.

References

[1] Yada T et al., 2021. 52nd LPSC, abstract#2008. [2] Arakawa M. et al. 2020, Science 368:67. [3] Tachibana S. et al. Submitted to Science. [4] Abe M. et al., 2021. This meeting. [5] Yada T. et al. Submitted to Nature Astronomy. [6] Yada T. et al., 2014. Meteoritics Planet. Sci. 49:135. [7] Cho Y. et al., Submitted to Planet. Space Sci.

Initial description of Ryugu returned samples: characteristics of individual grains by FT-IR analysis

Kentaro Hatakeda[1,4], Toru Yada[1], Masanao Abe[1,2], Tatsuaki Okada[1,3], Aiko Nakato[1], Kasumi Yogata[1], Akiko Miyazaki[1], Kazuya Kumagai[1,4], Masahiro Nishimura[1], Yuya Hitomi[1,4], Hiromichi Soejima[1,4], Kana Nagashima[1], Miwa Yoshitake[1], Ayako Iwamae[1,4], Shizuho Furuya[1,3], Tomohiro Usui[1], Shogo Tachibana[1,3], Kanako Sakamoto[1], Kohei Kitazato[5], Hisayoshi Yurimoto[6]

[1]*Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, Sagamihara 252-5210, Japan,*

[2] *The Graduate University for Advanced Studies (SOKENDAI), Hayama 240-0193, Japan*

[3] *University of Tokyo, Bunkyo, Tokyo 113-0033, Japan,*

[4]*Marine Works Japan, Ltd., Yokosuka 237-0063, Japan,*

[5]*The University of Aizu, Aizu-Wakamatsu 965-8580, Japan,*

[6]*Hokkaido University, Sapporo 060-0810, Japan.*

A total of ~5.4 g of sample was collected at the surface of the C-type asteroid 162173 Ryugu and successfully returned to Earth [1] [2]. The collected samples were transported to the curation facility in ISAS, Sagamihara, Japan, and stored in purified nitrogen condition, except for a few grains picked up under vacuum condition, to keep the samples as physically and chemically pristine as possible. Approximately 100 grains have been picked up from each of those in Chamber A, uppermost centimeter-scale layer of Ryugu collected during the first touch-down sampling (TD1), and in Chamber C, surface to subsurface layer (~1 m) of Ryugu collected close to the artificial crater during the second touch-down sampling (TD2). Then, initial descriptions, such as weighing, optical imaging, FT-IR spectroscopy in 1-5 µm range, MicrOmega as a hyperspectral NIR microscope, and visual multispectral imaging, have been performed for characterization of these samples. Here we present the preliminary result of FT-IR spectral analysis for individual grains.

The measurement system consists of the spectrometric unit outside the clean chamber and the sample chamber connected to the clean chamber (Figure 1). Although purified nitrogen gas flowed inside the spectrometric unit, absorption bands of O-H (e.g., H_2O) and that of C-O (CO_2) appeared in the reflectance spectra of reference material (Infragold) measured after the sample analysis, indicating the influence of spectral absorption in the atmosphere. In addition, the spot size of the incident beam, approx. 1 mm in diameter at the focal position, was slightly larger than the sizes of individual grains in many cases, and these data were contaminated by the reflectance from the sapphire dish at the bottom of the sample holder. The reflection from the sapphire dish increased the albedo, changed the spectral slope between 1 and 2.5 µm from positive to negative, and decreased the absorption band depth (Figure 2).

Except for the samples with significant effect of sapphire dish, reflectance spectra of individual grains generally show a similar trend to those of bulk samples [3] in the wavelength range between 2.5 and 4 µm. The depth of absorption bands varied between grains, and the band-depth variation is observed not only between the individual grains but also within the single grain. We also found grains with unique spectral profiles, of which abundance is ~1% or less. These grains basically contain relatively large inclusions, which are apparently different from the surrounding matrix.

We are now planning to modify the FT-IR system to extend to the mid to far-infrared wavelength range, and expect to get further information on the collected Ryugu samples.

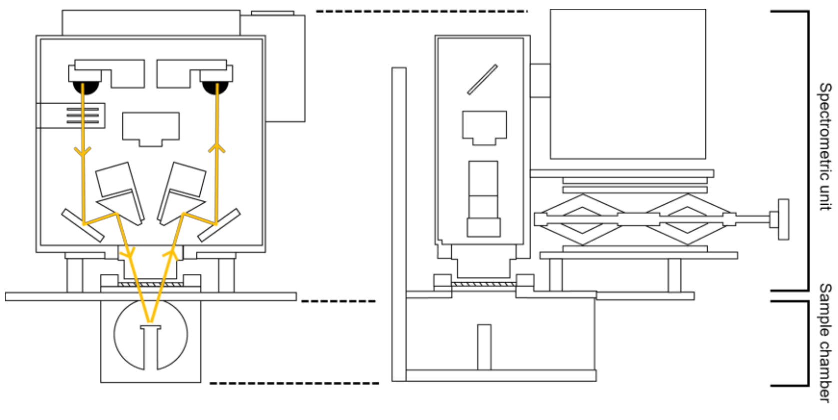


Figure 1. Overview of the FT-IR measurement system

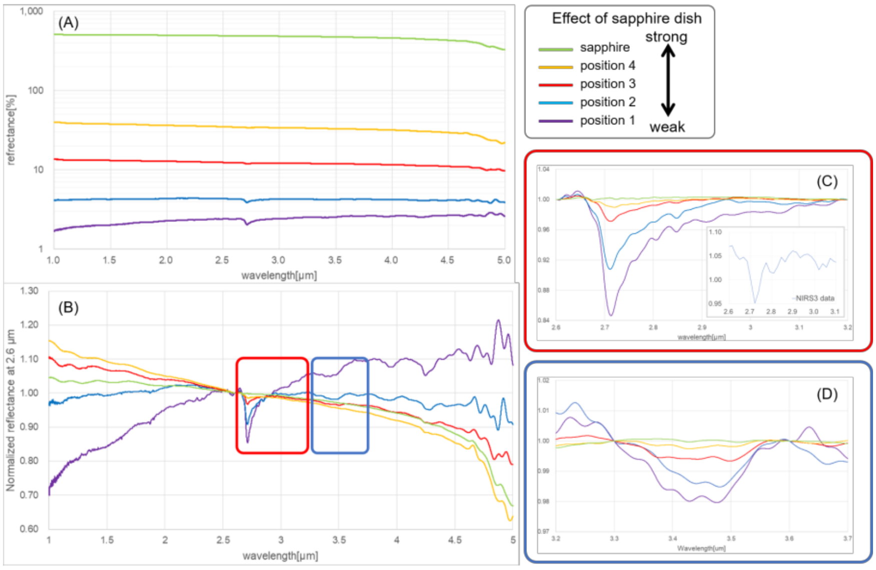


Figure 2. The mixing effect of the sapphire dish reflectance. The larger effect was observed with increasing the area where incident beam illuminated the sapphire dish; A) Reflectance spectra (%), B) Normalized reflectance at 2.6 μm, C) Normalized reflectance with continuum at 2.6-3.2 μm and NIRS3 spectral data [4], D) Normalized reflectance with continuum at 3.3-3.6 μm.

References

[1] Tachibana S. et al. (2021) LPS, XXXXXII, Abstract #1289. [2] Yada T. et al. (2021) LPS, XXXXXII, Abstract #2008. [3] Yada T. et al. in press. Nature Astronomy. [4] Kitazato et al. (2019) Science **364**: 272.

MicrOmega detections of C-rich phases in Ryugu returned samples within the Hayabusa2 JAXA Extraterrestrial Curation Center

Bibring[1], J.-P.; Brunetto[1], R.; Carter[1], J,; Gondet[1], B.; Pilorget[1], C.; Hamm[1], V.; Hatakeda[2], K; Langevin[1], Y.; Lantz[1], C., Le Pivert-Jolivet[1], T.; Loizeau[1], D.; Nakato[2], A.; Okada[2], T.; Riu[1,2], L.; Usui[2], T.; Yada[2], T.; Yogata[2], K., [1]*Institut d'Astrophysique Spatiale, Université Paris-Saclay, CNRS,* [2]*Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency*

The Ryugu samples brought back by the Hayabusa2 spacecraft in December 2020 have been delivered to the JAXA Extraterrestrial Curation Center [1, 2]. Bulk samples and then individual grains have been deposited onto sapphire dishes, weighted, and analyzed with optical microscopy, FTIR spectroscopy, and MicrOmega hyperspectral imaging [3] for initial description [2]. The MicrOmega instrument used in the JAXA Extraterrestrial Curation Center is a NIR hyperspectral microscope. It images samples ~ 5 mm x 5 mm large, with 250x256 pixels of ~22 µm in size. Its spectral capability covers the range from 0.98 µm to ~3.6 µm, which gives access to primary and secondary minerals and organic matter, in particular through their OH, CO_3, and CH features [4, 5].

As presented in the Yada et al. and Pilorget et al. talks (this conference), the averaged spectra of Ryugu returned samples present two major features, centered around 2.7 and 3.4 µm, attributed to OH-rich and CH-rich compounds respectively. Thanks to the MicrOmega capability to characterize the spectral signatures of returned grains down to the few tens of µm scale, a variety of C-rich compositions do show up, through the following features:
- variability in the central position and shape of the 3.4 µm dominant absorption, with a minimum varying from 3.35 µm to 3.45 µm, and the occasional presence of several local minima with varying spectral band areas. These observations suggest organic matter of varying composition and structure is present over the entire samples;
- the presence of coupled spectral features such as at around 2.85 µm, 3.1 µm or 3.55 µm, with their associated band ratios. Additional spectral structures < 2.7 µm are in some cases observed and correlate with them. These bands collectively suggest organic carbon is at times bound to non-C groups or intimately mixed with specific minerals.
- the ratio between the 2.7 µm and 3.4 µm band depths spans a very wide range of values, with some grains highly depleted in either OH-rich or CH-rich phases.

These spectral features are diagnostic of specific C-rich compositions and of their spatial heterogeneity in the collected samples at the scale of few tens to few hundred microns. We shall present a preliminary review of the observed diversity, and discuss it in terms of the composition and origin of the potential carriers.

References

[1] Tachibana S. et al. (2021) LPS, XXXXXII, Abstract #1289. [2] Yada T. et al. (2021) LPS, XXXXXII, Abstract #2008. [3] Bibring J.-P. et al (2017) Space Sci. Rev. 208, 401-412. [4] Pilorget C. and Bibring J.-P. (2014) PSS 99, 7-18. [5] Pilorget C. et al. (2021) this conference.

MicrOmega detections of carbonates in Ryugu returned samples within the Hayabusa 2 JAXA Extraterrestrial Curation Center

Loizeau, D.[1]; Bibring, J.-P.[1]; Brunetto, R.[1]; Pilorget, C.[1]; Okada, T.[2,3]; Carter, J.[1];Gondet, B.[1]; Hamm, V.[1]; Hatakeda, K.[2,4]; Langevin, Y.[1]; Lantz, C.[1]; Le Pivert-Jolivet, T.[1]; Nakato, A.[2]; Riu, L.[2]; Usui, T.[2,3]; Yada, T.[2]; and Yogata, K.[2];

[1]*Institut d'Astrophysique Spatiale, Université Paris-Saclay, CNRS, France*

[2]*Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, Japan* [3]*University of Tokyo, Bunkyo, Japan,* [4]*Marine Works Japan, Ltd., Japan*

The Ryugu samples brought back by the Hayabusa2 spacecraft in December 2020 have been delivered to the JAXA Extraterrestrial Curation Center [1, 2]. Bulk samples and then individual grains have been picked up and stored into sapphire dishes, weighted, and analyzed with an optical microscope, FTIR spectroscopy, and MicrOmega hyperspectral imaging [3] for initial description [2]. The MicrOmega instrument used in the JAXA Extraterrestrial Curation Center is a NIR hyperspectral microscope. It has a total field of view of 5 mm x 5 mm, with resolution of ~22 µm/pixel in the focal plane. It covers the spectral domain from 0.99 µm to ~3.6 µm. Its capabilities enable the identification of organic matter and of different minerals in the returned samples [4]. Initial analyses with MicrOmega were first made on the bulk samples from chambers A and C of the Hayabusa 2 returned capsule, and then on individual grains stored in their sapphire dishes. 137 out of the 205 extracted grains have been analyzed with MicrOmega as of September 30, 2021 [5].

In the spectral domain of MicrOmega, carbonates have a strong characteristic double absorption band in the 3.3-3.5 µm area, accompanied by two other weaker bands around 2.5 and 2.3 µm. The exact spectral position of these bands varies with the cation content of the carbonate [6]. Iron-bearing carbonates also show a strong absorption below 1.5 µm.

First detections of carbonates were made in grains included in the bulk samples from both chambers A and C. Some small grains seem to be entirely carbonate-rich and are up to ~450 µm, down to <50 µm in size. Carbonate inclusions were also detected in larger grains, with sizes up to ~380 µm in a >1.5 mm-sized grain, and down to <50 µm (figure 1-A).

From the first 130 analyzed extracted grains, MicrOmega detected carbonate inclusions with high confidence in 19 of those grains. The largest detection was made on grain C0041, covering ~0.25 mm , or ~10% of the visible surface of the grain (figure 1-B). This grain is one of the grains with "White regions" as described in Nakato et al. [7].

In terms of spectral characteristics, they all present a double band at 3.31-3.47 µm and a band centered at 2.71 µm. The largest grains and inclusions also exhibit spectral bands at 2.51 and 2.30 µm, also characteristic of carbonates, and a deep absorption below 1.5 µm. Some detections also have a band at 2.77 µm (present in many carbonate reference spectra), and some between 3.07 and 3.10 µm. The presence of a strong absorption below 1.5 µm indicates the likely presence of Fe^{2+} in the carbonate mineral, although the position of the bands around 2.3, 2.5 and 3.4 µm is shifted to shorter wavelength compared to a purely Fe^{2+} carbonate (siderite), and would better fit Mg-bearing carbonates like dolomite or magnesite. The iron-bearing magnesite breunnerite is a likely candidate for these detections. Smaller grains and inclusions do not show the absorption below 1.5 µm, while the other absorptions are centered around the same positions than for the larger grains (figure 1-C). Likely candidates include dolomite and magnesite.

Such carbonate grains and inclusions within the returned samples from Ryugu are a key to understand the evolution of the asteroid. MicrOmega can help mapping and quantifying the presence of these carbonates throughout the collection.

