Update of the initial descriptions and distributions of individual Ryugu samples and preparation for curation of OSIRIS-REx returned samples

Yada T.¹, Abe M.¹, Miyazaki A.¹, Yogata K.¹, Nagashima K.¹, Hatakeda K²., Nakato A.¹, Hitomi Y.², Sugiyama Y.¹, Tahara R.¹, Nakano A.¹, Ojima T¹, Nishimura M.¹, Okada T.¹, Tsuchiyama A.³, Michikami T.⁴, Sakamoto K.¹, Kanemaru R.¹, Kumagai K.², Soejima H.¹, Fukai R.¹, Ishizaki T.¹, Sugahara H.¹, Suzuki S.¹, Sugita S.⁵, Cho Y.⁵, Yumoto K.⁵, Yabe Y.⁵, Mori S.⁵, Aikyo Y.⁵, Furuichi K.⁵, Bibring J.-P.⁶, Pilorget C.⁶, Brunetto R.⁶, Riu L.⁶, Loizeau D.⁶, Lourit L.⁶, Hamm V.⁶, Lequertier G.⁶, Carter J.⁶, Le Pivert- Jolivet T.⁶, Lantz C.⁶, Tachibana S.⁵, Usui T.¹, and Fujimoto M¹
JAXA, 2. Marine Works Japan, 3. Ritsumeikan Univ., 4. Kindai Univ., 5. Univ. Tokyo, 6. Institut d'Astrophysique Spatiale

After the return of Ryugu samples by Hayabusa2 in Dec 2020, they have been described in the Extraterrestrial Sample Curation Center (ESCuC) of JAXA and distributed to the initial analyses and phase-2 curation teams for further detailed analyses. In order to provide fundamental information of the samples to researchers, a series of initial descriptions on bulk and individual Ryugu samples has been conducted non-destructively under purified nitrogen condition such as optical microscopic observations, weight measurements, infrared spectral measurements with an FT-IR, an infrared microscope MicrOmega, and visible spectral measurements using a monochronic microscope with six filters [1, 2]. These initial descriptions data are open to the public at the website of the Ryugu Sample Catalog (https://darts.isas.jaxa.jp/curation/hayabusa2/).

So far, 604 individual Ryugu grains are handpicked and described, which comprise nearly 40wt% of bulk samples recovered from the Chamber A and C. As noted previously [1], Chamber A samples corresponds to those from the first touchdown site and Chamber C corresponds to the second one where is close to the artificial crater produced on the asteroid by the Small Carry-on Impactor of Hayabusa2 [3]. Their mass distributions are shown in Fig. 1. The power index of the cumulative mass distribution of both Chamber A and C is -1.28, which is slightly steeper than the result of catastrophic impact experiments (-0.4 to -1.1) [4]. This indicates fragmentation after the past catastrophic disruption of the Ryugu parent body and re-accretion to the Ryugu body may have occurred on Ryugu's surface. The infrared spectral results with FT-IR (264 grains) and with MicrOmega (174 grains) are under detailed evaluations. So far, 202 grains have been analyzed for their visible spectra with the monochronic microscope with six filters. Their data are detailed in [5].

The first announcement of opportunity (AO) for Ryugu samples was announced from last Dec. In the 1st AO, 57 proposals were submitted and 40 of them were selected for sample distributions. The distributions of Ryugu samples to the selected PIs will be finished soon. The application of proposals for 2nd AO will be closed in the beginning of this Nov. After a series of reviewing and selection processes, the sample distributions to the selected PIs will start in the beginning of next year.

Based on the Memorandum of Understanding (MOU) between JAXA and NASA, JAXA will receive 0.5wt% of returned samples (estimated to be approximately 1.25g [6]) by the OSIRIS-REx. In order to curate the allocated OSIRIS-REx samples, a new clean room has been prepared in the ESCuC, and new clean chambers, which are designed based on the Hayabusa2 clean chambers, will be installed in the next fall. The initial analyses and subsequent distribution of the OSRIS-REx samples are still under discussion, though we aim to primarily focus on comparative studies between Ryugu and Bennu samples.



Fig. 1. A cumulative mass distribution of individual Ryugu grains from Chamber A, C, and A+C. The cumulative mass distribution from Chamber A shows a regular straight distribution whereas that from Chamber C appears irregular in >10mg weight range. This might indicate that the SCI impact by the Hayabusa2 might have disturbed the weight distribution of surface regolith on 2nd touchdown point [3].

References

[1] Yada T. et al. 2022. Nat. Astron. 6, 214. [2] Pilorget C. et al. 2022. Nat. Astron. 6, 221. [3] Arakawa M. et al. 2020. Science 368, 67. [4] Michikami T. et al. 2016. Icarus 264, 316. [5] Yumoto K. et al. 2022. this meeting. [6] Lauretta D. et al. 2022. Science 377, 285.

The Direct Asteroid Redirection Test (DART) – Preliminary Findings

O.S. Barnouin¹ and the DART Investigation and Engineering team.

The Double Asteroid Redirection Test (DART) is the first successful full-scale demonstration of the kinetic impactor technology to deflect an asteroid. While an asteroid impact large enough to cause regional devastation on Earth is unlikely, and no known asteroid poses a threat to Earth, the consequences of such an impact would be severe (e.g., <u>Defending Planet Earth</u>, 2010; <u>National Near-Earth Object Strategy and Action Plan</u>, 2018). Here we provide a quick overview of the objectives of the DART mission, and some preliminary results.

Acknowledgments: This research was supported by the the DART mission, NASA Contract No. NNN06AA01C to JHU/APL and the Italian Space Agency (ASI) within the LICIACube project (ASI-INAF agreement AC n. 2019-31-HH.0).

Radiolytic solar wind water in rims on an Itokawa regolith grain

John P. Bradley¹ and Hope A. Ishii¹

¹Hawaii Institute of Geophysics and Planetology, University of Hawai'i, Honolulu, HI 96922, USA

Introduction: The detection using electron energy-loss spectroscopy (EELS) of OH/H₂O *in-situ* in vesicles within sputtered rims on interplanetary exposed to the solar wind for $\sim 10^4$ - 10^5 years provided the first direct evidence that the interaction of the solar wind with oxygen-rich silicates produces water; additional confirmation was provided by detection of water using EELS in the sputtered rims on silicate mineral standards following proton irradiation at solar wind fluences [1]. The results are consistent with OH/H₂O signatures on the surface of airless bodies observed by remote spectroscopy, e.g. [2]. Regolith from the S-type asteroid Itokawa returned by the Hayabusa mission enables us to further explore the effects of solar wind irradiation on airless bodies. Enrichments in water and hydroxyl in the solar wind-irradiated rim of an Itokawa olivine grain and a lab-irradiated olivine standard have been detected using atom probe tomography [3]. Here we describe detection of OH/H₂O in the surface of another Itokawa olivine grain using electron energy loss spectroscopy (EELS).

Experimental procedure: Hayabusa regolith particle RA-QD02-0332 was carbon-coated for imaging and elementmapping in a focused ion beam-scanning electron microscope (FIB-SEM: FEI Helios 660 with Oxford Instruments EDS), and FIB sections of selected regions were extracted at Univ. Hawai'i using Pt protective straps. These were further analyzed on (scanning) transmission electron microscopes at the Molecular Foundry (S/TEM: FEI Titan ChemiSTEM with EDS, TEAM 1.0 with Gatan Continuum GIF for EELS).

Results: RA-QD02-0332 is a ~48 μ m grain that consists of olivine, pyroxene, plagioclase and, likely, K-feldspar. In SEM imaging, glassy melt splashes with degassing vesicles are visible in multiple locations on the surface. Fractures are observed as well as significant fine-grained adhering material, including angular fragments and spheroidal particles with melt droplet appearance. Two FIB sections crossing fine-grained material contain small mineral crystals of albitic plagioclase and fayalitic olivine with lesser amounts of high-Ca pyroxene and iron-sulfide. Fine grain sizes range from ~100 nm to several microns across, and grain shapes range from angular to euhedral to rounded, consistent with some brecciation on the parent body. Another FIB section contains a ~4 μ m plagioclase grain with fracture and defects in the interior consistent with shock, an amorphized rim on one face that has lost most of its Na and some Ca relative to the underlying crystal, and surficial lacy Ferich material that is likely remnants of the impactor.

A FIB section through an olivine crystal shows melt splash glass and a \sim 40 nm in thick vesiculated amorphous rim on the surface (Figure 1a). Energy dispersive spectral mapping shows that the amorphous rim has a composition similar to the underlying olivine but with minor additional Al and Ca present. An EELS spectrum from one of the vesicles shows features at \sim 8 and \sim 13.5 eV features. These features correspond to the energy gap and H-K core scattering edge from hydroxyl and/or molecular water, like those we previously observed in rims on IDPs, water in a liquid cell, proton irradiated silicate standards and electron beam-damaged talc and brucite [1,4]. Weaker features are observed in the amorphous rim off the vesicle.



Figure 1: (a) Darkfield image and highermagnification inset show vesicles in amorphous rim on Itokawa olivine, (b) EELS low-loss spectrum shows ~8 eV and ~13 eV features from one of the vesicles superimposed on the amorphous rim volume plasmon.

Discussion: The vesiculated amorphous rim on the olivine crystal in Itokawa grain RA-QD02-0332 establishes that it was exposed to the solar wind on the surface Itokawa. Detection of water by EELS confirms the prior atom probe tomography detection of water in another solar wind-irradiated rim on an Itokawa

olivine [3]. The relatively low intensity of the features observed here from the vesicle in the amorphous rim on Itokawa olivine compared to those observed in some vesicles in IDPs (Fig 1c), may be a consequence of a shorter (solar wind) exposure ages of Itokawa regolith grains relative to IDP orbital exposure ages.

References: [1] Bradley J.P. et al. (2014) *Proceedings of the National Academy of Sciences* 111:1732. [2] Li S. and Milliken R.E. (2017) *Science Advances* 3:e1701471. [3] Daly L. et al. (2021) *Nature Astronomy* 5:1275. [4] Zhu C. et al. (2019) *Proceedings of the National Academy of Sciences* 116:11165-11170.

Importance of Material Properties on the Thermal Evolution Models of Parent Bodies

Jonas Hallstrom¹ and Maitrayee Bose²

¹Department Of Physics, Arizona State University, Tempe, Arizona 85287, USA, jlhallst@asu.edu ²School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287, USA

Introduction: A majority of the chondritic materials in our solar system originated and were partially processed in the first ~10 million years after time 0, defined as the time when calcium-aluminum inclusions (CAIs) condensed [e.g., 1]. The primary heating mechanism for the parent body asteroids was radiogenic heating due to the decay of 26 Al [1]. Thermal evolution models alongside experimentally determined physical properties, such as the specific heat capacity, have been used to place constraints on the sizes and times of formation of various chondritic asteroid parent bodies [2–4]. These models allow an understanding of the processes in small bodies that formed early in the solar system history, and are a link to the shapes and geology of the asteroids observed during flyby or sample return missions.

While there are several sources of error in thermal evolution models that vary in their significance, we investigated the effect of uncertainty in some of the material properties, namely aluminum abundance, specific heat capacity, and thermal diffusivity. We adopted the thermal evolution model for the parent body of asteroid Itokawa described by [5], determined uncertainty ranges for the aforementioned material properties, and placed new constraints on the radius and formation time of Itokawa's parent body.

Methods: Our thermal evolution model follows the common approach of approximately solving the radial heat conduction equation using finite difference methods. This calculation also incorporates assumptions about the material properties and the initial and boundary conditions for the system, for which we followed the recipe from [5]. Temperature data from the thermal evolutions calculated by this model were interpolated over the whole range of realistic formation time and radius values, and then compared with known thermal constraints on the parent body of Itokawa [5]. Subsequently, we determined uncertainty ranges for the material properties from the literature: -10% to +10% for specific heat capacity [2, 6], -10% to +200% for thermal diffusivity [6, 7], and -14% to +16% for aluminum abundance [2, 8], and repeated the calculations to ascertain the effects of these uncertainties.

Results: Without accounting for any uncertainties, our model predicts a radius greater than 20.5 km and a formation time range between 1.87 and 2.24 Ma after the formation of CAIs for the parent body of Itokawa. This is in agreement with previous results [5; >20 km, 1.9-2.2 Ma]. Accounting for the uncertainty in all three parameters results in a minimum radius of 18.5 km and a formation time range between 1.6 and 2.5 Ma after CAIs.

Discussion: Although the minimum size for Itokawa's parent body reduced only by about 10%, the formation time range is significantly expanded, after taking the uncertainties into account. We observed that 10% uncertainties in both specific heat capacity and aluminum abundance contributed approximately an additional ± 0.1 Ma onto the computed range of valid formation times of the body. Though the exact effects of uncertainty in material parameters on the accuracy of thermal evolution models is likely highly dependent on the specific form of the model, and the values and conditions used therein, aluminum abundance and specific heat capacity are fundamentally important to all thermal evolution models. The efficacy of such models is therefore significantly dependent on the existence of precise measurements of these material properties.

References

[1] Desch S.J. et al. 2018. The Astrophysical Journal Supplement Series 238(1):11. [2] Henke S. et al. 2012. A&A 537:A45.
 [3] Sugiura N. and Fujiya W. 2014. Meteoritics & Planetary Science 49(5):772–787. [4] Blackburn T. et al. 2017. Geochimica et Cosmochimica Acta 200:201–217. [5] Wakita S. et al. 2014. Meteoritics & Planetary Science 49(2):228–236. [6] Yomogida K. and Matsui T. 1984. Earth and Planetary Science Letters 68(1):34–4. [7] Henke S. et al. 2016. A&A 589:A41.
 [8] Jarosewich E. 1990. Meteoritics 25(4):323–337.

Molecular descriptors for dictating the aqueous-alteration-induced organic decomposition in carbonaceous chondrites and return sample from Ryugu asteroid

Yamei Li¹, Hiroyuki Kurokawa¹, Yasuhito Sekine^{1,2}, Junko Isa³, Norio Kitadai^{1,4}, Yoko Kebukawa⁵, Kosuke Fujishima¹, and

Yuko Nakano¹

¹ Earth-Life Science Institute, Tokyo Institute of Technology

² Institute of Nature and Environmental Technology, Kanazawa University

³ Planetary Exploration Research Center, Chiba Institute of Technology

⁴ Super-cutting-edge Grand and Advanced Research (SUGAR) Program, Institute for Extra-cutting-edge Science and

Technology Avant-garde Research (X-star), Japan Agency for Marine-Earth Science and Technology (JAMSTEC)

⁵ Faculty of Engineering, Yokohama National University

Background. Carbonaceous chondrites (CCs) are among the most primitive material in our Solar System. Organics such as amino acids are ubiquitously found in CCs and have been invoked to serve as life's building blocks to promote the origin of life on Earth and possibly elsewhere. Meanwhile, the chemical diversity of amino acids records the chemical evolution events prior to and after the accretion of their parent bodies. In the past decade, the advancement of analytical instrumentations, an increasing supply of samples from various CC subgroups, and the development of a more accurate petrographic classification system of CCs have facilitated the study on how parent body processes have shaped the organic distributions. However, there is a large discrepancy between experimental results and meteoritic records. Previous studies show that amino acids can be synthesized in aqueous solution containing primordial molecules, suggesting that amino acids would have accumulated upon extended aqueous activity. Nevertheless, amino acids are found to be depleted in more aqueously altered CCs, pointing to a potential "Water Paradox".

In our previous study [1], we discovered a new low-temperature geo-electrochemical process which provides a possible solution to the "Water Paradox" and proposed a new molecular descriptor of aqueous alteration degree. The geo-

electrochemistry model was proposed based on the redox gradient that could be generated via water/rock interaction (Fig. 1). H_2 gas, generated through water/rock interaction, serves as the electron donor to drive the geo-electrochemical alteration of amino acids at the interface of mantle fluid and minerals. We found that three model amino acids (glycine, alanine, and valine) were decomposed to their amine and hydroxy acid analogs, and both of these two compound classes were found to coexist with amino acids and enriched in heavily aqueously altered CR chondrites. These results suggest that decomposition of amino acid dominates the chemical evolution of the parent body of CR chondrites. However, the discussion was only limited to CR chondrites due to insufficient data of amine and hydroxy acid abundances in other CC subgroups.



Figure 1. Model of geo-electrochemical alteration of amino acids induced by water-rock interaction in icy planetesimals (a parent body of CCs). A difference in the water/rock mass ratio (W/R) between the core (grey) and mantle (blue) leads to gradients in pH and redox.

Recently, we extended this model to other types of amino acids and found that the electrolysis of glutamate (Glu) and asparate (Asp) generates γ -aminobutyrate (γ -ABA) and β -alanine (β -Ala), respectively, via reductive decarboxylation. The enrichment of these products with respect to their amino acid precursors is found in heavily aqueously altered CR 2.0–2.4, CI as well as a return sample from asteroid Ryugu. These data suggest that the relative enrichment of derivative products can serve as a general descriptor of aqueous-alteration-induced organic decomposition. A geochemical model based on the waterrock differentiation in the parent icy plantesimals [2] was proposed to account for the observation.

Experiments and results. Electrolysis of amino acids was conducted at ambient temperature (25 °C) in an electrochemical cell made of two compartments separated by a proton-exchange membrane. In the cathodic chamber, iron or nickel sulfide catalysts were placed on a carbon paper electrode in a pH-7 phosphate buffer containing 20 mM of Glu or Asp. An anoxic condition was maintained by continuous argon gas flow during electrolysis. Using these two sulfides as catalysts, the conversion of Glu and Asp to various products, including decarboxylated products (γ -ABA and β -Ala, respectively), α -hydroxy acids (2-hydroxyglutarate and malate, respectively) was observed after 14-day electrolysis of amino acids at -0.5~-1.0 V versus standard hydrogen electrode (vs. SHE). The electrode potential represented the magnitude of the redox gradient (H₂ enriched core versus bicarbonate-buffered mantle) and is equivalent to the reduction potential of H₂/H⁺ redox

couple under specific pH and temperature conditions. A more negative electrode potential corresponds to a condition with more alkaline pH or higher temperature.

Discussion. The well-documented abundances of these four chemically related amino acids (namely, Glu, Asp, γ -ABA, and β -Ala) among different CC subgroups allow a general comparison of amino acid distribution and discussion on the impact of aqueous-alteration-induced decomposition processes (Fig. 2). Although no clear tendency can be deduced from the absolute abundances of these amino acids (Fig. 2a-2d) among different CCs, obvious enrichments of γ -ABA over Glu (Fig. 2f) and β -Ala over Asp (Fig. 2e) were discovered among heavily aqueously altered CR2.0-2.4, CI chondrites; contrastively, such enrichments are not observed in CM1-2.9 and primitive CR2.7-2.8 chondrites. Such difference implys that the impact of geoelectrochemical decomposition of amino acid highly depends on the chemical composition, degree of water-rock differentiation and the location of parent bodies in the early Solar System (Fig. 2i-2j). While we do not rule out parent body formation at various locations to account for different degree of aqueous-alteration-induced organic decomposition, here we propose another senario where CI, CM and CR sample different regions of water-rock-differentiated parent icy planetesimals formed beyond the CO_2 snow line. The accreted CO_2 ice and H_2O ice were melted by the heat generated via the decay of shortlived radionuclides. The icy planeteismal experienced water-rock differentiation and features a rock-rich core and water-rich mantle as discussed by Kurokawa et al. [2]. The low water/rock mass ratio (W/R) in the core generated alkaline, H₂-rich fluid upon water/rock interaction. In contrast, the high W/R ratio in the mantle generated neutral to weakly alkaline, CO₂-rich fluid where geo-electrochemistry proceeded and decomposed Glu and Asp to γ -ABA and β -Ala, respectively. Therefore, in light of the high abundance ratio of γ -ABA/Glu and β -Ala/Asp in CI and CR 2.0–2.4 chondrites, it is possible that these chondrites originally sourced from the mantle (Fig. 2i-2j). This is consistent with the observation of similarly high enrichment in the samples obtained from the surface of Ryugu asteroid (Fig. 2e~2h), which was suggested to be CI-like body with an outer Solar System origin [5, 6] and processed by low temperature aqueous alteration (30 °C) [6]. In contrast, the very low abundance ratios revealed in CM1-2 and CR2.7-2.8 chondrites indicate that they were sourced from the rock-rich core, as no geoelectrochemical alteration of amino acid could proceed there. CR chould span a wide range of rock/mantle transition region, thus show a wide range of decomposition degree. Based on these results and discussions, we propose that the relative abundance ratios of derivative products/organic precursors can serve as a general molecular descriptor for dictating the aqueous-alteration-induced organic decomposition as well as sheding insight into the water/rock differention status of icy planeteismals at their early evolution period [2]. This can shed implications on the chemical evolution and cycling within the parent bodies, as well as provide chemical models for guiding the future space missions to asteroids and return sample analyses.



Figure 2. The molar abundances of aspartate (a), glutamate (b), and the decarboxylated products β -Ala (c), and γ -ABA (d) in different carbonaceous chondrites and Ryugu sample reported recently [3]. FS_1-3 indicates the Formose-type synthesis results at 90–150 °C reported by Kebukawa et al. [4]. e, f, g, and h plotted the molar ratios of β -Ala/aspartate, γ -ABA/glutamate, aspartate/glutamate, and β -Ala/glutamate, respectively, in these samples. i and j depicted the model that can explain the different decomposition degree in e–h among different carbonaceous chondrite subgroups resulted from geo-electrochemistry in a water-rock differentiated parent body.

References

[1] Y. Li et al. *Nat. Commun.* **2022**, 13:4893. [2] H. Kurokawa et al., *AGU Adv.* **2022**, 3(1). [3] E. T. Parker et al., 53rd Lunar and Planetary Science Conference, **2022**, 2651. [4] Y. Kebukawa et al., *Sci. Adv.* **2017**, 3 : e1602093. [5] T. Yada et al., *Nat. Astron.* **2022**, 6(2). [6] M. Ito et al., *Nat. Astron.* **2022**.

The reproduction experiment of radial pyroxene chondrules using aerodynamic levitator furnace in a reduced condition

Tomoyo Morita¹, Tomoki Nakamura¹ and Kana Watanabe¹ ¹Tohoku University, Japan

We performed reproduction experiments of radial pyroxene chondrules (RP chondrules) using the aerodynamic levitator furnace in a reduced condition that simulates the environment in the protoplanetary disk [1]. Chondrules were formed by flash heating of solid precursors and crystallization during subsequent cooling. They show characteristic texture that refracts thermal histories and the local environment of the protoplanetary disk [2]. In this study, we attempt to constrain the thermal history of the RP chondrules, which formed at high temperature by total melting of the precursor material.