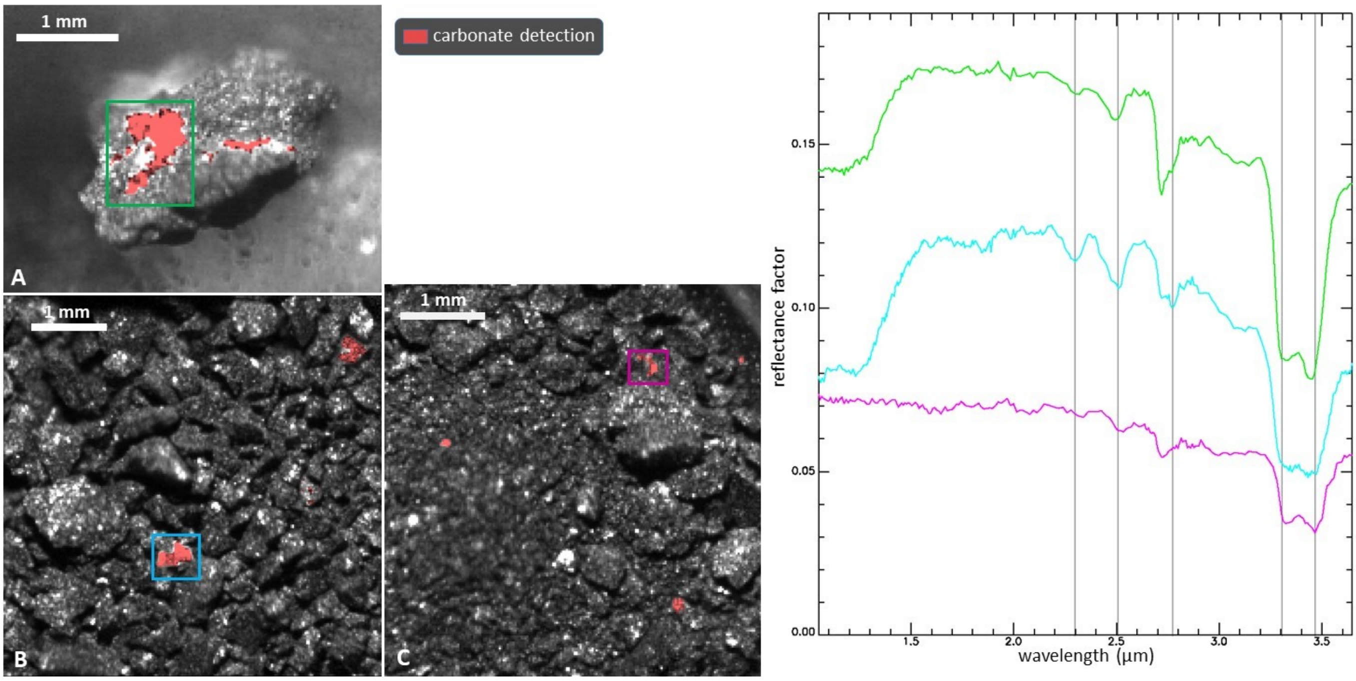


Figure 1. Example of carbonate detections with MicrOmega on bulks from chamber A and C, and on an extracted grain from chamber C. Left: MicrOmega images with red pixels where carbonate is detected. A: extracted grain C0041. B: bulk samples from chamber A. C: bulk samples from chamber C. Right: Average spectra of pixels with carbonate detections within the colored boxes in the left images.

References

[1] Tachibana S. et al. (2021) LPS, XXXXXII, Abstract #1289. [2] Yada T. et al. (2021) LPS, XXXXXII, Abstract #2008. [3] Bibring J.-P. et al (2017) Space Sci. Rev. 208, 401-412. [4] Pilorget C. and Bibring J.-P. (2014) PSS 99, 7-18. [5] Pilorget C. et al. (2021) this conference. [6] Hunt G.R. and Salisbury J.W. (1971) Visible and near infrared spectra of minerals and rocks. II. Carbonates. Modern Geology 2, 23–30. [7] Nakato A. et al. (2021) this conference.

The 2.7µm OH band in different grains of Ryugu from the two collection sites, as seen by MicrOmega in the Hayabusa2 Curation Facility

Tania Le Pivert-Jolivet[1], Jean-Pierre Bibring[1], Rosario Brunetto[1], Cedric Pilorget[1], Tatsuaki Okada[2], John Carter[1], Brigitte Gondet[1], Vincent Hamm[1], Kentaro Hatakeda[2,3], Yves Langevin[1], Cateline Lantz[1], Damien Loizeau[1], Aiko Nakato[2], Lucie Riu[1,2], Tomohiro Usui[2], Toru Yada[2] and Kasumi Yogata[2]

[1]IAS, Université Paris-Saclay, CNRS, France, [2]Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, [3]Marine Works Japan, Ltd

Hayabusa2 is the first space mission to study and collect samples from a C-type asteroid. In December 2020, the spacecraft brought back to Earth ~5.4g of materials from the surface of asteroid (162173) Ryugu. The samples were collected from two different sites TD1 and TD2 [1] at the surface of the asteroid, possibly sampling surface and subsurface materials. The samples were delivered to JAXA (Japan Aerospace eXploration Agency) Extraterrestrial Curation Center for preliminary analyses. Individual grains were extracted and analyzed in a controlled N_2 environment by an optical microscope, a FTIR microscope and MicrOmega, a near-infrared (0.99-3.65 µm) hyperspectral microscope. MicrOmega acquires images of 256x250 pixels with a spatial resolution of 22.5 µm. The total field of view covers ~5x5mm [2].

In addition to the bulk samples, observations of individual grains, extracted from the bulks, were performed with MicrOmega at different azimuth angles to optimize the coverage and avoid potential photometric biases. In order to extract average spectra of the individual grains (typical size 1-4.5 mm), we developed a novel procedure using thermal emission maps measured by MicrOmega: first the grains were isolated from the rest of the field of view (the sample holder) thanks to their difference in terms of thermal emission, then their pixels were averaged at each azimuth orientation. Spectral parameters were finally calculated to characterize the position and the depth of the 2.7 µm OH feature. This band is believed to be related to the presence of metal-OH stretching modes in phyllosilicates [3], and it is observed at large scale over the surface of Ryugu [4].

We shall present the distribution of the spectral parameters of the 2.7 µm feature observed by MicrOmega on grains extracted from chamber A and chamber C, corresponding to TD1 and TD2 respectively. We will discuss the potential variations of the spectral parameters, in particular with regards to the observations performed at a much larger scale by NIRS3, and their possible implications regarding the hydrothermal and space weathering history of the asteroid.

References

[1] Tachibana et al. (2020) LPS XXXXXI Abstract #2027. [2] Bibring et al. (2017) Space Sci. Rev. 208, 401-412. [3] Madejová et al. (2017) Developments in Clay Science, 8, 107-149. [4] Kitazato et al. (2019) Science, 364, 272-275

Microscale Diversity of H, C, and N Isotopes in Asteroid Ryugu

Larry R. Nittler[1], Jens Barosch[1], Bradley T. De Gregorio[2], Rhonda M. Stroud[2], Hikaru Yabuta[3], and The Hayabusa2-initial-analysis IOM team, Hisayoshi Yurimoto[4], Tomoki Nakamura[5], Takaaki Noguchi[6], Ryuji Okazaki[7], Hiroshi Naraoka[7], Kanako Sakamoto[8], Shogo Tachibana[8,9], Sei-ichiro Watanabe[10] and Yuichi Tsuda[8]

[1]*Carnegie Institution of Washington, Washington DC, USA,* [2]*US Naval Research Laboratory, Washington DC, USA,* [3]*Hiroshima Univ.,* [4]*Hokkaido Univ.,* [5]*Tohoku Univ.,* [6]*Kyoto Univ.,* [7]*Kyushu Univ.,* [8]*JAXA,* [9]*Univ. of Tokyo,* [10]*Nagoya Univ.*

Understanding the nature and origin of organic matter in asteroid 162173 Ryugu is one of the key science goals of the Hayabusa2 sample-return mission. Macromolecular organic matter (MOM) makes up to a few % of primitive meteorites and displays a wide range of H, C, and N isotopic ratios on whole-rock to sub-μm scales [1]. Both its origin (for example, whether in the protosolar molecular cloud or in the protoplanetary disk) and the degree to which it is modified on asteroidal parent bodies is debated, but it may represent the dominant form of C delivered to early Earth. NanoSIMS-based isotopic imaging surveys of both bulk CI, CR, CM, and CO chondrites and purified MOM residues from them [2-6] have revealed that, while bulk samples are typically modestly enriched in D and ^{15}N, relative to the Earth, a small fraction of the material shows much more extreme enrichments and/or depletions in these isotopes. Large ^{13}C enrichments and depletions are also seen in chondrites, both in presolar circumstellar SiC and graphite grains [7], and in rare cases in MOM particles [8].

We have begun conducting similar NanoSIMS surveys of Ryugu samples. Four grains from Chamber A aggregates (A0108) were embedded in S and sectioned with an ultramicrotome equipped with a diamond knife. Relatively thick (250-nm) slices were deposited onto Si wafers for NanoSIMS analysis while adjacent thin sections were kept for coordinated analysis by transmission electron microscopy (TEM) and synchrotron X-ray microscopy (STXM). After the S was sublimated, we applied a thin Au coat to the Si wafers and analyzed them with a NanoSIMS 50L ion microprobe in multicollection imaging mode. Microtome sections were first analyzed for C and N isotopes (as $^{12}C_2$, $^{12}C^{13}C$, $^{12}C^{14}N$, and $^{12}C^{15}N$, plus ^{16}O, ^{28}Si, MgO and secondary electrons) with a 0.4 pA, <200-nm Cs^+ beam. The sections were then re-analyzed at the same magnification with a 1-pA beam and collection of ^{1}H, D, and ^{12}C secondary ions and secondary electrons. Five of the sections were subsequently re-measured for C and N to improve the counting statistics. Total counting times varied but were typically of order ~0.1 s/0.01 μm^2 for each run.

The measurements reveal broadly similar results to similar data obtained on primitive carbonaceous chondrites. The four particles show modest bulk enrichments of D and ^{15}N, with D/H and $^{15}N/^{14}N$ ratios in general agreement with those of CI chondrites. The NanoSIMS images show that much of the C is present as particles typically a few hundred nm in size, but ranging up to 2 μm. As in chondrites, a fraction of these particles show more extreme enrichments or depletions ("hotspots" and "coldspots") which span ranges similar to those recently seen in the least-altered CM chondrites Asuka 12169, Asuka 12236, and Paris [3]. A much smaller fraction of C-rich grains shows ^{13}C anomalies, associated both with presolar grains and organic particles. The bulk and microscale isotopic distributions vary to some extent among the four Ryugu grains, indicating heterogeneity at the 100-μm scale. Planned TEM and STXM measurements of slices from the same grains will help unravel the chemical nature of the organic particles and their relationship to inorganic phases in the asteroid.

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Diversity of Insoluble Organic Matter at the Nanoscale in Asteroid Ryugu

Rhonda M. Stroud[1], Bradley T. De Gregorio[1], Larry R. Nittler[2], Jens Barosch[2], Hikaru Yabuta[3], and The Hayabusa2-initial-analysis IOM team, Hisayoshi Yurimoto[4], Tomoki Nakamura[5], Takaaki Noguchi[6], Ryuji Okazaki[7], Hiroshi Naraoka[7], Kanako Sakamoto[8], Shogo Tachibana[8,9], Sei-ichiro Watanabe[10] and Yuichi Tsuda[8]

[1]*US Naval Research Laboratory, Washington DC, USA,* [2]*Carnegie Institution of Washington, Washington DC, USA,* [3]*Hiroshima Univ.,* [4]*Hokkaido Univ.,* [5]*Tohoku Univ.,* [6]*Kyoto Univ.,* [7]*Kyushu Univ.,* [8]*JAXA,* [9]*Univ. of Tokyo,* [10]*Nagoya Univ.*

Acid-insoluble, macromolecular organic matter represents up to 4 wt% of the matrix of carbonaceous chondrites (CC). Many properties of the insoluble organic matter (IOM), including microstructure, functional group chemistry, and mineralogical associations strongly correlate with asteroid parent body grouping and alteration history [1]. However, the IOM of many chondrites shows significant variation in structure, chemistry, and isotopic composition at the nanoscale [2,3]. The microstructure of CC IOM ranges from discrete sub-micron blebs called nanoglobules; to micrometer and larger sized veins; diffuse intergranular material; OM intercalated into phyllosilicates, and poorly-graphitized carbonaceous grain coatings. In addition, the IOM can serve as host to inorganic carbonaceous phases, such as presolar nanodiamond [4] and phase-Q [5]. This variation results from a combination of inherited molecular cloud chemistry, nebular processing, parent body and terrestrial alteration. Studies of the nanoscale variation in the IOM in the returned samples of Ryugu provide the first chance to examine the IOM of a CC parent body largely free of terrestrial alteration signatures, in order to better constrain the alteration history of a specific asteroid, and provide unprecedented constraint on the evolution of carbon in the early solar system.

Our primary method for the Initial Analysis of the nanoscale diversity of Ryugu IOM microstructure and functional chemistry is scanning transmission electron microscopy (STEM), in coordination with scanning transmission x-ray absorption spectroscopy (STXM), and isotopic characterization with NanoSIMS. The STEM measurements are carried out with the Nion UltraSTEM 200-X at the Naval Research Lab, operated at 60 kV to minimize electron beam damage. STEM measurements include annular dark field (ADF) imaging, electron energy loss spectroscopy (EELS), and energy dispersive x-ray spectroscopy (EDS). The EELS and EDS data are collected as simultaneous spectrum images to allow direct correlation of the elemental composition with the C functional chemistry, and microstructure [6]. As of this abstract submission, we have examined slices of three grains from Chamber A (A0108), one prepared as a focused ion beam (FIB) lift-out section, and two prepared as sulfur-embedded ultramicrotome slices. The FIB section was analyzed with STXM at Photon Factory Bl-19 prior to the STEM analysis. Adjacent microtome slices of were prepared for coordinated STXM and NanoSIMS measurements at the Advanced Light Source and Carnegie Institution of Washington, respectively. Measurements of additional FIB and microtome slices of Chamber A and Chamber C particles are planned.