The experiments were performed using the aerodynamic levitator furnace at Tohoku University [3]. The sample spheres were levitated by Ar-H₂ gas (Ar = 97 %, H₂ = 3 %), heated to melt by a CO₂ laser (LC-100NV from DEOS), and cooled to crystallize in a non-contact state. The cooling rates were from 1 to ~1000 °C/s in the temperature range from 1600 °C to 500 °C. During cooling small glass particles called "seed" impacted the molten sample to crystallize pyroxene. The furnace was enclosed in an acrylic container and the inside of the container was replaced with Ar-H₂ gas to achieve a reducing atmosphere of Δ IW from -1.5 to -0.5. The starting material was a mixture of oxide powders (SiO₂, MgO, FeO, CaO, Al₂O₃, and Na₂O) with three different compositions similar to natural RP chondrules [4-6]. No metallic Fe was used. During the experiment, images of the samples were taken with a CCD camera (ELMO) and a high-speed monochrome camera (Photron FASTCAM-Net Max). The temperature of the samples was measured with a radiation thermometer (LumaSense Technologies ImpacIN140/5-H). After the heating experiments, the samples were then buried in an epoxy resin and polished. The microstructure was observed and chemical composition was determined using SEM/EDS (Hitachi S-3400N) and FE-SEM/EDS (JOEL JSM-7001F).

The experiment reproduced RP chondrules: radial pyroxene crystals growing from one or more points, mesostasis glass filling in between the pyroxene crystals, and two types of metallic iron with different morphological characteristics. Pyroxene crystals have dendritic shapes with linear surface contours, or are an aggregate of fine crystals similar to that in cryptocrystalline chondrules, indicating rapid crystallization from a supercooled melt. The Mg# of the pyroxene crystals reflect

Mg/(Mg+Fe) ratios of the starting materials. Some samples have Fe-rich overgrowth on large (> 1 μ m) Mg-rich pyroxene crystals, suggesting that the rapid crystal growth was followed by continued slow crystal growth due to slow cooling (1-10 °C/s).

The metallic iron in the samples was classified into two types based on the texture: one was primary metal which is variable in size from μ m to mm, crossing the radial pyroxene crystals. SEM observations showed that relatively small (< 10 µm) primary metals are incorporated into the pyroxene crystals and that radial crystals of pyroxene were aligned along the surface of the larger primary metals. The other was submicron-size metallic inclusions (hereafter secondary metal) that occurred only in mesostasis glass (Fig.1). The secondary metal is spherical or dendritic in shape, sometimes clinging to the surface of pyroxene crystals. In addition, they were found in a portion of the sample, not in the entire sample. Both primary and secondary metals were produced by reduction of Fe oxides due to low oxygen fugacity around the molten samples (Ar-H₂ ambient gas), because no metallic iron was added to the starting material. However, the timing of formation was different between the two inferred from their texture and observation.

The primary metal was formed during total melting of the starting material. We succeeded *in-situ* imaging of the formation of the primary metal using high-speed camera: the metal sphere forms in the melt when the sample was heated for about 10 or more seconds. In addition, the textural observation indicates that the metal solidified in a silicate melt during cooling, prior to the pyroxene crystallization. On the other hand, the



image of a RP chondrule produced by the experiment. Dendritic radial pyroxene crystals spread over the sample. (b) Enlargement view of the white box in (a). The spherical secondary metals are abundant in mesostasis glasses. Px; pyroxene and gl; glasses.

secondary metal is considered to have formed at temperature between the pyroxene crystallization and the glass transition (mesostasis glass formation). Secondary metal was observed in some samples cooled slowly (cooling rate is 1-10 °C/s) from the crystallization temperature to 500°C, while it was not observed in the glass of samples cooled rapidly after crystallization of pyroxene. The secondary metal formation only by slow cooling is interpreted as the time required for the reduction reaction and for the diffusion of Fe in the glass.

Similar primary type-metal inclusions are found in the natural RP chondrules, suggesting that the large metallic spheres were formed immediately after total melting by the reduction of iron oxide during chondrule formation, or they were present in the precursors. On the other hand, the metallic spheres of submicron size are universally found in natural RP chondrules, and their microstructure is similar to that of secondary metal produced in this experiment. This indicates that RP chondrules cooled at < 10 °C/s after crystallization of pyroxene and before glass solidification in a reduced condition to make secondary metallic inclusions.

References

[1] Villeneuve, J. et al. 2015. Geochim. Cosmochim. Acta 160:277. [2] Nagahara. H. 1981. Nature 292:135. [3] Nagashima. K et al. 2006. Journal of Crystal Growth 293:193. [4] Dodd. R.T. 1973. Earth and Planetary Science Letters 40:71. [5] Nagahara. H. 1981. Memoirs of National Institute of Polar Research 20:145. [6] Kita. N.T. et al. 2010. Geochim. Cosmochim. Acta 74:6610.

Curation Challenges Associated with the Apollo Next Generation Sample Analysis Program

Ryan A. Zeigler¹, Juliane Gross^{1,2}, Scott Eckley^{3,4}, Andrea Mosie³, Charis Krysher³, Jeremy Kent³, Cecilia L. Amick³, Ernest

K. Lewis³, and Francis M. McCubbin¹ and The ANGSA Science Team.

¹NASA Johnson Space Center, Houston, TX 77058, USA.

²Rutgers State University of New Jersey, Department of Earth & Planetary Sciences, Piscataway, NJ 08854, USA,

³ Jacobs Technology, Johnson Space Center, Houston, TX

⁴Jackson School of Geosciences, University of Texas at Austin, Austin TX,

⁵The ANGSA Science Team: <u>https://www.lpi.usra.edu/%20ANGSA%20/teams/</u>

Introduction and Overview

From 1969 to 1972, the Apollo missions collected 2196 individual samples of rock and regolith from the Moon (382 kg total mass). Over the past 50 years, there have been over 3300 Apollo sample requests, utilizing >10,000 subsamples from 2190 of the original 2196 samples. These myriad studies have shaped our understanding not only of the Earth-Moon system, but also of the terrestrial planets, airless bodies like asteroids, the formation locations of the gas giants, and have even acted as a record of the radiation history of our solar system as it has revolved around the galaxy for the past 4.6 Ga. Despite all of these studies and all of this knowledge gained, there is still more to be learned from the Apollo samples. To this end, NASA solicited proposals to study unopened or specially curated Apollo samples as part of the Apollo Next Generation Sample Analysis (ANGSA) Program. Prior to the ANGSA program being initiated there were six Apollo samples that had never been opened: (1) unsealed regolith drive tubes 73002 and 70012 (drive tubes are 35 cm long and 4 cm in diameter); (2) vacuum sealed regolith drive tubes 69001 and 73001; (3) vacuum sealed bulk soil sample 15014; and (4) frozen basalt sample 71036. Additionally, there were portions of other Apollo 17 regolith samples (15012/15013) that were opened, processed, and continuously stored since then in a He-purged environment (all other pristine Apollo samples are stored in N₂-purged environments). These samples were purposefully saved to be opened or studied at a future date where instrumentation had improved enough to give scientists the chance to maximize the scientific return on the samples.

NASA selected nine consortia of scientists to study a subset of the previously unexamined samples. The samples selected were: unsealed drive tube 73002, sealed drive tube 73001 (part of a double drive tube pair with 73002), and a suite of frozen samples including unexamined basalt sample 71036. These samples were selected for a variety of reasons, including: (1) The 73001/2 drive tubes were collected near Lara Crater at Station 3 in the Taurus Littrow Valley, and are spatially associated with both landslides and a fault; (2) the sealed and cold samples have obvious ties to the upcoming Artemis missions; and (3) from a practicality standpoint, having an unsealed core that could be studied immediately (without having to extract the gas) would allow for the program to start more quickly.

Curation Methodology

Each of the samples included in the ANGSA program had their own unique challenges during the curation process. Sample 73002 was the first drive tube sample to be opened in over 25 years. This meant that all of the equipment that was needed for the extrusion and dissection process had to located, cleaned, assembled, and tested (including procurement of replacement parts where needed). Similarly, the procedures for sample dissection had to be reviewed and modernized, which included building a full-sized cabinet mock-up and extensive testing with analog samples. During the actual dissection process, several non-standard dissection procedures were implemented such as time-sensitive sampling and mm-scale subsampling in the top two intervals (top 1 cm). Multi spectral imaging was performed on the 73002 core [1] during processing, as well as on the 73001 core from outside the cabinet [2], as well as inside the cabinet (after dissection was complete [3]).

After dissection was complete, making continuous core thin sections required that the entire core vacuum impregnation and curing devices had to be rebuilt. Additionally, a Keyance automated petrographic microscope was used to map all eight of the 73002 continuous core thin sections at a resolution of a few microns per pixel (and will similarly be used when the 16 of the 73001 sections are complete). These maps were provided to the ANGSA science teams to serve as base maps for the electron-and ion-beam work that would come later.

With sample 73001, the most obvious hurdles were related to how to get the gas out of the outer vacuum container (OVC) and Core Sample Vacuum Container (CSVC) prior to opening the samples. This involved building two bespoke pieces of hard-ware, a gas-extraction manifold built at Washington University in St. Louis [4] and a piercing tool built at ESA [5], as well as the actual assembly, integration, and operation of this equipment within the materials constrained environment of the JSC clean rooms.

The ability to process frozen samples at -20°C was not a capability that existed at JSC prior to ANGSA, and an existing Apollo glovebox had to be retrofit to work at those temperatures. Significant facility modifications to the walk-in freezer in the JSC Experimental Impact Lab to make it material and environmentally compliant with processing of Apollo samples was also required [6]. Similarly, the procedures for how to process the samples under these extreme conditions had to be developed and implemented [7].

This was the first time that X-ray Computed Tomography (XCT) was used as part of the curation process for drive tube dissection. Whole-core scans were made of both 73002 and 73001 prior to extrusion and dissection at the University of Texas High-Resolution X-ray Computed Tomography (UTCT) Facility for high-resolution scanning (Figure 1). Both of these scans had unique challenges that were overcome to give excellent data sets that proved invaluable to both the curation and mission science teams [8]. Over 350 particles in the 4-10 mm and >10 mm size particle size fractions were separated during dissection, individually bagged in Teflon (3 bags), and scanned by XCT at NASA JSC [9]. These scans allowed for the identification of different lithologies within the particles (Figure 1), which greatly helped with the request and allocation process [10].

Summary Summary

The ANGSA program was designed to help us prepare for the upcoming Artemis missions, while at the same time getting important new scientific results from the Apollo samples. Each of the samples included in the ANGSA program had their own unique challenges related to the curation process, and the work on this program has greatly enhanced our readiness for the next batch(es) of lunar samples to come back.

References

[1] Sun et al. (2021) MAPS, <u>https://doi.org/10.1111/maps.13715</u>.
[2] Sun et al. (2022) A17-ANGSA Workshop, #2017.
[4] Parai R. et al. (2021) LPSC 52, #2665.
[5] McDonald F. et al. (2022) EPSC2022, #1117.
[6] Amick C. et al. (2020) LPSC 51, #1632.
[7] Kent J. J. et al. (2022) Metsoc 85, #6497.
[8] Ketcham R. A. et al. (2022), A17-ANGSA Workshop, #2044.
[9] Zeigler R. A. et al. (2021) LPSC 52, #2632.
[10] Shearer C. K. et al. (2022), A17-ANGSA Workshop, #2003.



Figure 1. X-ray Computed tomography images of the entire 35 cm long 73001 core (top image), as well as individual soil particles sieved from the 73001 and 73002 cores representing a variety of lithologies observed.

Sample Return and Preliminary Examination Processes for the OSIRIS-REx Mission

Anjani T. Polit¹, Harold C. Connolly Jr^{1,2}, Dante S. Lauretta¹, and the OSIRIS-REx Sample Analysis Team

¹Lunar and Planetary Laboratory, University of Arizona, Tucson, Arizona, USA

²Rowan University, Glassboro, NJ, USA

The OSIRIS-REx spacecraft collected a sample of asteroid (101955) Bennu on October 20, 2020 [1, 2] and departed the asteroid in May 2021. On September 24, 2023, the spacecraft will fly by Earth and release the Sample Return Capsule (SRC), which will land four hours later in the desert of the U.S. state of Utah. Once the SRC is located within the landing ellipse, the OSIRIS-REx recovery team will be flown via helicopter to retrieve the SRC and take it to a temporary cleanroom for initial processing. In the cleanroom, the SRC will be opened, a high-purity nitrogen purge will be established, and the sample canister assembly will be packed for transport to the OSIRIS-REx curation facility at NASA's Johnson Space Center (JSC).

The Preliminary Examination (PE) period for sample analysis begins once the sample canister is opened at JSC. The focus during this time will be on disassembly of the sample canister, initial documentation of the sample, production of a sample catalog (to be completed within six months of Earth return), splits of sample for international partners, and the initial allocation of sample to the Sample Analysis Team (SAT). Within approximately one week after sample return, a Quick Look Tiger Team of the SAT will conduct a very preliminary characterization using a small amount of sample collected from the outside of the sample acquisition mechanism. Armed with information from the Quick Look sample analysis, the SAT will then focus on identification of distinct lithologies within the bulk sample using the mission imaging system known as QRIS (Quantitative Reflectance Imaging System), visual inspection, density calculations, and initial analysis on bulk oxygen isotope abundances as well as H, N, and C to enable decisions on which particles will be allocated to each planned science investigation. While the bulk sample is being processed for analysis, contact pads from the sample acquisition mechanism will also be processed.

The OSIRIS-REx team is preparing for sample return, recovery, and analysis with a series of reviews, team training activities, and readiness tests scheduled over the next year. The SAT is currently conducting a Sample Analysis Readiness Test (SART) which will conclude by June 2023, during which the SAT is demonstrating certification in key areas necessary for sample analysis. The SART is providing valuable lessons for revision of the mission Sample Analysis Plan (SAP) and is helping the team prepare for our July 2023 sample analysis readiness review. The SAT also completed two Sample Analysis Science Operational Proficiency Integrated Exercises (SA-SOPIEs), with a third scheduled in early 2023. These exercises use analog sample material to test instrumentation, initial sample characterization, and the selection of particles the SAT will use to address early mission science and the hypotheses outlined in the SAP.

References

[1] Lauretta, D.S. et al. 2021. In Sample Return Missions, Longobardo, A., ed. (Elsevier), pp. 163–194. [2] Lauretta, D.S. et al. 2022. Science Vol 377 pp. 285-291.

Coordinated Thermal and Physical Analysis of OSIRIS-REx Samples of Asteroid Bennu

Andrew Ryan¹ and the OSIRIS-REx Sample Analysis Team ¹University of Arizona, Tucson, Arizona, USA

Remote sensing and sample analysis both provide insight into the thermal and physical properties — and thereby the origin and evolution — of asteroidal material. Remote determination of thermal properties can be used to infer the physical characteristics of boulders and regolith on asteroid surfaces and to predict the evolution of an asteroid's orbit due to the Yarkovsky effect. Analysis of returned particles and particle assemblages informs the interpretation of remote sensing data and can powerfully constrain models of dynamic events such as robotic sampling and impacts at different scales.

It is well-known that the strength of stony material obeys scaling laws, such that larger boulders (or bodies) are weaker than smaller ones and thus are more susceptible to collisional damage. It is also likely (but not yet as widely recognized) that thermal properties of boulder materials may depend on the size of the sample and/or the length scale of the remote sensing observations. Therefore, to link the properties of returned samples and relevant meteorite analogs to remote sensing data of asteroid surfaces, a coordinated physical and thermal sample analysis campaign with measurements across multiple length scales is necessary.

Below (Figure 1) is a summary of the physical and thermal measurements that are planned for the returned samples from Bennu. In addition to addressing specific hypotheses related to the formation and evolution of Bennu's boulders and fine regolith, we seek to collect coordinated sample data that can contribute to the development of a broadly applicable multi-scale thermal and mechanical model for primitive rubble-pile asteroids.



Figure 1. Planned OSIRIS-REx sample measurements (green) feeding into a multi-scale model for regolith, boulder, and asteroid thermophysical properties (blue).

Contamination monitoring of the OSIRIS-REx ISO5 asteroid sample cleanroom

K. Righter¹, N.G. Lunning¹, K. Allums², M. Calaway², M. Rodriguez², R. Funk², L. Yan², T. Cala², J. McQuillan², A. Regberg¹, R. Davis², E.L. Berger^{1,2}, A. Burton¹, A. DeCuba², J. Ponce²

¹Astromaterials Curation, NASA Johnson Space Center, 2101 NASA Pkwy, Houston, TX 77058 USA ²Jacobs/JETS, Astromaterials Curation, NASA Johnson Space Center, 2101 NASA Pkwy, Houston, TX 77058 USA

The OSIRIS-REx mission to asteroid Bennu successfully collected hundreds of grams of asteroid regolith in October 2020 [1]. The spacecraft departed Bennu in May 2021 for Earth return and will release the sample canister to be recovered in Utah in September 2023 [2]. Samples will be transported to the curation facility at NASA Johnson Space Center, where an ISO5 equivalent cleanroom has been designed in 2017 and completed in 2021. Aspects of the design and material selection for the cleanroom and its supporting facilities (air handling system, cleanroom floors and walls, filters, paints, etc.) were optimized to minimize effects of organic and inorganic contaminants and offgassing [3]. Since its completion, the lab has been carefully monitored to understand and establish a baseline with respect to multiple environmental aspects – measurement of particle counts, deploying Si wafer witness plates for organic and inorganic contaminants, deploying aluminum foils for a focus on organics with JSC in-house expertise, gas samples, and regular microbial and fungal measurements on selected surfaces and air samples in the cleanroom. This contribution will report on nearly one year of monitoring and highlight several specific aspects that have led to a better understanding of the new cleanroom environment.

Particle counts: particle counts are taken weekly in 6 different locations in the cleanroom, in high traffic and low traffic areas and distributed representatively throughout the lab. The particle counts have remained well within the ISO5 rating of the cleanroom and have only exhibited higher counts (but still well within the ISO5 limits) in cases where there has been unusual activity. One such example is the repair of fan filter units (FFUs) in September 2022. Careful coordination of particle count measurements during servicing of the FFUs led to a better understanding of how the counts are affected when ceiling tiles were removed and FFUs were adjusted, as well as providing baseline information on how quickly the cleanroom environment is restored to background levels after the cease of repair activities. Monitoring of such off nominal events will be done in the future as opportunities arise.

Si wafer witness plates (Balazs, Inc): Large area Si witness plates have been deployed several times over this period, with the goal of detecting possible organic and inorganic contaminants. For inorganic and organics, 8-inch polished semiconductor silicon witness wafers were exposed to the laboratory air for 24 hours each. After exposure, the witness plate for organics was sent to Balazs for Thermal Desorption Gas Chromatography Mass Spectroscopy (TD-GC-MS), yielding results for organic compounds from C6 to C28 (with limit of 0.1 ng/cm²). The wafer for inorganics was analyzed by vapor phase decomposition inductively coupled plasma mass spectrometry (VPD-ICP-MS) which yielded data for 35 elements of interest (Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Fe, Ga, Ge, Hf, In, K, La, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Sn, Sr, Ta, Ti, W, V, Y, Zn, and Zr). Analyses for organics have yielded very low concentrations in general – lower than similar monitoring of the ISO4 equivalent Genesis lab, for example across a decade of monitoring. The few and very low species detected in early testing included TXIB (a plasticizer used in urethane elastomers and PVC piping), triacetin (a common plasticizer and solvent, 2-(2-butoxyethoxy) ethanol and texanol (used as a solvent for and in paints). These species have not been detected in measurementsts made in late 2022. Analyses for inorganics that were above detection limits included Al (from wall and ceiling struts), B (from the borosilicate glass in the Fan Filter Unit (FFU) ULPA filters), Cu, Sn, and Zn (could be from electrical or electrical conduit), and Fe (could be from stainless steel or electrical conduit). Continued monitoring of these elements will allow identification of problematic sources, but the levels detected are lower than other NASA curation labs, which is a testament to the careful selection of materials during the design and construction phase.

<u>Gas sampling (Balazs and JSC):</u> Cleanroom air samples were analyzed using two different approaches. Volatile organics in air were sampled with an adsorbent tube connected to a pump (100 mL/min.) for 6 hours. After exposure, the adsorbent tube was sent to Balazs for TD-GC-MS analyses for a wide range of hydrocarbons and volatile organic compounds (limit of 0.1 ng/L). A NASA-JSC based collection of 450 ml gas samples was followed by GC-MS. Both approaches have demonstrated very low levels of organics in general, with most species either (a) below detection limits, or (b) expected but present at very low levels (e.g., isopropanol, toluene, and xylene).

<u>Al foils deployment</u>: In addition to the Si wafers deployed for analysis by Balazs, the curation staff has also deployed monthly sets of aluminum foil witnesses that are being archived. These will also be analyzed using JSC in-house analytical techniques for amino acids. Results are not yet available at the time of writing of this abstract.

<u>Microbial and fungal monitoring</u>: Terrestrial contamination of asteroid or meteorite samples can lead to biological degradation, something we wish to avoid during short- and long-term curation. Swabs and sampling for microbial and fungal analysis have been collected regularly on various surfaces within the OSIRIS-REx cleanroom (as well as many other JSC cleanrooms [4]). Microbiological air samples were also collected by passing air through an electret filter at 200 L/min. Results of these analyses show very low levels in general, and decrease with time in any given area. When rates become more elevated, special cleaning procedures involving hydrogen peroxide have been developed to lower the fungal and microbial recovery rates.

Having the cleanroom completed more than a year in advance of sample return has allowed many important kinds of monitoring to be undertaken, lab environments characterized, and baseline established for any expected or unexpected contaminants. Future emphasis will be on maintaining the monitoring during outfitting of the lab (see details in [5]), as well as the presence of human processors in the lab for longer durations.

References

[1] Lauretta, D.S., et al. (2022) *Science 377*(6603), 285-291; [2] Lauretta, D.S., et al. (2017) *Space Science Reviews 212*, 925-984; [3] Calaway, M.J. and McQuillan, J. (2022) *LPI Contributions*, 2678, abstract #1148; [4] Regberg, A.B., et al. (2022) *LPI Contributions*, 2678, abstract #1686; [5] N. Lunning et al. (2022) this symposium.

A study of the curation protocol by sample analysis working team (SAWT) in Martian Moons eXploration (MMX) project

*R. Fukai¹, T. Usui², W. Fujiya³, Y. Takano⁴, K. Bajo⁵, A. Beck⁶, E. Bonato⁷, N. L. Chabot⁸, Y. Furukawa⁹, H. Genda¹⁰, M. Koike¹¹, M. Matsuoka¹², Y. N. Miura², F. Moynier¹³, S. S. Russell¹⁴, M. E. Zolensky¹⁵, H. Sugahara¹, S. Tachibana^{1,2}, K. Sakamoto¹, and M. Abe¹

¹Japan Aerospace Exploration Agency, ²The University of Tokyo, ³Ibaraki University, ⁴Japan Agency for Marine-Earth Science and Technology, ⁵Hokkaido University, ⁶Marietta College, ⁷German Aerospace Center, ⁸Johns Hopkins University, ⁹Tohoku University, ¹⁰Tokyo Tech, ¹¹Hiroshima University, ¹²National Institute of Advanced Industrial Science and Technology, ¹³Institut de physique du globe de Paris, ¹⁴Natural History Museum, ¹⁵National Aeronautics and Space Administration

Japan Aerospace Exploration Agency (JAXA) will launch a spacecraft in 2024 for a sample return mission from Phobos (Martian Moons eXploration: MMX). The major scientific goals of MMX are to constrain (1) the origin of Phobos and Deimos and (2) the evolution of the Mars-moon system [1]. The touchdown operations are planned to be performed twice at different landing sites on the Phobos surface to collect > 10 g of the surface materials [2]. After the return to the Earth, the Phobos samples will be collected from the individual sample canisters and introduced to the clean chamber installed at ISAS (Institute of Space and Astronautical Science). The Sample Analysis Working Team (SAWT) of MMX designed the procedure of Phobos sample analysis mainly conducted by the initial analysis teams [3]. For the next step, the SAWT will define the procedure of the curation process (mostly non-destructive analysis) of the Phobos samples, which will be presented here.