Overall, our STEM measurements indicate IOM microstructures and functional chemistry consistent with low temperature aqueous alteration, broadly consistent with CI and CM chondrites. Small nanoglobules (< 400 nm) are abundant, but larger nanoglobules > 1000 nm are less common. Diffuse carbon intercalated into phyllosilicates is also common. Carbonate and nanoscale Fe, Ni sulfides are also found in association with IOM Coordination of the STEM results with the ongoing STXM and NanoSIMS measurements of slices from the same grains will ultimately help constrain the nature of Ryugu and its relationship to known carbonaceous chondrites, and the history of the organic matter it contains.

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Infrared transmission spectra of Ryugu particles and their unique adsorption behavior

Yoko Kebukawa[1], Lydie Bonal[2], Eric Quirico[2], Emmanuel Dartois[3], Cécile Engrand[4], Jean Duprat[5], Jérémie Mathurin[6], Alexandre Dazzi[6], Ariane Deniset-Besseau[6], Hikaru Yabuta[7] and The Hayabusa2-initial-analysis IOM team, Hisayoshi Yurimoto[8], Tomoki Nakamura[9], Takaaki Noguchi[10], Ryuji Okazaki[11], Hiroshi Naraoka[11], Kanako Sakamoto[12], Shogo Tachibana[12,13], Sei-ichiro Watanabe[14] and Yuichi Tsuda[12]

[1]Yokohama National Uni., [2]IPAG, Univ. Grenoble Alpes, CNRS CNES [3]ISOM, [4]IJCLab, [5]IMPMC/MNHN, [6]ICP, [7]Hiroshima Univ., [8]Hokkaido Univ., [9]Tohoku Univ., [10]Kyoto Univ., [11]Kyushu Univ., [12]JAXA, [13]Univ. of Tokyo, [14]Nagoya Univ.

The Hayabusa2 spacecraft successfully obtained samples from two different locations from Ryugu, a C-type asteroid, and returned them 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 at ISAS/JAXA. The insoluble organic matter (IOM) subteam has so far conducted in-situ analyses of the Ryugu particles, in order to decipher the nature of the organic matter and its origin, parent body processing, and interaction with water and minerals. 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., 1-7]. IR spectroscopy is often employed for astronomical observations and remote sensing. The reflectance spectra of solar system bodies provide information of the compositions of their surfaces. To compare the laboratory samples and the surfaces of asteroids, IR reflectance spectra have been commonly used [e.g., 8-10]. Both IR transmission and reflectance spectra give intrinsically similar information as both reflect the absorptions of IR frequencies by the target samples, although some differences do exist. As a part of the initial analysis in the IOM team, IR absorption spectra were obtained using FTIR microspectroscopy, to provide initial characterization of the Ryugu particles and search for organic matter, as well as for comparison with the surface reflectance spectra of Ryugu. 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.

Each particle (sub-millimeter in diameter) from the aggregates in chamber A (A0108) or chamber C (C0109), was further decomposed by gently crushing between two glass slides, or by separation of a fragment with a scalpel. The small fragments were then further crushed between two diamond windows (YNU and IPAG) and in a diamond compression cell under an optical microscope to optimize the thickness for further atomic force microscope based infrared spectroscopy (AFM-IR) measurements (Orsay-lab). In YNU, IR absorption spectra were collected from each diamond window with a micro-FTIR (JASCO FT/IR-6100+IRT-5200), equipped with a ceramic IR light source, a germanium-coated KBr beam splitter, a mercury-cadmium-telluride (MCT) detector, and ×16 Cassegrain mirrors, with typically 20 × 20 µm aperture. The microscope and the FTIR were continuously purged with dry N_2. To remove adsorbed water further from the sample, a heating stage (Linkam 10036L) was employed. The IR absorptions from water were satisfactory removed typically by 60 °C under N_2 flow. Micro-FTIR measurements were also conducted at IPAG with a Hyperion 3000 Bruker FTIR microscope, operating with a ~50 × 50 µm spot and an environmental cell placing the sample under secondary vacuum (< 10^{-6} mbar) and gentle heating (< 80° C) to remove adsorbed water. IR spectra by the Orsay-lab team were taken during a week of beamtime at the SOLEIL synchrotron (SMIS beam line). The synchrotron beam was coupled to a Nicolet Continuum 2 IR microscope equipped with a MCT detector and a ×32 Cassegrain optics, under dry air. For these measurements, the IR spot size was optimized with an aperture of 6 × 6 µm, close to the diffraction limit, and hyperspectral maps of Ryugu samples were acquired over several hundreds of µm in size.

The IR absorption spectra of both A0108 and C0109 particles were almost identical, and typically consistent with CI chondrites. However, some local heterogeneity exists, e.g., IR spectra from some areas were dominated by carbonate features, and opaque minerals are seen in high resolution hyperspectral maps. They display Mg-rich phyllosilicate bands at ~1000 cm^{-1} (Si-O stretching) and ~3700 cm^{-1} (OH group in phyllosilicates), organic bands (aliphatic C-H) at 3000-2800 cm^{-1}. The position and narrowness of the OH band fit those observed in spectra collected in-situ by the spacecraft [11]. Compared to the reflectance spectra obtained by JAXA curation [12], the OH band and aliphatic C-H bands features in the absorption spectra were roughly consistent, but the abundance of aliphatic C-H peaks were lower than the reflectance spectra. Such differences could be due to the difference between reflectance spectra and transmission spectra of sample particles. Also, interesting behavior was observed during FTIR analysis, in that the aliphatic C-H peak increased during analysis for a few hours, likely due to adsorption of environmental volatile organic compounds (VOCs). It is known that porous OH bearing silicates adsorb

VOCs [e.g., 13-15], particularly when fresh surfaces are exposed by sample crushing [16], however the Ryugu samples appear unusually reactive and absorb VOC very rapidly, considering that the Ryugu sample analysis was conducted in a clean environment without abundant contamination sources. This behavior indicates that Ryugu samples are fresh and highly porous. Measurements conducted under vacuum and gentle heating reveal a rapid and dramatic disappearance of adsorbed water, along with an increase of the aliphatic band intensity. This has been previously observed for CI chondrites [6,17,18], and confirms the high adsorption properties of Ryugu samples. Tight interactions between organics and -OH in phyllosilicates may account for this spectral evolution.

Overall, the FTIR organic signatures of the Ryugu samples do not point to a significant post-accretional heating as observed in heated CM/CI chondrites [19]. Acid extraction of Ryugu samples very soon will provide a fresh IOM isolate, and thereby enable quantitative characterization of chemical group abundances.

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Thermal history of Ryugu based on Raman characterization of Hayabusa2 samples

Lydie Bonal[1], Eric Quirico[1], Mutsumi Komatsu[2], Gilles Montagnac[3], Hikaru Yabuta[4] and The Hayabusa2-initial-analysis IOM team, Hisayoshi Yurimoto[5], Tomoki Nakamura[6], Takaaki Noguchi[7], Ryuji Okazaki[8], Hiroshi Naraoka[8], Kanako Sakamoto[9], Shogo Tachibana[9, 10], Sei-ichiro Watanabe[11] and Yuichi Tsuda[9]

[1]*Institut de Planétologie et d'Astrophysique de Grenoble, Université Grenoble Alpes, CNRS CNES, Grenoble, France*

[2]*SOKENDAI, The Graduate Univ. for Advanced Studies*

[3]*Laboratoire de géologie de Lyon, CNRS/INSU - ENS de Lyon, Lyon, France*

[4]*Hiroshima Univ.*, [5]*Hokkaido Univ.*,[6]*Tohoku Univ.*, [7]*Kyoto Univ.*,[8]*Kyushu Univ.*, [9]*JAXA*, [10]*Univ. of Tokyo*, [11]*Nagoya Univ.*

Introduction: The degree of structural order of the polyaromatic carbonaceous matter present in extraterrestrial samples is a tracer of the thermal history they experienced (e.g., primitive chondrites: [1-4]; micrometeorites: [5-6]). To characterize Ryugu's thermal history (long vs. short thermal heating and extent of thermal heating), we thus perform Raman characterization of several Ryugu particles returned by the Hayabusa2 mission. In order to be fully confident in the obtained data and interpretation, Raman characterization was led independently by two groups of persons in Japan and in France on distinct Ryugu particles. The results were subsequently compared.

Samples and methods: Raman point analyses were performed on several fragments of six particles from Chamber A aggregates (A0108) and six particles from Chamber C aggregates (C0109). To be able to combine in situ IR and NanoSIMS measurements on the same samples, fragments of particles were manually selected under a binocular and pressed onto diamond windows. The Raman spectra were acquired with a 532 nm laser in both Japan and France. Because some Raman bands related to carbonaceous matter are dispersive, data for Ryugu particles and comparison samples have been acquired and analyzed consistently in both Japan and in France. In particular, a Renishaw InVia Reflex equipped with a 1800 l/mm grating at Materials Characterization Central Laboratory was used in Waseda University (Japan). The laser was focused at the sample surface through a 50× objective (spot size around 3-4 µm) and its power was set at 0.24 mW and 1 mW. Each acquisition comprised five integrations of 10 s that were averaged to make the final spectrum. In France, Raman measurements were performed at the Ecole Normale Supérieure de Lyon (Laboratoire de Géologie de Lyon—Terre, Planètes, Environnement) using a LabRam Raman spectrometer (Horiba Jobin-Yvon) equipped with a 600 g/mm grating. The laser was focused through a 100× objective to obtain a <2 µm spot size. The power on the sample was 0.3 mW. Each acquisition comprised six integrations of 15 s that were averaged to make the final spectrum.

Results and discussion: More than 200 spectra were acquired on 12 different particles. The Raman data acquired in Japan and in France are fully consistent. Each acquired spectrum is characterized by a high fluorescence background and by the presence of the Raman D- (~ 1350 cm^{-1}) and G-bands (~ 1580 cm^{-1}), related to the presence of polyaromatic carbonaceous matter. The spectral parameters derived from the mathematical fitting of the individual spectra, that is, the band widths (FWHM-D, FWHM-G), the band positions (ω_D, ω_G), and the band intensity ratio (I_D/I_G) are comparable between particles. No systematic differences have been observed to date between the spectral parameters of Chamber A and Chamber C particles. This point will be further investigated on insoluble organic matter isolated by acid treatment of Ryugu samples.

The Ryugu particles contain polyaromatic carbonaceous matter that is poorly structured, as reflected by the high fluorescence background superimposed to wide D- and G-Raman bands, present at relatively low Raman shifts. The comparison of these spectral parameters with similarly characterized chondrites shows that the structural order of the polyaromatic carbonaceous matter present in Ryugu particles is comparable to that in primitive (type 1, type 2) carbonaceous chondrites. Ryugu thus escaped significant degree of long duration radiogenic thermal metamorphism (as typically experienced by type 3 chondrites), as well as short-duration heating as experienced by some type 2 chondrites (e.g., [4]).

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Elemental and isotopic compositions of organic grains from asteroid Ryugu

Laurent Remusat[1], Maximilien Verdier-Paoletti[1], Smail Mostefaoui[1], Lydie Bonal[2], Hikaru Yabuta[3] and The Hayabusa2-initial-analysis IOM team, Hisayoshi Yurimoto[4], Tomoki Nakamura[5], Takaaki Noguchi[6], Ryuji Okazaki[7], Hiroshi Naraoka[7], Kanako Sakamoto[8], Shogo Tachibana[8, 9], Sei-ichiro Watanabe[10] and Yuichi Tsuda[8]

[1] Museum National d'Histoire Naturelle, CNRS, Sorbonne Université, Paris, France. [2]Institut de Planétologie et d'Astrophysique de Grenoble, Université Grenoble Alpes, CNRS CNES, Grenoble, France [3]Hiroshima Univ., [4]Hokkaido Univ.,[5]Tohoku Univ., [6]Kyoto Univ.,[7]Kyushu Univ., [8]JAXA, [9]Univ. of Tokyo, [10]Nagoya Univ.

Introduction: Isotope composition of organic material found in extraterrestrial samples is a powerful proxy for tracking its origin and evolution during the solar system events [1,2]. *In situ* investigation of isotope and elemental compositions unravel the heterogeneity and diversity of organic particles embedded within the fine-grained minerals of chondrites and IDPs [3,4]. Understanding the origin of organic matter on carbonaceous asteroids and its subsequent evolution due to secondary processes as well as space weathering is one of the prime goals of the Hayabusa2 sample-return mission [5]. To document Ryugu's inventory of organic material, we have employed NanoSIMS imaging of intact grains, without any chemical treatments, from both Chamber A and Chamber C. We present here the first set of data acquired on the NanoSIMS installed at the National Muséum of Natural History in Paris, and compare the composition of organic particles from the two sampling sites to evaluate the influence of space weathering and aqueous alteration.

Samples and methods: Several fragments of 3 particles from Chamber A aggregates (A0108) and 3 particles from Chamber C aggregates (C0109) were manually selected under a binocular and pressed on diamond windows. After their analysis by Raman and transmission FTIR, samples were gold coated (about 25 nm thick) before NanoSIMS imaging. In the first step, secondary ions of ^{16}O, $^{12}C_2$, $^{12}C^{14}N$, $^{12}C^{15}N$ and ^{32}S were imaged in multicollection mode, to investigate N-isotope distributions as well as N/C, O/C and S/C elemental ratios. A 2-3 pA primary Cs^+ beam with a spatial resolution around 200 nm was rastered over 20 by 20 μm^2, divided into 256 by 256 pixels, in association with an electron flooding gun for charge compensation. Dwell time was set at 2 ms/pixel and about 60 frames were stacked.

Results and discussion: About 11,600 and 9,600 μm^2 surface area were imaged, of Chamber A and Chamber C samples, respectively. Individual organic particles were identified using the L'image software developed by Larry Nittler (Carnegie Institution of Washington). The $^{15}N/^{14}N$ ratios of individual particles are comparable to the values for isotope anomalies in CI and CM insoluble organic matter [3,6,7] whilst samples from Chamber C tend to exhibit a slightly larger ^{15}N enrichment. In addition, bulk organic $\delta^{15}N$ is in the range of IOM in CI chondrites. These values are consistent with independent NanoSIMS measurements of other Ryugu aggregates [8]. The corresponding elemental ratios point to a larger content in N in the organic particles from Chamber A, while the particles from Chamber C are more O-rich. Overall, S content is similar in organic particles from both chambers. It must be noted that O/C and S/C may be biased by the occurrence of fine scale association of oxides/silicates and sulfides with the organic particles, as observed by TEM [9]. The elemental composition of particulate organic matter will be further investigated on insoluble organic matter isolated by acid treatment of Ryugu samples. Our data suggest differences between aggregates from the two sampling sites in terms of elemental and isotope compositions of individual organic particles.

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Exposure Conditions of Samples Collected on Ryugu's Two Touchdown Sites Determined by Cosmogenic Nuclides

Kunihiko Nishiizumi[1], Marc W. Caffee[2], Keisuke Nagao[3], Ryuji Okazaki[4], Hisayoshi Yurimoto[5], Tomoki Nakamura[6], Takaaki Noguchi[7], Hiroshi Naraoka[4], Hikaru Yabuta[8], Kanako Sakamoto[9], Shogo Tachibana[9, 10], Sei-ichiro Watanabe[9, 11], Yuichi Tsuda[9], and Hayabusa2 Initial Analysis Volatile Team

[1]Space Sci. Lab., Univ. of California, Berkeley, CA 94720-7450, USA., [2]Dept. of Phys. & Astro., Purdue Univ., West Lafayette, IN 47907-2036, USA., [3]KOPRI, Incheon 21990, Korea, [4]Kyushu Univ., Fukuoka 819-0395, Japan, [5]Hokkaido Univ., [6]TohokuUniv., [7]Kyoto Univ., [8]Hiroshima Univ., [9]ISAS/JAXA, [10]Univ. of Tokyo, [11]Nagoya Univ.

Hayabusa2 arrived at the C-type asteroid 162173 Ryugu in Jun. 2018, and successfully collected surface samples from two sampling sites, returning ~5.4 g of samples to Earth on Dec. 6, 2020. Surface samples stored in Chamber A were collected by the 1st touchdown (TD) on Ryugu's surface on Feb. 21, 2019. A crater (diameter of ~14 m) on Ryugu's surface was made using a collision device - denoted "Small Carry-on Impactor (SCI)" - on Apr. 5, 2019 [1]. Samples in Chamber C were collected proximal to this artificial crater and are possibly ejecta from the north side of the crater by the 2nd TD on Jul. 11, 2019 [2].

Our studies are based on the measurement of those nuclides produced in asteroidal surface materials by cosmic rays - both solar and galactic cosmic rays. Cosmic-ray-produced (cosmogenic) nuclides are used to determine the duration and nature of the exposure of materials to energetic particles. Our goals are to understand both the fundamental processes on the asteroidal surface and the evolutionary history of its surface materials. They are also key to understanding the history of Ryugu's surface and asteroid-meteoroid evolutionary dynamics. For Hayabusa2 samples, there are several specific questions we aim to address: (1) are the Chamber C samples, collected during the 2nd touchdown ejecta deposits from the artificial crater, (2) if so, what is the original depth of each recovered sample in the Ryugu regolith, and (3) what is the surface exposure time, mixing rate, and erosion/escape rate of Ryugu's surface? To answer these questions, we were allocated and received 2 particles from Chamber A (A0105-19 and -20) and 3 particles from Chamber C (C0106-09, -10, and -11) for measurements of cosmogenic radionuclides and noble gases. Each sample is several hundred µm in size.

We transferred the individual grains to acid cleaned sapphire containers, with ~2 mm diameter hole, using a vacuum tweezer at the JAXA curation facility. The five samples were hand carried to the Space Sciences Laboratory (SSL), University of California, Berkeley. Each sample was gently crushed by a mortar and pestle made from sapphire and then divided into two fractions, one fraction for cosmogenic radionuclides and one for noble gases. The samples were individually transferred to a small Al weighing boat and the masses were determined using an ultra-micro balance. For cosmogenic radionuclide analysis, the sample was transferred to a Teflon bomb from the Al boat and dissolved with a few drops of HF-HNO_3 mixture in the presence of clean Be, Al, Cl, and Mn carriers. After Cl was separated as AgCl, a small analysis aliquot was taken for chemical analysis by ICP-OES (Table 1). Beryllium and Al were separated by ion chromatography, using 1 mL anion and cation ion exchange columns, and purified for accelerator mass spectrometry (AMS) measurements. To serve as a baseline comparison, three grains of the Nogoya CM2 chondrite were analyzed using the same protocols.

Beryllium-10 ($t_{1/2}$ = 1.36 x 10^6 yr) AMS analysis was performed at PRIME lab, Purdue University [3] and result was shown in Table 1. Analyses of ^{26}Al (7.05 x 10^5 yr) and ^{36}Cl (3.01 x 10^5 yr) as well as noble gases will be done in the near future.

Table 1. Chemical compositions and cosmogenic nuclide ^{10}Be concentration in Hayabusa2 samples and Nogoya CM2 chondrite.

Sample	Mass (mg)	Mg (%)	Ti (ppm)	Mn (ppm)	Fe (%)	Co (ppm)	Ni (%)	^{10}Be (dpm/kg)
Hayabusa2 A0105-19	0.2429	8.18	470	-	17.6	590	1.00	12.76 ± 0.37
Hayabusa2 A0105-20	0.2061	8.41	720	(2010)	18.0	460	1.03	12.75 ± 0.29
Hayabusa2 C0106-09	0.1228	6.05	690	(2090)	19.5	580	1.36	7.10 ± 0.30
Hayabusa2 C0106-10	0.1543	7.97	490	-	21.0	440	1.43	7.48 ± 0.26
Hayabusa2 C0106-11	0.1898	8.45	450	-	21.5	430	1.29	7.21 ± 0.43
Nogoya CM2	0.4594	9.96	480	1800	20.0	580	1.18	2.09 ± 0.13
Nogoya CM2	0.3437	9.61	480	1680	19.9	540	1.17	2.12 ± 0.09
Nogoya CM2	0.2049	11.27	410	1710	19.8	380	1.20	2.00 ± 0.13

Mn concentrations in parentheses are large uncertainty.

Although the chemical compositions of all 5 Hayabusa2 particles are very similar, the concentrations of Fe and Ni of the 3 Chamber C samples are ~10 % higher than that of Chamber A samples. Our measurements of the 5 Hayabusa2 samples indicate that the chemical composition of Ryugu is closer to those of CI or CM carbonaceous chondrites, rather than CV or CO.

To validate our procedures we measured the ^{10}Be concentrations in 3 individual grains from Nogoya. The concentrations from the Nogoya grains are nearly identical and in good agreement with our previous measurement of 2.22 ± 0.10 dpm/kg. The measurements reported here used ~3 orders of magnitude less sample mass than the measurements made years ago, have essentially the same uncertainties. For Ryugu, we were able to obtain high quality ^{10}Be measurements using ~100 μg sample.

The surface of Ryugu is bombarded by cosmic ray in a 2π exposure geometry, similar to surface of the Moon. On the Moon, the production profile of cosmogenic ^{10}Be from the surface to a depth of over 400 g/cm^2 is well established by measurements of ^{10}Be concentrations in the Apollo 15 drill core and 15008/7 core, shown in Fig. 1 [4, 5]. The ^{10}Be concentrations in A0105-19 and -20 are equivalent to the saturation value measured at the surface of the Moon. The simplest scenario is that both A0105-19 and -20 were collected from a depth of 0-30 g/cm^2 on Ryugu. Both samples have been continuously exposed to cosmic ray at a similar depth for more than several Myr. A more precise depth can be obtained by measurement of ^{26}Al, which has a different production profile than ^{10}Be, and is also produced by solar cosmic ray at shallow depth (≤ several g/cm^2). Since the ^{10}Be activity is saturated, the total exposure age must be obtained by measurements of longer half-life (3.7 x 10^6 yr) ^{53}Mn and cosmogenic noble gases. Beryllium-10 concentrations in three Chamber C samples are lower than that of the Chamber A samples but nearly the same as each other. The sampling location of the 2nd TD is close to the "ejecta ray 3" described by [1]. Assuming that the Chamber C samples were shielded during their exposure to cosmic rays and then were incorporated into the ejecta deposits from the artificial crater by SCI impact, we can calculate the depth at which they were exposed. All three Chamber C samples were ejected from a depth of 150 – 180 g/cm^2 from Ryugu (see Fig. 1). This depth corresponds to 1.3 – 1.5 m, assuming the regolith density is the same as Ryugu's bulk density of 1.2 g/cm^3 [6]. Since the depth of the crater floor from the initial surfaces was determined 1.7 m by a digital elevation map (DEM) [1], three Chamber C samples were ejected from near bottom of the crater. Alternatively, if we assume these were not ejecta, but were resident on the surface, the lower ^{10}Be activities would indicate that these grains have shorter exposure ages, ~ 1 Myr. Based on their location near the artificial crater ejecta ray, we consider this scenario unlikely. Aluminum-26 and ^{36}Cl measurements of these samples will further constrain ejection depth and condition.

For our work, we obtained 5 similar sized, ~0.5 – 1 mm, grains. We don't know whether the sizes we observe now are representative of the grain's original sizes on Ryugu's surface; it is possible that they were broken during the collection process or during sample handling. We are certain though that independent of their original size on Ryugu, the three Chamber C grains were exposed to cosmic rays at the same depth. These grains had ample ^{10}Be for measurement, ^{10}Be measurements are possible in smaller grain sizes. A logical next step would be the measurement of ^{10}Be in grains of different sizes to investigate whether any possible association of grain size and ejection depth.

Based on saturated ^{10}Be in surface samples and from ejecta samples we conclude that the surface of Ryugu has been exposed to cosmic rays for more than several Myr and that the upper 1 - 2 m of regolith have been relatively undisturbed for more than several Myr. Our observation shows that the surface of Ryugu is more stable than the surface of Itokawa and the estimation by geomorphological indicators [7]. Additional cosmogenic nuclide measurements, especially stable noble gases, will allow a detailed understanding of the surface evolution of Ryugu.

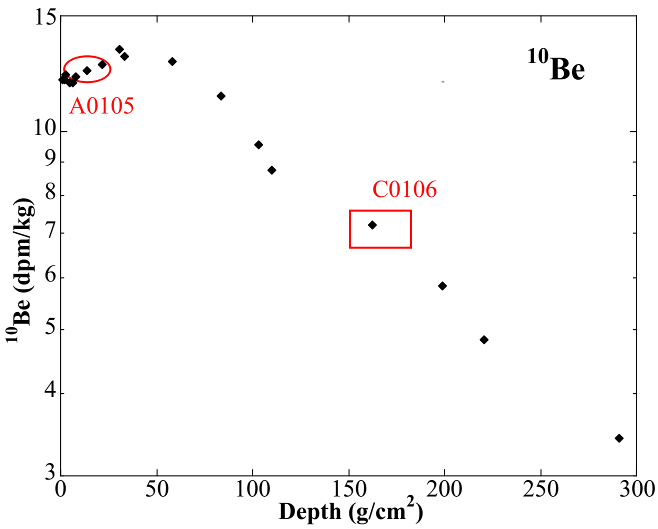

Figure 1. The depth profile of ^{10}Be production on the Moon. Black diamonds indicate ^{10}Be concentration vs. depth on the Moon measured in undisturbed Apollo 15 drill core and 15008/7 core [4, 5]. Observed ^{10}Be concentrations in Hayabusa2 samples are plot at estimate depths on Ryugu and marked red circle (A0105) and square (C0106).

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Small grains from Ryugu: handling and analysis pipeline for Infrared Synchrotron Microspectroscopy

Stefano Rubino[1], Zélia Dionnet[1], Alice Aléon-Toppani[1], Rosario Brunetto[1], Tomoki Nakamura[2], Donia Baklouti[1], Zahia Djouadi[1], Cateline Lantz[1], Obadias Mivumbi[1], Ferenc Borondics[3], Stephane Lefrançois[3], Christophe Sandt[3], Francesco Capitani[3], Eva Héripré[4], David Troadec[5], Megumi Matsumoto[2], Kana Amano[2], Tomoyo Morita[2], Hisayoshi Yurimoto[6], Takaaki Noguchi[7], Ryuji Okazaki[7], Hikaru Yabuta[8], Hiroshi Naraoka[7], Kanako Sakamoto[9], Shogo Tachibana[9-10], Sei-ichiro Watanabe[11], Yuichi Tsuda[9], and the Hayabusa2-initial-analysis Stone team

[1]*IAS, Université Paris-Saclay, CNRS, France,* [2]*Tohoku University, Japan,* [3]*SMIS-SOLEIL, France* [4]*CentraleSupélec, Université Paris-Saclay, CNRS, France,* [5]*IEMN, Université de Lille, France,* [6]*Hokkaido University, Japan,* [7]*Kyushu University, Japan,* [8]*Hiroshima University, Japan,* [9]*ISAS/JAXA, Japan,* [10]*The University of Tokyo, Japan,* [11]*Nagoya University, Japan*

Introduction: In December 2020, the sample return mission Hayabusa2 (JAXA) brought 5.4g of matter from the surface of C-type primitive asteroid (162173) Ryugu [1]. This extremely precious material is now the object of multiple studies with state-of-the-art techniques in laboratories all around the world (Initial Analysis phase). These studies will grant new insight on the origin and evolution of primitive hydrated planetesimals, and ultimately on the early stages of our solar system. Within the Hayabusa2-initial-analysis "Stone" team [1] led by T. Nakamura, we received several microscopic particles in July 2021, with the goal of performing IR hyper-spectral imaging and IR micro-tomography studies.

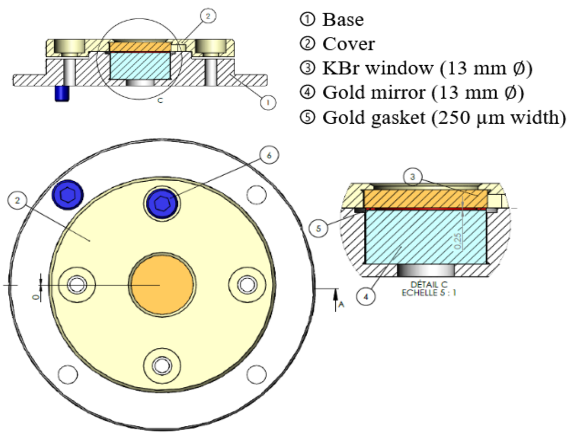

Figure 1. Sample-holder description

Samples transfer and handling: Ryugu samples are kept in a controlled N_2 environment at Sagamihara (JAXA) in order to avoid exposure to the terrestrial atmosphere. We took several steps in order to minimize the samples' exposure to air, before, during and after measurements. Prior to receiving the samples, we designed a custom sample-holder (Figure 1) for transferring particles from Japan to France and for their preliminary analysis. Particles from Ruygu were deposited on a gold mirror inside the sample-holder at Tohoku University (Japan). A KBr window installed in the cover of the sample-holder allowed us to acquire measurements of the particles while the sample-holder was still sealed. This custom-made sample-holder was kept as clean and sterile as possible (to avoid terrestrial contamination) and it had to fulfill two major requirements: fit on the microscope stages for our IR imaging and microspectroscopy studies and keep the samples in a dry N_2 environment (to avoid alteration from the atmosphere). The sample-holder was assembled inside a glovebox under N_2 atmosphere ($\Delta P \sim 6$ mBar, $H_2O = 1.0$ ppm, $O_2 = 1.2$ ppm). Multiple interfaces were used in order to prevent the mixing of the clean N_2 atmosphere and the ambient air (gold gasket, cleanroom static shielding bags), but also to avoid issues from shocks and vibrations (membrane boxes, foam-padded case). Once in Sendai, the empty sample holders were opened in a glovebox, and were loaded with 32 microscopic particles from Ryugu (distributed among four sample-holders: 14 particles from the first touchdown site in SH2 and SH3, and 18 particles from the second touchdown site in SH1 and SH4).