The protocols of the Phobos sample curation are illustrated in figure 1. First, the headspace gas from the sample container will be collected during the Quick Analysis phase. The Quick Analysis will be operated by the sampler and curation teams in ISAS/JAXA. The terrestrial leak and contamination from the sampling systems will be tested using a quadrupole mass spectrometer equipped with a gas sampling system. Second, the bulk Phobos sample will be observed in the clean chamber under purified-N₂ gas with an ambient condition (Pre-basic Characterization) within three weeks. This phase will be operated by the curation team in ISAS/JAXA and the instrument team of the MMX mission. The consistency between the data from the instruments in the clean chamber and the spacecraft will then be evaluated.

Subsequently, the curation will distribute the small amount of Phobos samples to the Initial analysis team of MMX to conduct the "Preliminary Examination". The objectives of the preliminary examination are to provide (1) feedback on the subsequent sample allocation process, (2) preliminary scientific results that will address parts of MMX mission goals, and (3) evaluation of the sampling system and terrestrial alteration on Phobos samples. Because multiple models are proposed for the origin of Phobos [1] (e.g., giant impact, the capture of asteroids), the chemical and mineralogical characteristics of Phobos must be assessed before the allocation of the sample return. Simultaneously, the curation team in JAXA will observe the individual grains and aliquots of the samples in the clean chamber (Basic Characterization). The results, the curation team will decide on the sample amounts to allocate to the Initial Analysis team. After 6 months from the Preliminary Examination, Initial Analysis will be started to perform the comprehensive analysis for Phobos samples within 1 year.

The curation protocols the SAWT proposes here are partly based on those in Hayabusa & Hayabusa2 missions [4]. However, our strategy enables us to utilize larger amounts of return samples compared to the previous sample return missions. Also, the chemical/mineralogical characteristics of Phobos will be quickly understood throughout the non-destructive and destructive analyses in the curation process.



Fig. 1: Curation protocols for the Phobos samples.

References: [1] K. Kuramoto et al. (2022) *Earth, Planets, and Space*, 74 (12). [2] T. Usui et al. (2020) *Space Science Review*, 216 (49). [3] W. Fujiya et al. (2021) *Earth, Planets and Space*, 73 (120). [4] T. Yada et al. (2022) *Nature Astronomy*, 6, 214.

Bridging the gap - linking remote sensing, in-situ and laboratory spectroscopy

Maturilli A.¹, Schwinger S.², Bonato E.¹, Hamm M.², Baque M.¹, Helbert J.¹, Alemanno G.¹, D'Amore M.¹

¹Department of Planetary Laboratories, Institute for Planetary Research, DLR, Berlin

²Department of Planetary Physics, Institute for Planetary Research, DLR, Berlin

Sample return provides us with "ground truth" about the visited body, verifying and validating conclusions that can be drawn by remote sensing (both Earth-based and by spacecraft) and via landed instruments on other bodies. The detailed investigation of the mineralogy and geochemistry of Ryugu plays a fundamental role in the understanding of its formation processes, and thereby gather further knowledge about the building blocks of the solar system. Based on the preliminary data from remote sensing measurements and laboratory-based measurements, Ryugu is rich in hydrated carbonaceous chondrite (CC) like material and more specifically it is very similar to Ivuna-like (CI) carbonaceous chondrites [1]. These meteorites are characterized by a high abundance of phyllosilicates and organic matter [2], which makes them have a low albedo. However, Ryugu seems to be even darker than CIs, as well as being more porous and fragile [1].

Back in August 2022, the Institute of Planetary Research at DLR (Berlin) received a fragment retrieved by the Hayabusa2 mission from asteroid Ryugu. The fragment assigned to us for analyses is sample A0112, from chamber A. Our investigation is based on two main goals. The first goal is to address a fundamental challenge in the interpretation of remote sensing data which was seen during the initial analysis of the Hayabusa 2 samples. Observations of planetary surfaces using spectroscopy have shown subdued contrast compared to measurements performed under laboratory conditions on analog materials. A strong focus of the work performed at PSL over the last decade has been to understand - and if possible minimize - the difference between laboratory and remote sensing observations (e.g. [3, 4, 5, 6]). Simulating the conditions on the target body as well as accurately reproducing the observing geometries have gone a long way towards that goal, however differences remain. A suggested explanation is the difference between terrestrial analog materials including even meteorites and the surfaces of planetary bodies. With Ryugu samples this hypothesis can be tested further, leading to a deeper understanding of the link between laboratory and remote sensing observations and thus benefiting not only the analysis of Hayabusa 2 data but of all remote sensing observations of planetary surfaces using spectroscopy. The second goal building on this is an investigation of the mineralogy and organic matter of the samples collected by Hayabusa 2, to better: a) understand the evolution of the materials characterizing asteroid Ryugu and therefore advance our knowledge of the mineralogy of the protoplanetary disk and organic matter (OM); b) investigate the aqueous alteration that took place in the parent body that lead to its current chemical and mineralogical characteristics; c) compare the results with data collected from pristine carbonaceous chondrite meteorites rich in hydrated minerals and organic matter.

We are currently collecting the first datasets, and for doing so we are applying a strict protocol to maintain the grain as pristine as possible. The first set of measurements is taking place keeping the sample within the N_2 filled sample holder it was delivered in. Just afterwards, we will open the protective holder to transfer the sample in the anaerobe bench to the Hayabusal holder (that we hosted in our institute too) and we will repeat those measurements. As a final step, we will remove the sample from this

holder and let the sample be in contact with laboratory atmosphere.

Here is a description of the protocol:

- The first step of our investigation consists in 3D imaging of the sample (Figure 1) with the use of a Keyence VHX-7000 4K High Accuracy digital microscope;
- 2. Mapping of the sample with Raman spectroscopy (Figure 2);
- 3. Mapping of the sample with IR microscope in the wavelength range $0.25 25 \mu m$;
- Collection of reflectance data in the wavelength range 0.25 – 25 μm;



Figure 1: 3D scan of particle A0112 with a Keyence VHX-7000 4K High Accuracy digital microscope.

- Transfer of the sample to a dedicated holder previously created for the analysis of Hayabusa1 samples and repetition of the previous steps;
- Sample open and exposed to air: stored in dry cabinets, spectroscopy measured in vacuum;
- 3D imaging with the use of a Keyence VHX-7000 4K High Accuracy digital microscope
- 8. IR data collection in the wavelength range $0.25 25 \,\mu m$
- Raman mapping: in this case after the acquisition of IR data to minimize the reaction of organic matter with the laser;
- 10. SEM and EDX mapping at low voltage of uncoated and unprepared sample.



Figure 2: Raman preliminary results. A. WITec Alpha 300 confocal microscope setup with JAXA's sample holder containing particle A0112. B. Typical Raman spectra of polyaromatic carbonaceous matter measured under N2 atmosphere in the unopened container showing typical D and G carbon bands and fitted with a Lorentz function to extract parameters such as bands' position, full width at half maximum (FWHM), and bands' intensities. Inlet: measurement points on particle's surface.

Up to now, step 1 has been successfully executed as can be seen in Figure 1. The 3D measurements will help planning the next steps of the measurements. They are also an interesting result in itself as they will allow to determine the volume and thereby the density of this particle.

Step 2 has been started and Raman spectra were successfully acquired on the particle without opening the original container (as was executed for Hayabusa1 particles previously). Preliminary data show the typical carbonaceous matter signature typical of CCs from which their thermal history can be derived [8].

References

Yada T., et al., 2022. Nat Astron 6, 214–220. [2] Cloutis E. A., et al., 2011. Icarus, 212:1. [3] Maturilli A., et al., 2016a.
 Earth, Planets and Space 68(1). [4] Maturilli A., et al., 2016b. Earth, Planets and Space 68(1). [5] Beck P., et al., 2018. Icarus 313: 124-13. [6] Yesiltas M. et al., 2020. Meteoritics & Planetary Science, 55(11): 2404–2421. [7] Ray D. and Shukla A.D., 2018. PSS 151, 149-154. [8] Bonal L. et al., 2016. Geochimical et Cosmochimica Acta, 189:312-337.

An infrared look at Ryugu returned samples in the meteorite/asteroid perspective

R. Brunetto¹, A. Aléon-Toppani¹, T. Nakamura², C. Lantz¹, Z. Dionnet¹, F. Borondics³, D. Baklouti¹, Z. Djouadi¹, S. Rubino¹, K. Amano², M. Matsumoto², Y. Fujioka², Y. Fukuda², T. Morita², M. Kikuiri², E. Kagawa², R. Milliken⁴, M. Matsuoka⁵, H. Yurimoto⁶, T. Noguchi⁷, R. Okazaki⁷, H. Yabuta⁸, H. Naraoka⁷, K. Sakamoto⁹, S. Tachibana⁹⁻¹⁰, S. Watanabe¹¹, Y. Tsuda⁹ and the Hayabusa²-initial-analysis Stone team.

¹IAS, Université Paris-Saclay, CNRS, France, ²Tohoku University, Japan, ³SMIS-SOLEIL, France, ⁴Brown University, USA, ⁵LESIA, Observatoire de Paris-Meudon, France, ⁶Hokkaido University, Japan, ⁷Kyushu University, Japan, ⁸Hiroshima University, Japan, ⁹ISAS/JAXA, Japan, ¹⁰The University of Tokyo, Japan, ¹¹Nagoya University, Japan

Laboratory analyses of materials originating from asteroids give us the opportunity to directly study the components that formed in the protoplanetary disk. However, collections of extraterrestrial materials available on Earth have strong biases, and the link between laboratory samples and their asteroidal parent bodies is often ambiguous. Furthermore, many classes of small bodies are likely absent from our collections [1]. Some of these limitations are overcome by sample return missions, such as Hayabusa2/JAXA that targeted and sampled the small and dark near-Earth asteroid Ryugu [2]. Ryugu has retained valuable information on the formation and evolution of planetesimals at different epochs of our Solar System history [3].

Samples originating from asteroids can be analyzed thanks to modern analytical techniques [4]. Among them, infrared spectroscopy is important for comparing lab measurements to remote sensing observations of small bodies. In addition, midand far-infrared (MIR, FIR) reflectance spectra of asteroids and meteorites contain fundamental vibrational bands which are diagnostic of their mineral and organic compositions. Infrared spectra of Ryugu were measured by NIRS3 on board Hayabusa2 in the near-IR range [5], however the MIR-FIR range was not available. The return of Ryugu samples collected by Hayabusa2 provide an excellent opportunity to measure the MIR-FIR spectra of Ryugu materials and to compare them with similar observations of meteorites and asteroid, in particular the remote sensing MIR-FIR spectra of B-type asteroid Bennu acquired by the OSIRIS-REx mission [6].

In this study we report IR reflectance measurements of two mm-sized Ryugu stones (A0026 and C0002), acquired at the SMIS beamline of synchrotron SOLEIL (France) and at Tohoku University (Japan), and we compare them with meteorite spectra acquired with similar setups, and with the available remote sensing spectra of different asteroids.

Generally speaking, the MIR and FIR reflectance spectra of the two Ryugu stones show similitudes with spectra of CI meteorites, both in terms of overall spectral shape and in terms of peak position of the main reststrahlen silicate features, although some differences are observed probably due to a different history of alteration (both in space and on Earth). The IR spectra of Ryugu samples are clearly different from those of CM meteorites and other ungrouped primitive meteorites. They also differ from the remote sensing spectrum of asteroid Bennu. Overall, the results indicate that Ryugu has both a mineral composition and a history of aqueous alteration that are more similar to those of CI chondrites than to those of CM chondrites and of asteroid Bennu. These observations confirm that Ryugu and Bennu, two small near-Earth asteroids that are so similar in many ways (size, morphology, density, etc.), have distinct IR spectra also in the mid-IR and far-IR, in agreement to what was previously shown in the near-IR range from orbital data [5,6].

Finally, the presence of different lithologies in C0002 [3] allows to trace the early evolution of Ryugu materials and the corresponding IR spectral variations. The parameters extracted from the micro-IR spectra of different clasts in C0002 draw an alteration pattern which is different from that of CM meteorites [7,8], and which helps to reconsider the general asteroid-meteorite connection in a different perspective.

References

[1] Greenwood R.C. et al. 2020. Geochimica et Cosmochimica Acta 277, 377–406. [2] Watanabe S. et al. 2019. Science 364, 268–272. [3] Nakamura T. et al. 2022. Science 10.1126/science.abn8671. [4] Brunetto R. et al. 2021. In: Sample Return Missions: The Last Frontier of Solar System Exploration. Editor: Andrea Longobardo. Elsevier 315–342. [5] Kitazato K. et al. 2019. Science 364, 272–275. [6] Hamilton V. et al. 2019. Nature Astronomy 3, 332-340. [7] Hanna R.D. et al. 2020. Icarus 346. [8] Dionnet Z. et al. 2022. Meteoritics and Planetary Science 57, 965–988.

P-rich compounds within the Ryugu sample collection: a perspective from joint MicrOmega/Curation, the OU and Phase2 Kochi curation activities

^{1,2}Pilorget, C.; ¹Loizeau, D.; ³Ito, M., ¹Bibring, J.-P.; ¹Carter, J.; ¹Le Pivert-Jolivet, T.; ^{1,4}Riu, L.; ¹Brunetto, R.; ³Tomioka, N.; ⁵Uesugi, M.; ⁶Yamaguchi, A.; ⁶Imae, N.; ^{7,8}Hatakeda, K.; ⁷Yogata, K; Y.; ¹Baklouti, D.; ^{7,9}Okada, T.; ⁷Yada, T.; ^{7,9}Usui, T.; ¹⁰Greenwood, R.; ¹¹Liu, M., and the Ph2K team, the OU team and the MicrOmega Curation Team.

¹IAS, Université Paris-Saclay, CNRS, France, ²Institut Universitaire de France, ³JAMSTEC, Kochi Inst. Core Sample Research, ⁴ESAC, ESA, Madrid, Spain, ⁵JASRI, ⁶National Institute of Polar Research, ⁷Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, ⁸Marine Works Japan, Ltd, ⁹University of Tokyo, Bunkyo, Tokyo 113-0033, Japan, ¹⁰Open U. UK, ¹¹UCLA US

The JAXA Hayabusa2 mission has returned for the first time samples collected at the surface of a C-type asteroid, Ryugu [1,2]. They are now preserved at the Extraterrestrial Samples Curation Center of JAXA at ISAS in Sagamihara, Japan, where they are submitted to a first round of non-destructive and non-invasive analyses, while maintained in a purely non-altering environment since their collection [3]. Some of these grains have also been extracted to be further analyzed by - initially - 8 analytical teams, including Phase2 Kochi (Ph2K) curation [4,5], and later open to AOs.

The MicrOmega hyperspectral microscope operating in the near-infrared (NIR) range $(0.99 - 3.65 \ \mu\text{m})$ is performing the mineralogical and molecular characterization of the samples present in the Curation Center, down to the scale of a few tens of micrometers [6]. By the end of September 2022, >375 individual grains (a few mm in diameter) and 25 sub-bulks (a few tens of mg each) have been analyzed with MicrOmega, in addition to the 6 initial bulks from chamber A and C. It offers a global view on the Ryugu samples, preserved from any terrestrial contamination, and can be used to target specific grains and areas of interest with complementary techniques. In particular, while strong features at 2.7 μ m – translating their OH-rich content - and 3.4 μ m – diagnostic of the presence of organics – dominate at a global scale, key distinctive signatures have been identified at sub-mm scale [7,8,9,10]. Here we present the international collaborative curation work conducted with the Ph2K and the OU on Ryugu samples and focused on the P-rich compounds.

Specific grains of interest/inclusions have been identified with MicrOmega within the Curation Facility, for having a bright aspect (reflectance of ~10-20%) coupled to a very peculiar spectrum in the NIR: a broad and deep band at ~3 μ m, with additional features, in particular a sharp band at ~2.7 μ m shifted by ~10 nm compared to the one observed in the matrix [7]. Grains with such properties tend to occur as inclusions or loose grains with sizes up to a few hundreds of microns, similar to carbonates observed by MicrOmega [8] but with a much lower occurrence. Such signatures have been identified in the C0209 sub-bulk delivered to the Ph2K team in April 2022. Grains presenting these properties have been manually extracted and analyzed by SR-XRD at Spring-8 and then combined SEM/EDX at Kochi JAMSTEC, which revealed an enrichment in P, O and Mg elements, possibly pointing towards Mg-phosphates as suggested by other observations on a few samples [11,12]. These grains and the C0209 sub-bulk were then re-analyzed by a MicrOmega unit present at IAS [13]. The results confirmed the correlation between the IR signature and the P, O, Mg content detected by the EDX. Slight modifications of the IR spectra in the 2.7-3.0 μ m range points towards a contact with the terrestrial atmosphere after the extraction of the grains from the Curation Center.

These results offer a new perspective on the characterization of the distribution and properties of such compounds over the entire collection. Further analysis of the grains is on-going to assess the possible couplings of the P-rich phases with other compounds (minerals and/or organics) and their origin by H, O isotopic ratios.

References

[1] Watanabe et al. (2019) Science 364 268-272. [2] Morota et al. (2020) Science 368 654-659. [3] Yada et al. (2022) Nat Astron, 6, 214-220. [4] Ito et al. (2022) Nat Astron, [5] Liu et al. (2022) Nat Astron, [6] Bibring et al. (2017) Space Sci. Rev. 208, 401-412. [7] Pilorget et al. (2022) Nat Astron, 6, 221-225. [8] Loizeau et al. (2022) 53rd LPSC contrib. N°2017 [9] Carter et al. (2022) 53rd LPSC contrib. N°1495. [10] Bibring et al. (2022) this conference. [11] Nakamura et al. (2022) Proceedings of the Japan Academy, Series B 98, 227–282. [12] Ma et al. (2022) MetSoc contrib. N°2695. [13] Loizeau et al. (2020) Planetary and Space Science 193 article id. 105087.

Overviews of the Hayabusa2 mission and its integrated science

Sei-ichiro Watanabe¹, Hayabusa2 Science Team, Hayabusa2 Curation Team, and Haybusa2 Initial Analysis Team ¹Nagoya University

The asteroid explorer Hayabusa2 performed its proximity operation around Cb-type asteroid (162173) Ryugu from June 2018 to November 2019, and returned to Earth with the surface sample in December 2020. More than 5 g of the particles in the sample catchers were successfully retrieved and the initial description and initial analysis were performed. The formation of the Solar System and the subsequent history of asteroid Ryugu will be discussed based on the proximity observations of Ryugu and analysis of the return sample.

From the initial analysis, the Ryugu sample was confirmed to be similar to CI (Ivuna-type) chondrites in terms of mineral assemblages and composition, and isotopic ratios [1-4]. Some differences were attributed to the effects of weathering and contamination on the ground suffered by CI chondrites, so that the Ryugu sample is considered to preserve the chemical and isotopic state of CI chondrites as they were in space. The presence of grains having large anomalies in the stable isotope ratios of H, C, and N was confirmed [5], suggesting that these particles were produced in the low-T environment of the solar parental molecular cloud and retained without undergoing isotopic equilibrium on the parent body. The organic carbon of the Ryugu sample is comparable to that of CI chondrites, whereas the carbonate content is significantly higher, and therefore the total carbon content is somewhat higher. The presence of CO₂-bearing aqueous fluid inclusions in a large iron sulfide (phyrrhotite) crystal [3], the IR absorption of NH in ammonium salts or organic nitrogen compounds [6], and the very low content of chondrules and CAIs [3] suggest that the parent body of Ryugu may have originated outside the snow lines of CO₂ and NH₃ (presumably outside Saturn's orbit). Near infrared spectrometer NIRS3 found a global 2.72 µm absorption on Ryugu, indicating omnipresence of Mg-rich phyllosilicates [7]. Return sample analyses clarified that aqueous alteration in the parent body had progressed in alkaline water with a temperature of $\sim 310 \text{ K}$ [1] generated by the decay heat of ^{26}Al in the interior of an about 100-km sized icy body at 5-6 million years after the formation of CAIs in the protosolar disk [3]. The presence of less altered grains in Ryugu particles suggests the difference in temperature between the near-surface and interior of the icy parent body at the stage of aqueous alteration [3]. Some of these less altered grains have particularly high micro-porosity, suggesting the formation of planetesimals from fluffy ice and stone particles. It is noteworthy that franboidal magnetite grains with a remanent magnetization of ~100 µT were found in several Ryugu particles [3], suggesting that the parent body had moved from the outer Solar System to the asteroid belt, where disk magnetic field is expected to have been strong enough, before/during a period of aqueous alteration.

These results are consistent with the scenario that carbonaceous chondrites' parent bodies are icy planetesimals with diameters of ~100 km that formed in the outer Solar System and were brought to the inner Solar System through scattering by giant planets. However, based on the reflection spectra and orbital analysis of Ryugu, its parent body is considered to be one of the collisional families in the inner asteroid belt [8]. Therefore, it is necessary to verify whether the scattering by giant planets could bring planetesimals to such an inner region of the asteroid belt. In any case, it is a great discovery that the parent bodies (at least one of them) of CI chondrites are collisional families in the inner asteroid belt.

Contrary to the parent body processes, the sample analysis information about the formation and evolution of Ryugu itself is rather little and the results from remote sensing observations are important. Low bulk density and abundant large boulders indicate that Ryugu is a rubble-pile object formed through re-accumulation of fragments produced by catastrophic disruption or cratering of the parent body [9]. Surface mean visible spectrum of Ryugu is similar to that of (495) Eulalia, and spectrum of the largest boulder Otohime is similar to (142) Polana, both asteroids are the largest members of the Polana-Eulalia collisional families. Assuming the collision frequency model for the asteroid main belt, the surface age of Ryugu is about 10 Myr based on crater chronology using crater-to-impactor size ratio of 130 after the SCI experiment [10]. The surface age is much younger than the estimated ages of the parent collisional family of Ryugu, either the Polana or Eulalia family. Thus, the surface age is considered to correspond to the top shape formation, probably global resurfacing events [9, 11], induced by the YORP spin-up long after the formation of Ryugu.

Much has also been learned about the post-formation history of Ryugu. From the analysis of the YORP effect using the shape models, Ryugu is now slowly spinning down and had a fast rotation in the past (~10 Ma) [12]. The analysis of the tilt angle distribution on the surface of Ryugu suggests that the top shape was formed by surface landslides when the rotation period was 3.5 to 3.75 hours [9]. Following a previous study [13], which suggested that the east-west asymmetry of the crater rims on Ryugu was caused by the Coriolis forces acting on crater ejecta during a high-speed rotation era, the analysis with precise topographic correction revealed that three large craters on Ryugu have significant higher rims both on the west and

equatorial sides [14]. These craters are more susceptible to the Coriolis force than other craters at the stage of high-speed rotation, and the average tilt angle of each surrounding terrain is larger than that of other craters. These results as well as numerical simulations of top-shape formation [15] suggest that the top shape of Ryugu was formed during high-speed rotation era about 10 million years ago, and that the crater formation and space weathering were proceeded during the spin-down phase.