To monitor the atmosphere's changes in our sample-holders, these were accompanied by a "control"-holder, with grains of olivine and Fe dust (to monitor hydration and oxidation). A second "control"-holder, loaded with drierite (calcium sulfate) and some Fe dust, was kept in France, to monitor hydration and oxidation when not under dry N_2 conditions.

Samples reception and characterization: Upon arrival at synchrotron SOLEIL (France) in early July, the sample holders were inspected with a binocular through the KBr windows. We were able to identify at least 24 out of 32 of the original Ryugu particles, either based on their morphological correspondence with the grains prepared at Tohoku, and/or thanks to their clear IR "Ryugu-like" spectral signatures (mainly the 2.7 µm feature [2]). The particle size range was from 20 to 80 µm, with a particularly large particle in SH4 larger than 100 µm.

The analytical pipeline started with a full spectral characterization using the IR synchrotron beam while keeping the sample-holder closed, in order to minimize exposure to air. During the first three weeks of July, we analyzed all the identified Ryugu grains in their sample holders using three different FTIR microscopes: (1) a mid-IR large wavelength range MCT/B-equipped and synchrotron-radiation-fed microscope, (2) a far-IR bolometer-equipped microscope, (3) an FPA-equipped imaging microscope. Multiple detectors were used to access different wavelength ranges, covering from near-IR to far-IR (1 µm to 35 µm). This large spectral coverage allowed us to detect carbonates, organics, and phyllosilicates with different band positions [3]. Most of the IR spectra showed interesting features. Hyperspectral maps in the mid-IR of the individual particles were also acquired, in order to assess the compositional heterogeneity at the 5-10 µm scale. A few Raman spectra and maps were also acquired on isolated fragments, to assess the presence and structure of endemic organics in Ryugu's particles and to get complementary information on the mineralogy.

Thanks to a Raman measurement on a µm-spot on the gold substrate, we managed to detect remotely molecular oxygen inside SH2, which indicates the holders at some point lost their air-shut condition, probably in flight from Japan to France. We estimate that the grains were exposed to air for about 72-96 hours, before we received them and we put them again into a dry N_2 environment. However, we did not observe any modification of the KBr (a control KBr window we exposed to air for 24h showed clear modifications), and the anhydrous control samples we sent along the Ryugu sample holders showed no evidence of water adsorption nor hydration. So we inferred that Ryugu grains remained in a relatively dry environment, although in presence of O_2, probably thanks to the presence of desiccants that prevented an increase in humidity.
In mid- and late-July, we opened sample holders SH2 and SH3, and we mounted 6 Ryugu grains on W or Al needles using two different FIB-SEM microscopes in Saclay and in Lille [4]. These grains were then measured in both transmission and reflectance mode, by Infrared Computed Tomography [5] (IR-CT) and Infrared Surface Imaging [6] (IR-SI) respectively. IR-CT allows us to assess the compositional heterogeneity of small particles in a 3D space, while IR-SI allows us to assess the surface composition for larger particles, treating the grain as a planetary surface by projecting the 2D IR hyper-spectral maps on a 3D shape model. Data processing and analysis of this large set of data is still ongoing. Our primary method of analysis, IR spectroscopy, is totally non-destructive, which implies that after our measurements a few particles can be sent to other analytical teams in the scope of combining different studies on the same sample. Some of these particles are now being analyzed by X-ray computed tomography at SPring-8 (Japan) [7].
Overall, the outcome of the last months has shown that the agreed handling, transfer and analysis pipelines are valid and may be applied for future sample-return missions.

Acknowledgements: We thank Moe Matsuoka for her precious help in preparing and sending Ryugu's particles from Sendai-Japan all the way to Orsay-France. This work is part of the multi-analytical sequence of the Hayabusa2 "Stone" MIN-PET group, led by Tomoki Nakamura. Zélia Dionnet was supported by a CNES postdoctoral allocation and this work was supported by the Centre National d'Etudes Spatiales (CNES-France, Hayabusa2 mission). The micro-spectroscopy measurements were supported by grants from Region Ile-de-France (DIM-ACAV) and SOLEIL.

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Preliminary results from FTIR hyper-spectral imaging campaign on Ryugu small grains and fragments.

Zélia Dionnet[1], Stefano Rubino[1], Alice Aléon-Toppani[1], Rosario Brunetto[1], Tomoki Nakamura[2], Donia Baklouti[1], Zahia Djouadi[1], Cateline Lantz[1], Ferenc Borondics[3], Christophe Sandt[3], Eva Héripré[4], David Troadec[5], Megumi Matsumoto[2], Kana Amano[2], Tomoyo Morita[2], Hisayoshi Yurimoto[6], Takaaki Noguchi[7], Ryuji Okazaki[7], Hikaru Yabuta[8], Hiroshi Naraoka[7], Kanako Sakamoto[9], Shogo Tachibana[9-10], Seiichiro Watanabe[11], Yuichi Tsuda[9] and the Hayabusa2-initial-analysis Stone team.

[1]IAS, Université Paris-Saclay, CNRS, France, [2]Tohoku University, Japan, [3]SMIS-SOLEIL, France [4]CentraleSupélec, Université Paris-Saclay, CNRS, France, [5]IEMN, Université de Lille, France, [6]Hokkaido University, Japan, [7]Kyushu University, Japan, [8]Hiroshima University, Japan, [9]ISAS/JAXA, Japan, [10]The University of Tokyo, Japan, [11]Nagoya University, Japan

Introduction: Hayabusa2 is the first sample return mission to study and return samples from a primitive carbonaceous asteroid. It thus allows the study of the same small body at very different scales, from the km down to the atomic scale. Infrared (IR) spectroscopy plays a crucial role in this respect, helping to build a bridge between the remote sensing observations of the asteroid's surface, performed by NIRS3 [1,2] and the chemical and physical processes operating at a smaller scale and characterized in the laboratory on the returned samples. In December 2020, the Hayabusa2 reentry capsule delivered 5.4 g of material coming from asteroid Ryugu. This extremely precious material was then recovered by JAXA and pre-characterized inside the ISAS curation facility [3,4]. A fraction of this material was then given to six Initial Analysis sub teams, including the "Stone" team led by T. Nakamura which studies mineralogy and petrology at a large scale [5].

Material and Methods: We will present the result of FTIR hyperspectral imaging on six micrometric Ryugu fragments (ranging from 30 to 80 µm in size). These fragments originate from 2 bigger millimetric grains (A0064 and C0046). We analyzed these small grains in multiple configurations (see detailed analytical plan and transportation issues in [6]). After the first characterization in reflectance mode on their gold substrate, we mounted these small grains at the top of metallic needles to analyze them at different rotating angles both in transmission and reflection modes. The obtained data in transmission mode, IR-CT [7] (Infrared Computed Tomography), were then analyzed to reconstruct 3D distributions of the molecular components inside the grains, while reflectance data were projected on a 3D shape model of the grains. In this case, the fragments were treated as a planetary surface, which will also help to reinforce the link between remote sensing and laboratories measurements. Taking advantage of each configuration, the preliminary results of the combination of the different measurements will be shown and discussed.

Results and Discussion: We will present the average spectra in the 2.5 – 30 µm range. Several grains have IR signatures at 2.7 µm, 3.0-3.1 µm, 3.4 µm, and 3.9 µm, in a good agreement with the bands identified by NIRS3 or by MicrOmega and FTIR in the JAXA curation facility [3, 4], plus several mid-IR signatures of great interest, such as bands attributed to Si-O stretching in phyllosilicates, and C=O stretching in organics and carbonates. A comparison of the IR spectra of the different grains with those of a large variety of carbonaceous chondrites acquired with the same set-up will be presented. Finally, we will discuss the heterogeneity within individual grains, with particular emphasis on the following issues: (i) detection and heterogeneity of the 2.7 µm band (ii) spatial correlation between phases (phyllosilicates, carbonates, opaque phases, organics) and (iii) identification and quantification of the carbonates. These spectral observations and parameters will help to better constrain the 3D µm-scale assembly of minerals and organics in Ryugu, and will provide information on the origin and evolution of Ryugu.

Perspectives: Our multi-analytical sequence started with non-destructive IR hyperspectral imaging and continues now with more destructive techniques. One grain has been sliced into 3-µm thin sections and will be analyzed in 2D with higher resolution IR hyperspectral imaging and complementary analyses [8]. The rest of the samples have been sent back to Japan, to be analyzed at the BL47XU of SPring-8 synchrotron by XCT [9] in order to obtain complementary information concerning the 3D physical, chemical and morphological properties.

Acknowledgments: We thank Moe Matsuoka for her precious help in preparing and sending Ryugu's particles from Sendai-Japan all the way to Orsay-France. This work is part of the multi-analytical sequence of the Hayabusa2 "Stone" MIN-PET group, led by Tomoki Nakamura. Zélia Dionnet was supported by a CNES postdoctoral allocation and this work was supported by the Centre National d'Etudes Spatiales (CNES-France, Hayabusa2 mission). The micro-spectroscopy measurements were supported by grants from Region Ile-de-France (DIM-ACAV) and SOLEIL.

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Iron valence state and mineralogy in particles from asteroid Ryugu

Jean-Christophe Viennet[1], Mathieu Roskosz[1], Pierre Beck[2], Esen Ercan Alp[3], Barbara Lavina[3,4], Michael Hu[3], Jiyong Zhao[3], Tomoki Nakamura[5], Kana Amano[5], Mizuha Kikuiri[5], Tomoyo Morita[5] Hisayoshi Yurimoto[6], Takaaki Noguchi[7] Ryuji Okazaki[8] Hikaru Yabuta[9], Hiroshi Naraoka[8], Kanako Sakamoto[10], Shogo Tachibana[10,11], Seiichiro Watanabe[12], Yuichi Tsuda[10], and the Hayabusa2-initial-analysis Stone team.

[1] *Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Museum National d'Histoire Naturelle, CNRS, Sorbonne Université, Paris, France.* [2]*Institut de Planétologie et d'Astrophysique de Grenoble, Université Grenoble Alpes, CNRS CNES, Grenoble, France.* [3]*Center for Advanced Radiation Sources, The University of Chicago, Chicago, IL 60637, USA.*[4]*Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA.* [5]*Tohoku Univ.* [6]*Hokkaido Univ.*[7]*Kyoto Univ.* [8]*Kyushu Univ.* [9]*Hiroshima Univ.* [10]*JAXA.* [11]*Univ. of Tokyo,* [12]*Nagoya Univ.*

Introduction: Iron is a major element in rocky material from the solar system that can occur under multiple valence state. As such it can be used to trace geological processes that occurred on asteroid Ryugu, including thermal metamorphism and aqueous alteration. Observations of the mineralogy of carbonaceous chondrites have revealed the presence of minerals assemblages that are barely in thermodynamic equilibrium. Even at the micron-scale, iron is often present under multiple valence state (most frequently 0, +2, or +3) in a wide range of minerals (primary or secondary in nature), including silicates, oxy-hydroxide, sulfides, sulfates, clay minerals and carbonates. Such heterogeneous assemblages are the results of post-accretion processes that often triggered a partial textural and chemical equilibration, associated to a modification of primary Fe-bearing minerals and their valence state. It is therefore tricky to disentangle the different processes recorded by the iron mineralogy of chondritic materials. Furthermore, since most Fe-bearing phases are redox-sensitive, exposure to terrestrial atmosphere may also induce iron oxidation and additional, late modifications of the iron mineralogy. In this context, Hayabusa2 sampled Ryugu, an asteroid that did not suffer extensive thermal metamorphism, and returned rocks to Earth with minimal air exposure. It offers a unique opportunity to study the redox state of carbonaceous asteroids and evaluate the overall redox state of the most oxidized primitive rocks of the solar system.

Samples and methods: Here, we determine the mineralogy and the redox state of Fe-bearing minerals from ten Ryugu samples (five from the chamber A used for the first sampling and five from the chamber C for the second sampling) prior to and after exposure to air. We use Synchrotron Mössbauer Spectroscopy (SMS) technique that enables to probe the bonding environment of iron at the microscopic scale. These measurements are combined with co-aligned X-ray diffraction, permitting to assess locally the mineralogy and valence state of iron in Ryugu particles. We also apply conventional Mössbauer spectroscopy on a couple of large (mm-size) Hayabusa returned samples from the chambers A and C.

Results and discussion: We will present the bulk proportions of iron-bearing minerals and the Fe redox state (Fe^{3+}/Fe_{tot}) at the 'Stone' scale. We will then provide the first estimate of the redox state of Ryugu as compared to the large array of bulk redox data collected over several decades on meteorites. We will also describe the redox states of iron-bearing clay minerals before any air contamination. The first clues on the ageing of these minerals after exposure to air will be discussed based on data collected on the same sample before and after exposure to air. We will compare in greater details Ryugu samples to a series of well-known chondritic meteorites including Orgueil and Murchison. We will show, more specifically, that most of the iron is accommodated in magnetite and sulfides (pyrrhotite and pentlandite). Clay minerals also contain a fraction of the total iron. Overall, the investigated Ryugu samples appears to be (or are) more reduced than the Orgueil, both considering the bulk composition and the clay minerals fraction. The redox state recorded in a pristine sample and in the same sample exposed to air for more than two months do not show clear evidence of oxidation suggesting that, as far as iron is concerned, samples can be prepared and analyzed at ambient conditions at least for several weeks if stored in vacuum or in inert gas after preparation.

Three-dimensional analysis of Ryugu sample particles using X-ray nanotomography.