Several bluer (negative spectral slope in visible wavelengths) craters are sccattered in red (flat spectral slope) areas on Ryugu. Stratigraphic relationship between craters reveals that bluer craters are younger in this region, suggesting primordial material of Ryugu is bluer and distributed underground [16]. Suface reddening of the bluer material occurred by space weathering due to solar wind [17]. On the other hand, on (101955) Bennu, the OSIRIS-REx target, redder, flat spectral slope craters are scattered in blue areas, and the craters changed from red to blue due to space weathering, so younger craters are redder on Bennu [18]. This means that space weathering progressed in the opposite direction on the two bodies from the similar flat-spectral material.

The thermal infrared imager (TIR) onboard Hayabusa2 revealed flat diurnal brightness temperature profiles caused by surface roughness and derived global thermal inertia of 225 ± 45 J m⁻² s^{-1/2} K⁻¹ [19, 20], indicating higher porosity of boulders on Ryugu than that of carbonaceous chondrites. In situ measurement by the Mobile Asteroid Surface Scout (MASCOT) also found low thermal inertia of 295 ± 18 J m⁻² s^{-1/2} K⁻¹ [21]. In contrast, return sample measurement showed that the thermal inertia of a Ryugu particle with the thickness of < 1 mm is 890 J m⁻² s^{-1/2} K⁻¹ [3], which is higher than the values on the asteroid surface. The thermal skin depth for the diurnal temperature change of Ryugu is about 10 mm, so that mm-scale cracks may be responsible for the thermal shielding effect on the surface layer of Ryugu. Some dark boulders on Ryugu have thermal inertia lower than 100 J m⁻² s^{-1/2} K⁻¹, which correspond to porosity >70% [22]. These boulders are considered to be the least processed materials on Ryugu and may preserve the structure of grain aggregates on the parent porous planetesimal.

References

[1] Yokoyama T. et al. 2022, Science abn7850. [2] Nakamura E. et al. 2022, Proc. Jpn. Acad. Ser. B 98:227. [3] Nakamura T. et al. 2022, Science abn8672. [4] Ito M. et al. 2022, Nat. Astron. doi:10.1038/s41550-022-01745-5. [5] Yabuta H. et al. 2022, Abstract #2241, 53rd LPSC. [6] Pilorget C. et al. 2021, Nat. Astron. doi:10.1038/s41550-021-01549-z. [7] Kitazato K. et al. 2019, Science 364, 273. [8] Sugita S. et al. 2019, Science 364, aaw0422. [9] Watanabe S. et al. 2019, Science 364, 268. [10] Arakawa, M. et al. 2020, Science 368, 67. [11] Sugiura, K. et al. 2021, Icarus 365, 114505. [12] Kanamaru M. et al. 2021, JGRE 126. [13] Hirata N. et al. 2021, Icarus 354, 114073. [14] Yamada R. 2022, Master Thesis, Nagoya Univ. [15] Sugiura K. et al. 2021, Icarus 365, 114505. [16] Morota T. 2022 Science 368, 654. [17] Tatsumi et al. 2021, Nat. Comm. 12, 5837. [18] DellaGiustina, D. N. et al. 2020 Science 370, eabc3660. [19] Okada, T. et al. 2020, Nature 579, 518. [20] Shimaki, Y., et al. 2021, Icarus 348, 113835. [21] Hamm et al. 2020, Mon. Not. R. Astron. Soc. 496, 2776. [22] Sakatani, N. et al. 2021, Nat. Astron. 5, 766.

MMX samples curation in Europe

Enrica Bonato¹, Jörn Helbert¹, Ansgar Greshake², Lutz Hecht², Tomohiro Usui³ ¹German Aerospace Centre (DLR), Institute for Planetary Research, Berlin, Germany ²Museum für Naturkunde, Berlin, Germany ³ISAS, JAXA, Japan

In 2024 the Martian Moons eXploration (MMX) mission from JAXA will be launched to the Martian Moons Phobos and Deimos to investigate their nature and improve our understanding about their formation. In 2029 samples from Phobos will be returned back to Earth as MMX is the latest JAXA's sample return mission. Samples returned to Earth by the MMX mission will be retrieved by JAXA and transferred to the JAXA ISAS Sample receiving laboratory for initial description, followed by initial proprietary analyses performed by the MMX Science Sub-Teams (SSTs), which will include a number of ESA-appointed MMX participating scientists from ESA Member States. The duration of these activities is determined by the MMX Sample Allocation Committee (SAC), and it is estimated to last approximately one year. It is planned that JAXA will thereafter transfer an allocation of samples to ESA for use by scientists and laboratories in the ESA Member States. Sample Curation Facilities (hereafter SCFs) at the German Aerospace Centre (DLR) and at the National Centre for Space Studies (CNES) will host and handle the MMX Samples provided to the ESA Science Program. After transfer to the SCFs the samples will be catalogued (if not done by JAXA) in preparation for an ESA Announcements of Opportunity (AOs) to allocate the Samples to scientists and laboratories in the ESA Member States.

In preparation to this major effort, we are working on the setup of an analytical and curation facility in Berlin, in cooperation between the DLR and the Museum für Naturkunde (MfN). Within the analytical facility it will be possible to carry out the basic characterization of the samples in controlled environmental conditions, for then being able to move on to more specialized facilities for more in depth examination. The curatorial expertise is being developed on the existing expertise from the Meteorite Collection based at the MfN and in collaboration with the JAXA curation facilities. Current curators, together with the younger generation are being trained and working on skillset exchange.

Can SIMS measurements constrain the D/H ratio of water on Ryugu?

Larry R. Nittler^{1,2}, Jens Barosch,¹ and Rhonda M. Stroud^{3,2}

The Hayabusa2-initial-analysis Organic Macromolecule and Core Teams

¹Earth and Planets Laboratory, Carnegie Institution of Washington, USA.

²School of Earth and Space Exploration, Arizona State University, USA

³US Naval Research Laboratory, Washington DC, USA

We have previously reported the use of the Cameca NanoSIMS ion microprobe to characterize H, C, and N isotopes on a sub-micrometer scale in particles returned by the Hayabusa2 spacecraft from C-asteroid Ryugu [1, 2]. These data show that macromolecular organic-rich particles in Ryugu samples are remarkably isotopically heterogeneous on μ m scales with compositional distributions similar to those of carbonaceous chondrites (CCs), including CIs, the closest meteorite analog to Ryugu [3]. Recently, Piani et al. [4] have used large-geometry SIMS (Cameca ims-1280) data to conclude that Ryugu water has $\delta D/H = +74 \pm 117$ ‰. Since the NanoSIMS has much higher spatial resolution than the ims-1280, we have re-examined our data to investigate whether they can provide additional information on Ryugu's water composition. Our results agree well with those of [4], but we argue below that it is not possible with current ion probe data sets to infer the H₂O D/H composition on Ryugu with any degree of confidence.

Prior work on CCs and Ryugu samples [4-6] has assumed that ~10- μ m-scale SIMS H-isotope measurements represent two-component mixtures between water of hydration (with C/H=0) and organic matter (with higher C/H), based on observed correlations between measured C/H and D/H ratios. Extrapolation of fitted linear trends to the data to C/H=0 then yields the inferred D/H of the intrinsic H₂O. Shown as grey circles in Fig. 1d are the C/H ratios and δ D values we have previously found in organic-rich particles, typically a few 100 nm in diameter, based on 20 fragments of Ryugu particles A0108-13 (12 fragments) and C0109-2 (8 fragments) pressed into Au foils. The instrumental mass fractionation and C/H calibration were corrected based on a terrestrial organic standard. The large scatter in these data precludes linear extrapolation. We thus chose to bin the imaging data by defining regions-of-interest (ROIs) in each image whose C/H ratios spanned specific intervals (e.g., Figs. 1a-c). The C/H and D/H ratios are generally correlated within an image (e.g., Fig. 1c) but the variable presence of anomalously D-rich or D-poor grains (hot/coldspots) often leads to non-linear trends. Nevertheless, when the data are combined for all 20 particles, clear linear trends are observed below C/H~1 for both the Chamber A and Chamber C grains (green and orange symbols in Fig. 1d-e). Outliers are due to the presence of D hotspots or coldspots. The solid green and orange lines indicate linear fits to the data below C/H=1 (excluding outliers). The fit lines intersect the Y-axis at δ D=142 ‰ and 82 ‰, respectively, in excellent agreement with the results of [4] (red error bar), acquired with a different instrument on different samples.

The linear trends seen in Fig. 1d,e support the idea that, when averaged over relatively large areas, the data represent two-component mixing. At the high C/H end, the endmember is clearly the average of the ubiquitous C-rich particles present throughout the Ryugu samples, i.e., the grey symbols in Fig. 1d. We note that insoluble organic matter (IOM) extracted from CI chondrites [magenta star; 7] lies close to but slightly above the Ryugu trend lines. This supports previous measurements indicating that Ryugu IOM has lower D/H than IOM from CIs [8] but could also reflect a possible mis-calibration of the C/H ratios from measured C/H secondary ion signals in the NanoSIMS. The identification of the low C/H endmember is more ambiguous. Transmission electron microscopy and synchrotron-based transmission x-ray microscopy studies have shown that in Ryugu samples the phyllosilicates are intimately mixed with a "diffuse" organic material [9-11]. This diffuse C ("dC") is spectroscopically distinct from the larger particulate organic grains, for example showing a CO₃ feature (not associated with carbonate minerals) and often showing a higher abundance of aliphatic compounds [11]. The intimate association of the dC with the clay minerals means that even at the highest NanoSIMS spatial resolution, one cannot distinguish H coming from the dC and that coming from the water. Thus, the trend in fact represents *3-component* mixing where the low C/H endmember is itself a mixture of H₂O and dC. Since the two forms of organics (dC and particles) are spectrally distinct, they also could

have distinct C/H and D/H ratios on average. For example, the black lines on Fig 1e indicate mixing between water with δD = -200 or -500 ‰ (as inferred for CI chondrites by [12]) and supposed diffuse C components arbitrarily assumed to have C/H~0.6 (based on assumed higher aliphatic content) and δD ~2000 or 3000‰, respectively. Since these lines intersect with the low-C/H end of the Ryugu trends, the data are fully consistent with Ryugu water having a D/H much lower than inferred by [4], *if the dC indeed has higher D/H and/or lower C/H on average than the larger organic grains and the mixing ratio between dC and phyllosilicates is roughly constant on the scale of the measurements*. Without a way to independently determine the composition of the dC, we conclude that SIMS measurements like those used here and by [4-6] cannot unambiguously resolve the D/H of water in Ryugu samples. Moreover, dC has also been seen to be present in CI, CM, and CR chondrites [13], suggesting that previous SIMS D/H measurements of these should be revisited. Finally, we note that under O⁻ primary ion bombardment, the secondary ion yield of H⁺ is higher from hydrated silicates than from organics [14]. High-resolution NanoSIMS



measurements of Ryugu samples with the Hyperion RF plasma O source, compared with Cs-based measurements of the same materials, may allow for better discrimination of the water endmember from the dC and provide a better estimate of the D/H of Ryugu water.

Figure 1. a) Color-coded NanoSIMS map of H and C in a Ryugu particle b) ROIs defined by pixels within selected C/H ratio bins. c) δD versus C/H for ROIs from panel b. d,e) δD versus C/H for 20 analyzed Ryugu fragments. Vertical red error bar is y-intercept reported by [4].