Akira Tsuchiyama[1,2], Megumi Matsumoto[3], Junya Matsuno[1], Tomoki Nakamura[3], Takaaki Noguchi[4,5], Kentaro Uesugi[6], Akihisa Takeuchi[6], Masanori Yasutake[6], Miyake Akira[4], Shota Okumura[4], Yuri Fujioka[3], Mingqi Sun[2], Aki Takigawa[7], Toru Matsumoto[4], Satomi Enju[8], Itaru Mitsukawa[4], Yuma Enokido[3], Tomoyo Morita[3], Naoto Nakano[4] and Stefano Rubino[9], Tsukasa Nakano[10] Hisayoshi Yurimoto[11], Ryuji Okazaki[12], Hikaru Yabuta[13], Hiroshi Naraoka[12], Kanako Sakamoto[14], Shogo Tachibana[7,14], Seiichiro Watanabe[15] and Yuichi Tsuda[14], and the Hayabusa2-initial-analysis Stone and Sand teams

[1]*Research Organization of Science and Technology, Ritsumeikan University*, [2]*CAS, Guangzhou Institute of Geochemistry*, [3]*Guraduate School of Science, Tohoku University*, [4]*Guraduate School of Science, Kyoto University*, [5]*Faculty of Arts and Science, Kyushu University*, [6]*SPring8/JASRI*, [7]*Guraduate School of Science, University of Tokyo*, [8]*Guraduate School of Science and Engineering, Ehime University*, [9]*Université Paris-Saclay, CNRS, Institut d'Astrophysique Spatiale,* [10]*GSA/AIST,* [11]*Guraduate School of Science, Hokkaido University*, [12]*Guraduate School of Science, Kyushu University*, [13]*Guraduate School of Advanced Science and Engineering, Hiroshima University*, [14]*ISAS/JAXA*

We have performed initial analysis of samples returned from asteroid 162173 Ryugu by the Hayabusa2 spacecraft using synchrotron radiation-based X-ray nanotomography to elucidate the 3D structures and features of the samples with sub-micron spatial resolution as parts of the Hayabusa2 initial analysis Stone and Sand sub-teams.

We analyzed 29 and 20 particles from the first and second touchdown sites (chambers A and C), respectively. Particles of 10 ~ 150 μm in apparent size were picked up and attached to the tips of Ti needles with Pt deposition using FIB or amorphous carbon fibers with glycol phthalate. They were imaged by two different methods (dual-energy tomography (DET) [1] and scanning-imaging X-ray microscopy (SIXM) [2]) at BL47XU of SPring-8 [3]. In DET, X-ray absorption contrast images were obtained as the spatial distribution of linear attenuation coefficient (LAC) at two different X-ray energies of 7 and 7.35 keV, which are below and above the K-absorption energy of Fe (7.11 keV), respectively. The LAC images at 7 keV correspond closely to compositional (Z) contrasts, except for Fe, and those at 7.35 keV strongly depended on Fe content. In SIXM, we obtained X-ray differential phase contrast images as the spatial distribution of refractive index decrement (RID), which is the difference between the X-ray refractive index (RI) and unity (RI = 1 - RID), at X-ray energy of 8 keV. The RID image is closely proportional to the density of the object. The voxel sizes of LAC 7 keV, LAC 7.35 keV and RID images are $47.4\times 47.4\times 47.4$ nm^3, $51.1\times 51.1\times 51.1$ nm^3 and $111.1\times 111.1\times 109.2$ nm^3, respectively.

The image analysis was made by combining ImageJ and codes made with C and Python. The registration among the three types of images was made with the reference of LAC 7 keV images. Then, RGB-CT images were made by assigning blue, red, and green to LAC 7 keV, LAC 7.35 keV, and RID images, respectively. Different phases including organic materials show different colors in the RGB-CT images. Minerals are quantitatively discriminated by comparing the LAC and RID values of the objects in CT images and those of minerals with known chemical compositions and densities. The solid portions of the sample particles images were extracted in LAC 7.35 keV using Chan-Base segmentation. The volume, V, surface area, S, 3-axial lengths, $A\geq B\geq C$, fractal dimension, FD, and closed porosity, p_0, were then obtained. Porosity by considering pores and cracks that are open to the outside, named as open porosity, p_∞, were also estimated by a wrapping method [4]. The density, ρ, was estimated from the averaged RID value of the particle as the lower limit. Density considering open pores, ρ_∞, was calculated as $\rho\times(1-p_\infty)$. Sphere-equivalent diameter, D, was calculated from V and sphericity, Ψ, from V and A.

No distinct difference between the samples from chambers A and C was recognized. The sample particles are mainly composed of Mg-rich phyllosilicates (serpentine and/or saponite; Mg#~0.8-0.9) in the matrix (Fig. 1A). The phyllosilicates are not homogeneous in some particles (Fig. 1B) probably due to the difference of Mg# and/or nanoporosity below the spatial resolution. FeS (mostly pyrrhotite and minor pentlandite) grains are commonly present as hexagonal plates shown as a rectangle shape in a slice image (Fig. 1A). We found whiskers of probably FeS (Fig. 1C) in some matrices as well. Magnetite grains with different morphologies (framboidal, spherulitic, plaquette and equant) are also commonly present (Fig. 1A). Sub-micron grains of FeS and magnetite are usually present in the matrix. Dolomite is usually present mostly as aggregates of euhedral or subhedral grains (Fig. 1A) and contains minor amounts of Fe and some heavy element (possibly Mn). Aggregates of micron-sized dolomite grains are also present (Fig. 1B). Breunerite is present as a rhombohedron in shape and have the composition roughly estimated as $(Mg_{0.6}Fe_{0.4})CO_3$ (Fig. 1D). $CaCO_3$ (aragonite or calcite) is rarely present. Apatite is usually present mostly as aggregates of subhedral or anhedral grains (Fig. 1E). Small grains of forsterite or enstatite (Mg#~1) are rarely observed. Small objects (mostly <1 μm) of probably organic materials are commonly present in the matrix (Fig. 1B) but their abundance is small (probably a few % or less). Inclusions, which are empty or filled with low-Z materials, were observed in FeS, dolomite, breunerite and apatite grains (Fig. 1D). Spherical objects of phyllosilicate surrounded by fine grains of FeS or dolomite (Fig. 1E) and object composed of Fe-rich and mostly anhydrous silicates (Fig. 1E) and fine grains of FeS and/or magnetite named “dark inclusion” (Fig. 1A) were sometimes observed. In addition to the above phases, several unidentified phases are observed as well. Some sample particles are unique; a low-density material (~1 g/cm^3) with a lot of fine cracks and organic-like material with embedded mineral grains. Porous objects like the ultra-porous lithology in Acfer 094 [3] were not observed.

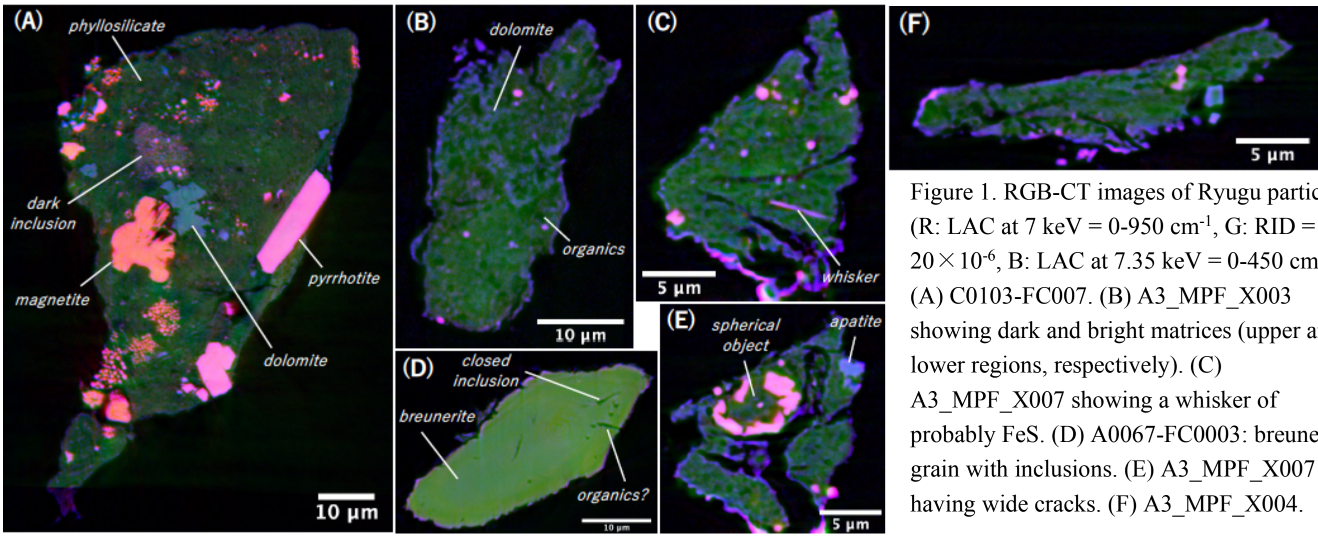

Figure 1. RGB-CT images of Ryugu particles (R: LAC at 7 keV = 0-950 cm^{-1}, G: RID = 0-20$\times$10^{-6}, B: LAC at 7.35 keV = 0-450 cm^{-1}). (A) C0103-FC007. (B) A3_MPF_X003 showing dark and bright matrices (upper and lower regions, respectively). (C) A3_MPF_X007 showing a whisker of probably FeS. (D) A0067-FC0003: breunerite grain with inclusions. (E) A3_MPF_X007 having wide cracks. (F) A3_MPF_X004.

D ranges from 9 to 60 µm. The 3D shape distribution indicates that the Ryugu particles (B/A =0. 66 and C/B =0.65 in average) are less spherical in shape than the Itokawa particles and fragments of impact experiments (*c.f.*, silver ratio: B/A=C/B=0.71) [1]. Some particles examined here may not be the original impact fragments on the Ryugu surface but artificial fragments during the sampling by the space craft and/or in the laboratory. Ψ is small (<0.4) and *FD* of some particles are <3 together with a weak correlation between them, indicating that the particle shapes are irregular and complicated. Some surfaces of the particles are convexo-concave indicating fragmentation, while some are more or less smooth and may be formed by mechanical abrasion on the asteroid as proposed for Itokawa particles [4]. Cracks less than a few µm in width are commonly present in all particles except for those composed of single crystals. Some cracks develop along the boundaries of some objects and mineral grains (Fig. 1E), implying that they are cracks formed due to shrinkage by dehydration. Some cracks are subparallel to flattened particle surfaces probably due to impact (Fig. 1F). p_0 is usually less than a few%. p_∞ mostly ranges from 5 to 20% (Fig. 2), which is less than the porosity of the CI chondrite Orgueil (34.9% [5]). This can be explained by the different size of pores; the p_∞ counts relatively large pores (>~a few hundred nm) while that of CI counts nanopores. ρ mostly ranges from 1.3 to 1.8 g/cm^3 and and ρ_∞ from 1.1 to 1.6 g/cm^3 (Fig. 2). They are not inconsistent with the bulk density of Orgueil (1.57 g/cm^3 [5]) if we consider ρ and ρ_∞ as the lower limits.

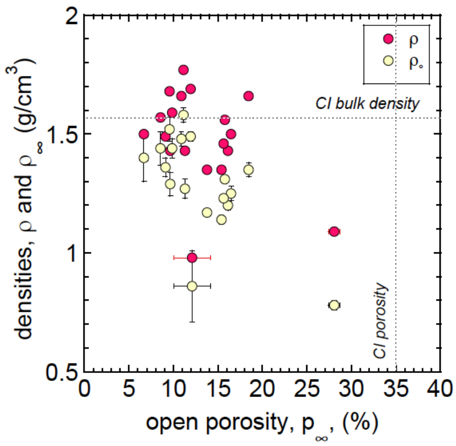

Figure 2. Density, ρ, estimated from the averaged RID value (lower limit) and density considering open pores, ρ_∞, plotted against open porosity, p_∞.

The examined samples closely resemble CI in mineralogy and textures although we did not surely find any sulfates, such as gypsum, epsomite and blödite. The porosity and density are also consistent with those of CI. Any signature of dehydration as suggested from the IR spectrum [6] was not recognized. Highly porous materials as expected from the low thermal inertia [7] were not observed. FIB sections were prepared based on the 3D information and examined by TEM [8, 9]. The present examination is ongoing and we note that some of the ranges of physical properties, such as D, B/A, C/B, Ψ, FD, p_0, p_∞, ρ and ρ_∞, are still preliminary.

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Surface morphologies and space weathering features of Ryugu samples

T. Matsumoto[1], T. Noguchi[1], A. Miyake[1], Y. Igami[1], M. Haruta[1], H. Saito[2], S. Hata[2], Y. Seto[3], M. Miyahara[4], N. Tomioka[5], H. A. Ishii[6], J. P. Bradley[6], K. Ohtaki[6], E. Dobrică[6], T. Nakamura[7], M. Matsumoto[7], A. Tsuchiyama[8, 9]; M. Yasutake[10], J. Matsuno[8], S. Okumura[1], K. Uesugi[10], M. Uesugi[10], A. Takeuchi[10], M. Sun[9], S. Enju[11], A. Takigawa[12], H. Leroux[13], C. Le Guillou[13], D. Jacob[13], M. Marinova[13], F. de la Peña[13], F. Langenhorst[14], D. Harries[14], P. Beck[15], T. H. Van Phan[15], R. Rebois[15], N. M. Abreu[16], T. Zega[17], P.-M. Zanetta[17], M. Thompson[18], M. Lee[19], L. Daly[19], P. Bland[20], R. Stroud[21], K. Burgess[21], J. C. Bridges[22], L. Hicks[22], M. E. Zolensky[23], D. R. Frank[6], J. Martinez[24], H. Yurimoto[25], K. Nagashima[6], N. Kawasaki[25], R. Okazaki[2], H. Yabuta[4], H. Naraoka[2], K. Sakamoto[26], S. Tachibana[12], S. Watanabe[27], Y. Tsuda[26], and the Hayabusa2 Initial Analysis Team

[1]*Kyoto Univ., Japan;* [2]*Kyushu Univ., Japan;* [3]*Kobe Univ., Japan;* [4]*Hiroshima Univ., Japan;* [5]*Kochi Core Center, JAMSTEC, Japan;* [6]*Univ. of Hawaii, USA;* [7]*Tohoku Univ., Japan;* [8]*Ritsumeikan Univ., Japan;* [9]*Guangzhou Institute of Geochemistry, China;* [10]*JASRI, Japan;* [11]*Ehime Univ., Japan;* [12]*Univ. of Tokyo, Japan;* [13]*Univ. de Lille, France;* [14]*Univ. of Jena, Germany;* [15]*Univ. Grenoble Alpes, France;* [16]*Penn State, USA;* [17]*Univ. of Arizona, USA;* [18]*Purdue Univ., USA;* [19]*Univ. of Glasgow, UK;* [20]*Curtin Univ., Australia;* [21]*US Naval Research Laboratory, USA;* [22]*Univ. of Leicester, UK;* [23]*JSC/NASA, USA;* [24]*Jacobs Engineering,* [25]*USA, Hokkaido Univ., Japan;* [26]*JAXA/ISAS, Japan;* [27]*Nagoya Univ., Japan*

Introduction: Asteroids are leftover remnants of planet formation and provide clues as to the origin and evolution of the early solar system. C-type asteroids have been expected to be parent bodies of carbonaceous chondrites, containing hydrated silicates and volatile compounds that could be the origin of water and life on the Earth. JAXA's *Hayabusa 2* spacecraft explored C-type asteroid Ryugu and collected surface materials at two landing sites on Ryugu [1]. The spacecraft delivered its re-entry capsule to the Earth, and subsequent initial investigation of the *Hayabusa 2* sample container found that millimeter pebbles and fine grains were successfully recovered from the surface of Ryugu [2]. Geologic maps and variations in the reflectance spectra of Ryugu's surface suggest that geologic activities and alteration of regolith occur over time [3]. Ryugu samples will provide an opportunity to understand the dynamic evolution of surface materials on C-type asteroids. Materials exposed to the space environment are expected to have altered optical, physical, or chemical properties. This process is defined as space weathering, which includes alteration by micrometeoroid bombardments, solar wind implantation, and solar radiation heating [4]. Analyses of lunar soils and regolith particles from S-type asteroid Itokawa have revealed that the uppermost surfaces of regolith grains record the space weathering features, such as amorphization, melting, and vapor-deposition [5,6]. Thus far, the space weathering of carbonaceous asteroids is not well understood. The surface microstructures of Ryugu samples will offer insight into the ongoing alteration of the regolith on Ryugu. In this study, we report the surface morphologies and mineral structures of Ryugu samples investigated in the initial analysis by the Mineralogy-Petrology Fine (Sand) sub-team.

Samples and methods: Ryugu samples from the two sampling sites were preserved in chambers A and C of the sample catcher inside the sample container [2]. We have mainly investigated the fine grains (< 300 μm) picked up from both chambers at the Extraterrestrial Sample Curation Center of JAXA. After the samples were allocated from JAXA, we handled them in a dry glove box filled with nitrogen at Kyoto University. For surface observation, the fine grains were fixed on gold plates using an Araldite adhesive. We examined the surface features of the Ryugu samples using a field emission scanning electron microscope (FE-SEM: JSM-7001F). We then extracted electron-transparent sections of regions of interest on the Ryugu grains for transmission/scanning transmission electron microscopy (TEM/STEM) studies, using a focused ion beam (FIB) system (Helios NanoLab G3 CX at Kyoto University, Thermo Scios at Kyushu University). We are now performing TEM/STEM analysis, synchrotron radiation X-ray absorption fine structure analysis, nano-tomography, and atom probe analysis.

Results: *Surface features of Ryugu grains*: Fine Ryugu grains have massive, platy, and granular shapes. The majority of the grain surfaces consist of phyllosilicates with rough surfaces. Coarse and fine surface textures are identified on the phyllosilicates. Cracks/gaps exist between phyllosilicates and other mineral phases. TEM analysis shows that the phyllosilicates are composed mainly of serpentine and saponite (detailed TEM observations are described in [7]). The second major mineral phases on the grain surfaces are sulfides, magnetite, and carbonates. These minerals are ubiquitous, although their abundance varies from grain to grain. Most of the sulfides are pyrrhotite crystals. They appear as hexagonal plates, cuboids, and irregular shapes with sizes up to a few tens of micrometers. The pyrrhotite plates exhibit sharp growth steps on their surfaces. Some pyrrhotite crystals with irregular surfaces have numerous voids. Pentlandite often coexists with pyrrhotite. Tiny sulfides (< 1μm), including zinc, chromium, and/or copper, occur as minor phases. Magnetite appears as framboidal aggregates, plaquettes, spherulites, and irregular shapes. The framboidal magnetite on Ryugu grains have distinct sharp edges, when compared to framboidal magnetites with rounded morphologies in thermally metamorphosed CI chondrites (e.g., Y980115) in which thermal sintering has likely occurred. The carbonate phases found on the Ryugu grains are mainly dolomite and minor magnesite-breunnerite. They have euhedral, fractured, and irregular surfaces. Calcium phosphate, oxides (chromite, ilmenite), and iron phosphides are found as minor phases. Na-Mg bearing phosphate with an irregular shape is present as a rare phase and is commonly attached loosely to the grain surfaces. Anhydrous minerals found on Ryugu grains are forsteritic olivine, low-calcium pyroxene and pure spinel with sizes up to a few micrometers. These phases are rare. Most of them have fractured surfaces.

Space weathering features: We found impact craters, melted drops, splashes, melt sheets, glassy spherules on Ryugu grains by SEM observation (Fig. 1). Studies of lunar soils and Itokawa particles have shown that these objects are likely products of micro-impacts on airless bodies [8, 9]; hence, the grain surfaces with the impact products may have been exposed to the space environment. The abundance of the impact products varies from grain to grain. Phyllosilicates on the grain surfaces are altered to have smooth surface textures with tiny voids (Fig. 1 in [7]). TEM analysis shows that the uppermost surface is surrounded by an amorphous rim with a thickness from 50 nm to 2-3 μm. Tiny vesicles and iron compounds appear in the rim. EDX analysis shows a change in chemical composition near the surface. The altered surfaces of pyrrhotite and pentlandite have shallow depressions (200 nm – 300 nm in depth) with rugged textures (Fig. 1). Iron metals protrude from the iron sulfide surfaces, and some are in the form of curved whiskers (Fig. 1). Dark-field TEM imaging suggests disordering of the lattice near the sulfide surface. Carbonates and magnetite have altered surfaces with rough textures. The breunnerite grain we examined by TEM has a distinct rim with disordered lattice and a thickness of approximately 90 nm. Selected area diffraction patterns obtained from the rim imply the appearance of periclase ((Mg,Fe)O) particles in the rim.

Discussion: The dominance of phyllosilicates and the scarcity of anhydrous minerals indicate that Ryugu samples have experienced a high degree of aqueous alteration. The morphologies of the major mineral phases, such as the unique shapes of magnetite, suggest a close similarity between Ryugu samples and CI chondrite [10].

Previous ion irradiation experiments simulating space weathering suggest that the uppermost surface of phyllosilicates can be modified by space weathering [11]. The altered phyllosilicate rim found in our analysis may have been formed by solar wind implantation and impact events [7]. Iron metallic whiskers on iron sulfides have recently been identified as space weathering products in lunar soils and Itokawa particles [12,13]. The iron metals are likely to have formed via selective sulfur loss, accumulation of excess iron atoms, and subsequent growth of iron metals. These alteration processes may be caused by various phenomena including solar wind implantation, thermal effects produced by micrometeoroid bombardments and solar heating [12]. The appearance of iron whiskers on Ryugu samples implies that the space weathering of iron sulfides on Ryugu is similar to that on the Moon and Itokawa. The thickness of the altered rim on breunnerite is roughly consistent with the maximum depth at which extensive atomic displacement is produced by implanted solar wind ions (~ 1 keV/nucleon) [6]. Hence, solar wind implantation may have contributed to the rim formation of the carbonate. Based on our initial analysis, we tentatively conclude that the Ryugu samples record the combined processes of space weathering on the aqueously altered asteroid, implying that remote sensing data should be reassessed considering the space weathering effect.

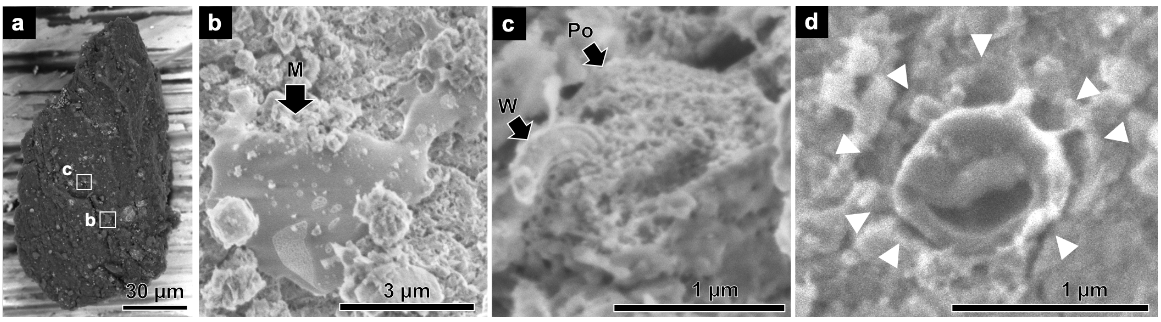

Fig. 1 Space weathered Ryugu grain. (a) Backscattered electron image of a fine Ryugu grain. (b-d) Secondary electron images of a melted drop (b), pyrrhotite with an iron whisker (c), and an impact crater with a residue on phyllosilicates (d). The image (d) was obtained from another fine Ryugu grain. M: melted drop, Po: pyrrhotite, W: iron whisker. Triangles in (d) indicate the crater rim.

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CNHOS contents with their isotopic compositions and preliminary organic profiles from the Hayabusa2 samples

Yoshinori Takano[1], Hiroshi Naraoka[2], Nanako O. Ogawa[1], Yasuhiro Oba[3], Toshiki Koga[1], Toshihiro Yoshimura[1], Saburo Sakai[1], Naohiko Ohkouchi[1], Hisayoshi Yurimoto[3], Tomoki Nakamura[4], Takaaki Noguchi[5], Ryuji Okazaki[2], Hikaru Yabuta[6], Kanako Sakamoto[7], Shogo Tachibana[7,8], Sei-ichiro Watanabe[9], Yuichi Tsuda[7] and the Hayabusa2-initial-analysis SOM team

[1] JAMSTEC, [2] Kyushu Univ., [3] Hokkaido Univ., [4] Tohoku Univ., [5] Kyoto Univ., [6] Hiroshima Univ., [7] JAXA, [8] Univ. Tokyo, [9] Nagoya Univ.

The successful collection and recovery of the Ryugu sample [1,2] are leading us to a valuable opportunity for revealing the properties of the carbonaceous asteroid in the Solar System history; -What is Ryugu? -What are the origins and characteristics of light elements (C, N, H, O, and S)? -What do their isotopic compositions tell us? -How do they record the primordial chemical evolution on the asteroid? -How did the interaction of water, organic matter, and minerals affect the evolution and diversity of indigenous molecules? To answer those important issues by using state-of-the-art small-scale analysis, the SOM (Soluble Organic Matter) team have been firstly focusing on (i) the initial bulk profiles, especially for the elemental abundance of carbon (C), nitrogen (N), hydrogen (H), oxygen (O), sulfur (S) with the isotopic compositions of δ^{13}C, δ^{15}N, δD, δ^{18}O and δ^{34}S, respectively, and (ii) the molecular profiles to understand more deeply for nature of indigenous SOM [3-5]. For instance, if endogenous water-mineral interactions occurred in the asteroid, some aqueous alteration signatures (e.g., process relevant products including carbonates and other precipitates) should have been recorded to the pristine sample in the bulk and molecular levels. Assuming the interactions above mentioned, we can trace the potential *in-situ* temperature of the alteration process by using clumped isotope surveys of minerals [6]. To assess the objectives, we have been conducting rehearsal analyses for analytical optimizations and sequential sample processes [3-5, e.g., Figure 1], with a scope of solid and soluble organic aspects [6-9]. In order to deal with samples of unknown identity, especially for bulk nitrogen scale, we validated the dynamic range of δ^{15}N profiles covered on the basis of pioneering works and compilations for the Inner and Outer Solar System [e.g., 10].

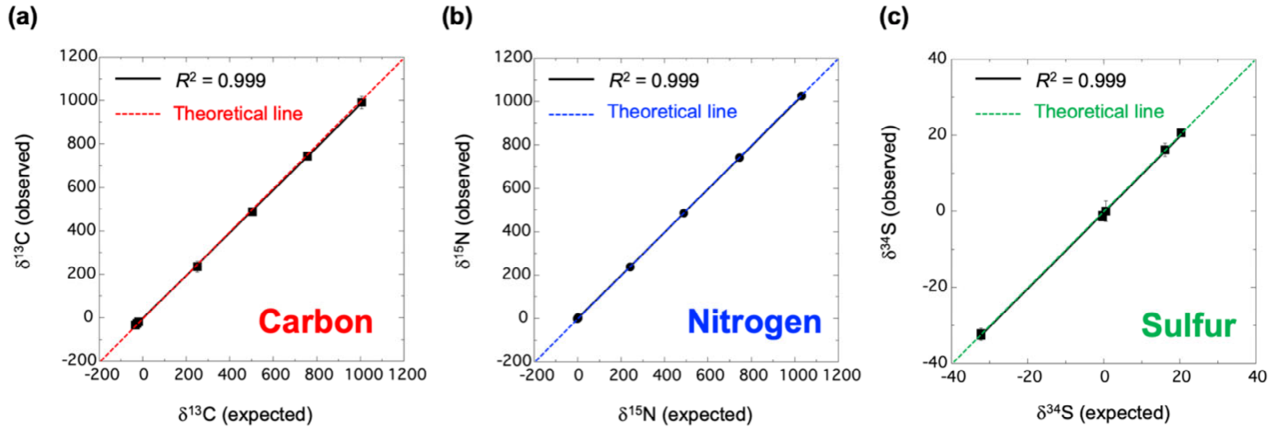

Figure 1 The high precision and high accuracy analytical optimization using reference standards of carbon (C), nitrogen (N), and sulfur (S) for covering wide range isotopic compositions: **(a)** δ^{13}C, ‰ vs. VPDB; within ^{13}C-enriched and ^{13}C-depleted profiles, **(b)** δ^{15}N, ‰ vs. Air; within ^{15}N-enriched and ^{15}N-depleted profiles, **(c)** δ^{34}S, ‰ vs. VCDT; within ^{34}S-enriched and ^{34}S-depleted profiles. The x-axis and y-axis stand for the nominal value (= expected) and the measured value (= observed), respectively. Prior to the Hayabusa2 samples, those analytical validations using the nano-EA/IRMS system [3,4,7] were performed during the rehearsal analyses (e.g., several carbonaceous chondrite of CM2 and C2-ungrouped: unpublished data) at JAMSTEC. We have confirmed that there was no memory effect in the analytical lines due to sequential process. For further of optimization ultra-small-scale sulfur (S) quantification with δ^{34}S validation, please see the latest update [11].

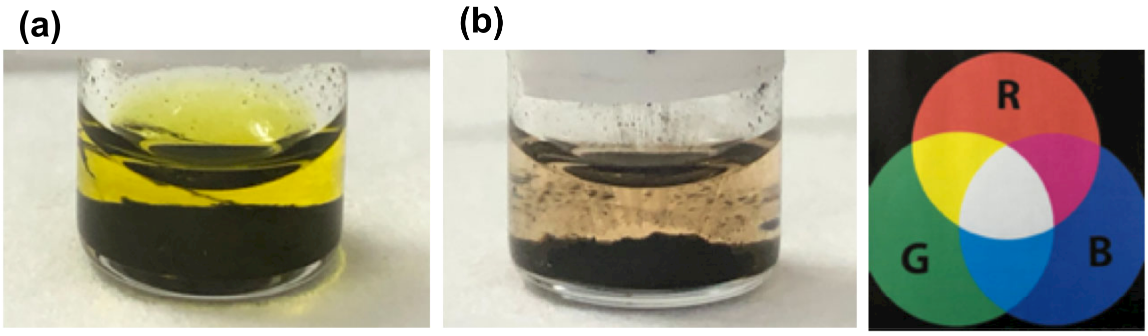

Figure 2 (a, b) Capturing the representative colors during the sequential solvent extraction and the wet chemical treatment for the Hayabusa2 samples (Ryugu, sample ID: A106 & C107). After solid-liquid separation, the colored supernatant with yellowish and pinkish colors were observed in both A106 and C107, the photo taken in the cleanroom at Dept. Earth Planet Sci., Kyushu Univ. Since dissolved inorganic elements and organic-inorganic complex molecules also have some kind of chromaticity depending on the affinity of the solvent, we are in the process of conducting detailed verification. Please see also the residue of insoluble organic matter (IOM, black color) on the bottom of the vial. The onsite RGB color scale is shown.

We observed some of the colored supernatant during the sequential solvent extraction processes of Ryugu sample (Figure 2). These extraction samples have been safely distributed to the SOM team members and are being analyzed in detail at their laboratories [12]. The residue of IOM fraction has been also seamlessly transported to the other initial analysis team for further description [13]. Here, we note that the colors of the extract show the chemical responses of the extractable indigenous organic molecules to the inherent affinity of the solvent from low to high polarity (i.e., dependent on hydrophilicity, hydrophobicity, and amphiphilicity with both properties). Also, the colored supernatant may indicate that there is a certain amount of components with a significant absorption spectrum (e.g., chemically various carbon skeleton with N-, S-, O-hetero structures). Regarding the molecular-level analysis, we are currently in the process of combining the pieces of the raw data profiles [12], and we expect synergistic discussions at this symposium in terms of native organic properties within the history of the Ryugu.

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Compound distribution determined by nanoLC-Orbitrap MS

Francois-Regis Orthous-Daunay[1], Cédric Wolters[1], Véronique Vuitton[1], Roland Thissen[1], Junko Isa[2], Hiroshi Naraoka[3], Hisayoshi Yurimoto[4], Tomoki Nakamura[5], Takaaki Noguchi[6], Ryuji Okazaki[7], Hikaru Yabuta[8], Kanako Sakamoto[9], Shogo Tachibana[9,10], Seiichiro Watanabe[11] and Yuichi Tsuda[9] , and the Hayabusa2-initial-analysis SOM team

[1]Univ. Grenoble Alpes CNRS IPAG, [2]Tokyo Inst. Tech., [3]Kyushu Univ., [4]Hokkaido Univ., [5]Tohoku Univ., [6]Kyoto Univ., [7]NASA Goddard Space Flight Center, [8]Hiroshima Univ., [9]JAXA, [10]Univ. Tokyo, [11]Nagoya Univ

The Hayabusa2 mission is no less than the first opportunity to infirm or confirm theories about the formation of C-type asteroids [1], [2]. The origin and nature of the organic molecules Ryugu bears will tell which part of this chemistry takes place on this type of airless bodies and which part in inherited by accretion. The comparison with carbonaceous chondrite will be the method to evaluate if what has been interpreted from well-studied meteoritical samples is still valid for actual asteroid regolith.
This study focuses on the molecular mixture complexity observed thanks to the combination of two analytical methods: liquid phase chromatography and high-resolution mass spectrometry [3]. Samples from the first (named A106) and second (C107) encounter with Ryugu were washed with different solvents in order to extract the soluble organic compounds in a sequence of increasing polarity in Kyushu University. Each extract was separated on an amide column with limited volume and flow in a so-called nano-liquid-chromatography (nano-LC) protocol. The chemical separation is monitored through time by Orbitrap-mass-spectrometry (Orbitrap-MS).
This provides three observables for each compound present in the Ryugu soil extract: an intensity evaluating its relative abundance, a retention time depending on its structure and a molecular weight equivalent to its atomic composition. With thousands of different compounds, mixtures usually exhibit peculiar patterns in this three-dimensional framework. For instance, the relative abundance of phospholipids in terrestrial living cells varies by orders of magnitude if the carbon atoms number is odd or even, making contamination by fingerprints easy to detect. We used the ATTRIBUTOR routines developed at University of Grenoble Alpes to extract relevant patterns in the Ryugu extracts chromatograms [4].
The most remarkable feature found in both meteorites and Ryugu samples is a ubiquitous polymerization pattern [5]. Almost each measured mass is part of a network linking it to other molecules with one more carbon atom, two more hydrogen atoms or any combination of these. A typical bell-shaped intensity distribution indicates that the whole mixtures are likely to be of one single synthesis origin [6]. Variability of the distribution characteristics goes with a complex origin of subsequent processes. This type of mass and intensity patterns is difficult to find in other terrestrial natural samples.
The less polar molecules found in Murchison have extremely broad distributions, only matched by some of the Ryugu's compounds and other chondrites. For these molecules, the best analogues are solid residues generated out of gas mixtures in plasma chambers [7]. Experimental polymers synthesized in liquid phase or by irradiation of ices have significantly different polymerization patterns [8].
The chemical structure of compounds found in Ryugu slightly differs from the one in the CM2 Murchison chondrite. As of preliminary identification, the less polar compounds are similar between Ryugu and Murchison while the most polar molecules have significantly different retention times. Assuming polar compounds are more likely to be part of a reaction in liquid water, the discrepancy between Murchison and Hayabusa2 samples could be due to different degree of aqueous alteration on their parent bodies.

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Highest molecular diversity and structural complexity revealed with ultrahigh resolution mass spectrometry and nuclear magnetic resonance spectroscopy of Ryugu´s samples

Philippe Schmitt-Kopplin[1, 2], Norbert Hertkorn[2], Marianna Lucio[2], Marco Matzka[2], Mourad Harir[2], Philippe Diederich[2], Hiroshi Naraoka[3], Hisayoshi Yurimoto[4], Tomoki Nakamura[5], Takaaki Noguchi[6], Ryuji Okazaki[3], Hikaru Yabuta[7], Kanako Sakamoto[8], Shogo Tachibana[8,9], Seiichiro Watanabe[10] and Yuichi Tsuda[8] and the Hayabusa2-initial-analysis SOM team

[1] *Technische Universität Muenchen, Germany,* [2] *Helmholtz Zentrum Muenchen, Germany,* [3]*Kyushu Univ., Japan,* [4]*Hokkaido Univ., Japan,* [5]*Tohoku Univ., Japan,* [6]*Kyoto Univ., Japan,* [7]*Hiroshima Univ., Japan,* [8]*JAXA, Japan,* [9]*Univ. Tokyo, Japan,* [10]*Nagoya Univ., Japan.*

The surface and possible sub-surface materials of the asteroid Ryugu were recovered during the two touch-down sampling by the Hayabusa2 spacecraft. Here we present the first results on the solvent soluble organic matter (SOM) using ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectroscopy (FTICR/MS) complemented with high field nuclear magnetic resonance spectroscopy (NMR) [1-3]. The two samples A106 (first touchdown) and C107 (second touchdown) were sequentially extracted in the Hayabusa2-initial-analysis SOM team with various polar and apolar solvent extracts and demonstrate a never seen molecular complexity and diversity.

We confirm herewith the close similarity and the possible comparison of the solvent extracts with meteoritic material to the Hayabusa2 return samples. We analyzed the sequential hexane, dichloromethane (DCM), methanol and water extracts with NMR and with electrospray ionization (ESI) and atmospheric pressure photoionization (APPI) [4] FTICR/MS systematically for both negative and positive ions. The hundred thousands of signals were filtered, converted and assigned into more than 24,000 elementary compositions consisting of carbon (C), hydrogen (H), nitrogen (N), oxygen (O) and/or sulfur (S). Organomagnesium compounds (CHOMg, CHOSMg) were not found and this reflects the low temperature processes on the parent body [5, 6]. As shown for carbonaceous chondrites previously, our results confirm that the extraterrestrial chemical diversity is much higher compared to terrestrial biological and biogeochemical spaces and consists in a regular continuum (i) of small to macromolecules (ii) of carbon oxidation states from apolar (CH, polycyclic aromatic hydrocarbons and branched aliphatics) to polar small molecules (CHO) with increasing functionalized oxygen and heteroatom contents (CHN, CHS, CHNO, CHOS) leading to the observed differential solvent type solubility. We revealed specific known molecular targets (CHN^+, $CHNO^+$) [4] and show evidences of multiple chemosynthesis pathways in describing the carbon oxidation state distribution and heteroatom contributions to the assembly of multiple complex endogen molecules; these also reflect cold hydrothermalism involved on the parent body [5,6]. We also confirm the high importance of chemical processes involving specific nitrogen and sulfur chemistry [7, 8]. The two fractions analyzed show an extreme coverage in structural features in APPI and only slight differences in the apolar solvents in ESI. The A106 sample showed slight differences only with higher mass range and more oxygenated compounds. The C107 sample had increased abundance and uniqueness of more unsaturated carbon and low oxygenated compounds that may have disappeared due to surface processing (some hypothesis could be cosmic irradiation at the surface). These samples presents a unique opportunity of having a direct and low invasive insight into the complex organic diversity present on 162173 Ryugu.

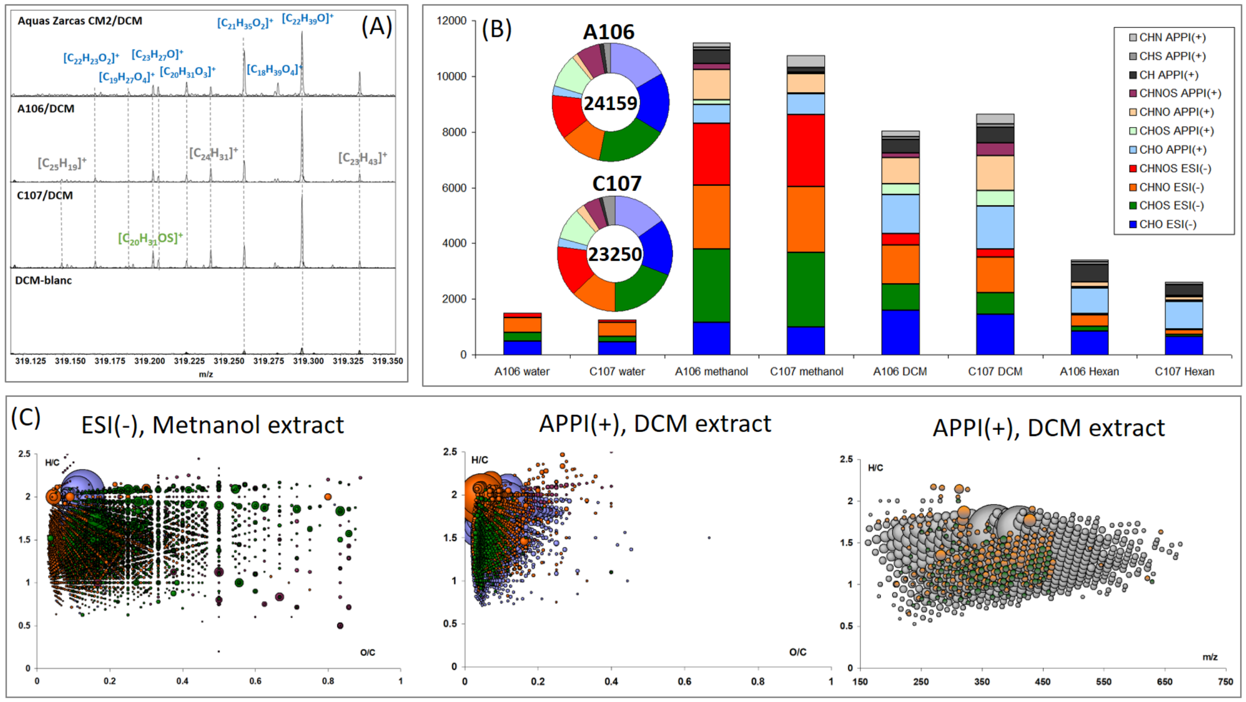

Figure 1. Selected results from the analysis of the solvent extracts of A106 (24159 formula) and C107 (23250 formula) analyzed with Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) in electrospray ionization negative mode (ESI(-)) and atmospheric pressure photoionization (APPI(+)). **(A)** nominal mass 319 details of dichloromethane (DCM) extracts of the CM2 Aguas Zarcas, A106, C107 and the DCM-blank with the annotated elementary compositions as CH, CHO and CHNO from ultrahigh resolution. **(B)** counting of the thousands of elementary compositions in the C, H, O, N, S space as obtained from ESI(-) and APPI(+) and there abundance variations within the different extraction solvents for the A106 and C107 samples. **(C)** visualization of the structural information retrieved from the elementary compositions as van Krevelen diagram plots describing the differences in oxygenations between the two ionization modes ESI(-) and APPI(+) and the profiles of the non-oxygenated CH, CHS and CHN compounds.

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