References

[1] Barosch J. et al. 2022. Abstract #2050. 53d LPSC. [2] Nittler L. R. et al. 2022. Goldschmidt Conference. [3] Yokoyama T et al. 2022. Science abn7850. [4] Piani L. et al. 2022. Abstract #6058. 85th MetSoc Meeting. [5] Piani L. et al. 2021. Earth & Planetary Science Letters 567: 117008. [6] Piani L. et al. 2018. Nature Astronomy 2:317-323.
[7] Alexander C. M. O'D. et al. 2007. Geochimica et Cosmochimica Acta 71: 4380–4403. [8] Remusat L. et al. 2022. Abstract #6197. 85th MetSoc Meeting. [9] Yabuta H. et al. 2022. Abstract #2241. 53d LPSC. [10] De Gregorio B. T., et al. 2022. Abstract #1634. 53rd LPSC. [11] Stroud R. M., et al. 2022. Abstract #2052. 53d LPSC. [12] Alexander C. M. O'D. et al. 2012. Science 337: 721–723. [13] Le Guillou C. et al. 2014. Geochimica et Cosmochimica Acta 131: 368–392. [14] Deloule E. and Robert F. 1995. Geochimica et Cosmochimica Acta 59: 4695–4706.

The Hayabusa2-initial-analysis Organic Macromolecule and Core Teams: H. Yabuta, G. D. Cody, C. Engrand, Y. Kebukawa, B. De Gregorio, L. Bonal, L. Remusat, R. Stroud, E. Quirico, L. R. Nittler, M. Hashiguchi, M. Komatsu, E. Dartois, J. Mathurin, J. Duprat, T. Okumura, Y. Takahashi, Y. Takeichi, D. Kilcoyne, S. Yamashita, A. Dazzi, A. Deniset-Besseau, S. Sandford, Z. Martins, Y. Tamenori, T. Ohigashi, H. Suga, D. Wakabayashi, M. Verdier-Paoletti, S. Mostefaoui, G. Montagnac, J. Barosch, K. Kamide, M. Shigenaka, L. Bejach, T. Noguchi, H. Yurimoto, T. Nakamura, R. Okazaki, H. Naraoka, K. Sakamoto, S. Tachibana, S. Watanabe, and Y. Tsuda

Pentlandite: A Compositional Indicator of Oxygen Fugacity for Chondrites

D. L. Schrader¹, T. J. Zega², J. Davidson¹, T. J. McCoy³, and K. J. Domanik²

¹Buseck Center for Meteorite Studies, School of Earth and Space Exploration, Arizona State University, AZ 85287, USA (devin.schrader@asu.edu), ²Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721, USA. ³Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, Washington, DC 20560-0119, USA.

Introduction: Fe-sulfides are ubiquitous in chondrites and are sensitive indicators of formation and alteration conditions in the protoplanetary disk and small Solar System bodies [e.g., 1–14]. We previously constrained a minimum oxygen fugacity (fO_2) needed to form pentlandite, (Fe,Ni)₉S₈, [6,7] and identified trends with pentlandite compositions between distinct meteorite groups [6,7]. We also identified a relationship between the at.% Fe/S ratio of pyrrhotite group sulfides and the fO_2 of formation, either in the protoplanetary disk or the parent body during aqueous or thermal alteration [13]. Since pentlandite formed with pyrrhotite (they are typically intergrown in these chondrite groups [1–14]; Figure 1), fO_2 may have also influenced pentlandite compositions. Here we report the chemical compositions of pentlandite in chondrites that experienced a wide range of formation and parent body alteration conditions (including fO_2 [13]). This compositional analysis enables investigation of potential trend(s) with the pyrrhotite at.% Fe/S ratio, and by extension fO_2 .



Figure 1. Backscattered electron image of a pyrrhotite (Po) – pentlandite (Pn) intergrowth in Tarda (C2-ung). Mag = magnetite.

Samples and Analytical Procedures: We determined the major and minor element compositions of pentlandite in each of the following 54 chondrites: CI (Alais), a C1-ungrouped (Miller Range [MIL] 090292), C2-ungrouped (Tarda and Tagish Lake), CY (Belgica [B]-7904), CM1/2 (Allan Hills [ALH] 83100 and Kolang [two lithologies]), unheated CM2s (Aguas Zarcas [multiple lithologies], Mighei, Queen Alexandra Range [QUE] 97990, Theil Mountains [TIL] 91722, and D'Angelo Bluff [DNG] 06004), stage I heated CM2 (Asuka [A]-881458), stage II heated CM2 (Yamato [Y]-793321), CM-like (Sutter's Mill), CO3.00 (Dominion Range [DOM] 08006), CR1 (Grosvenor Mountains [GRO] 95577), CR-an (Al Rais), CR2 (Elephant Moraine [EET] 87770, EET 92048, EET 96259, Gao-Guenie (b), Graves Nunatak [GRA] 95229, LaPaz Ice Field [LAP] 02342, LAP 04720, MIL 090657, Northwest Africa [NWA] 801, Pecora Escarpment [PCA] 91082, QUE 99177, Shişr 033, and Y-793495), shock-heated CR2 (GRO 03116), CV3_{OxA}

(Allende), CV3_{0xB} (Bali), and CV3_{Red} (Vigarano), CK4 (ALH 85002 and Karoonda), CK5 (Larkman Nunatak [LAR] 06868), CK6 (Lewis Cliff [LEW] 87009), L3.05 (EET 90161 and QUE 97008), LL3 (Semarkona and Vicência), LL4 (Hamlet and Soko-Banja), LL5 (Chelyabinsk and Siena), LL6 (Appley Bridge and Saint-Séverin), R3 (MET 01149), R3.6 (LAP 031275), R5 (LAP 03639), and R6 (LAP 04840 and MIL 11207) chondrites. We acquired high-resolution backscatter electron images (e.g., Figure 1) and quantitative chemical compositions with the JEOL-8530F Hyperprobe electron microprobe analyzer (EPMA) at Arizona State University (ASU) and the Cameca SX-100 EPMA at the University of Arizona (UA) following [13]. Some pentlandite compositions were previously reported [6,7,10,11].

Results and Discussion: Our data show that there is a relationship between the at.% Fe/S ratio of pyrrhotite (data from [13]) and pentlandite compositions. Moreover, because the at.% Fe/S ratio of pyrrhotite is a proxy for fO_2 [13], these results indicate that there must also be a relationship between fO_2 and pentlandite composition. This relationship holds whether pentlandite formed: (1) during chondrule formation in the protoplanetary disk (i.e., during chondrule cooling, as previously noted by [6,8,10,11] for CR2, CO3.00, and LL3.00 chondrites), (2) during thermal alteration on the parent asteroid under relatively reducing (i.e., LL4–6 chondrites) or oxidizing (i.e., R4–6 and CK chondrites) conditions, or (3) during oxidizing aqueous alteration (i.e., as in CI, CM1, C1-ung, and C2-ung chondrites). Therefore, in addition to the at.% Fe/S ratio of pyrrhotite, the chemical compositions of pentlandite can also be used as a proxy for the fO_2 of formation. This discovery has implications for the interpretation of pentlandite compositions in meteorites and in asteroid returned samples from Ryugu and Bennu.

References: [1] Zolensky M. E. et al. (2002) *Meteorit. Planet. Sci.* 37:737–761. [2] Bullock E. S. et al. (2005) *Geochim. Cosmochim. Acta* 69:2687–2700. [3] Schrader D. L. et al. (2008) *Geochim. Cosmochim. Acta* 72:6124–6140. [4] Berger E. L. et al. (2011) *Geochim. Cosmochim. Acta* 75:3501–3513. [5] Harries D. and Langenhorst F. (2013) *Meteorit. Planet. Sci.*

48:879–903. [6] Schrader D. L. et al. (2015) *Meteorit. Planet. Sci.* 50:15–50. [7] Schrader D. L. et al. (2016) *Geochim. Cosmochim. Acta* 189:359–376. [8] Schrader D. L. et al. (2018) *Earth Planet. Sci. Lett.* 504:30–37. [9] Singerling S. A. and Brearley A. J. (2018) *Meteorit. Planet. Sci.* 53:2078–2106. [10] Davidson J. et al. (2019) *Geochim. Cosmochim. Acta* 265:259– 278. [11] Davidson J. et al. (2019) *Geochim. Cosmochim. Acta* 267:240–256. [12] Singerling S. A. and Brearley A. J. (2020) *Meteorit. Planet. Sci.* 55:496–523. [13] Schrader D. L. et al. (2021) *Geochim. Cosmochim. Acta* 303:66–91. [14] Holt M. C. and Herd C. D. K. (2022) *Meteorit. Planet. Sci.* 57:1267–1287.

Acknowledgements: We thank the Smithsonian Institution, NASA/NSF, the ASU Buseck Center for Meteorite Studies (BCMS), and the National Institute of Polar Research (NiPR) for the loan of the meteorites used in this study, and NASA grant NNX17AE53G (DLS PI, TJZ Co-I) and the BCMS for funding this research. US Antarctic meteorite samples are recovered by the Antarctic Search for Meteorites (ANSMET) program which has been funded by NSF and NASA, and characterized and curated by the Department of Mineral Sciences of the Smithsonian Institution and Astromaterials Curation Office at NASA Johnson Space Center.

¹H and ¹³C Solid state Nuclear Magnetic Resonance (NMR) spectroscopy of an HCl extracted Ryugu C0002 particle

G. D. Cody¹, H. Yabuta², and the Hayabusa2-initial-analysis IOM team

¹Earth and Planets Laboratory, Carnegie Institute for Science, Washington, DC, USA ²Hiroshima University, Hiroshima, Japan

Introduction: ¹H and ¹³C solid state NMR studies of extraterrestrial organic solids (Insoluble Organic Matter, IOM) in carbonaceous chondritic meteorites has the potential to reveal the extent of IOM's molecular evolution that occurred due to parent body processing (largely hydrothermal) in the interior of the original planetesimal from which the meteorite was derived. For example ¹H and ¹³C NMR studies of IOM from CR, CI, CM, and an ungrouped C meteorites (Tagish Lake, TL) reveal that there is a wide range of molecular evolution where the least evolved was the CR IOM and the degree of molecular evolution increased from CI to CM to TL (Cody and Alexander, 2005). Subsequent NMR studies of discrete TL clasts with differing degrees of alteration revealed a high degree of molecular evolution across them (Herd et al., 2011). In all previous studies, relatively large (10's of mg) samples of pure IOM were available (note for typical CC meteorites, recoverable IOM constitutes ~ 1 wt % of the meteorite, 10 mg of IOM would require ~ 1gm of meteorite). For studies of Ryugu we were provided with a single particle that had been treated with aqueous HCL (to remove any carbonate) from C0002 that was ~ 1 mg where in principle 10 ng of IOM is expected. Notwithstanding the obvious challenges we endeavored to see what could be seen.

Experimental: All NMR experiments were performed at the W. M. Keck Solid State NMR facility at the Earth and Planets Laboratory at a static magnetic field of 7.05 Tesla. ¹H NMR analysis was performed using 2.5 mm rotor diameter Magic Angle Spinning (MAS) probe with the resonant frequency of ¹H being 300 MHz. The samples were spun at 22 KHz to reduce line broadening associated with H dipolar coupling. In order to reduce ¹H background signal arising from hydrogen outside the rotor we applied the DEPTH pulse sequence. The rotors capable of spinning faster than 20 KHz use endcaps and drive tips made of an aromatic polymer, Torlon, that is inside the rotor and will contribute some background ¹H signal. This background signal is generally negligible with 10-20 mg of pure organic matter. With the very small Ryugu sample it was expected and observed that the Torlon's ¹H back ground signal would be substantial. ¹³C solid state NMR was attempted using a 5 mm probe (with MAS = 11.5 KHz) with Teflon (no H) inserts and a background suppression pulse scheme before Variable Amplitude Cross Polarization to maximize signal. We were unable to obtain any ¹³C signal which is not unexpected given how little organic carbon is in a 1 mg Ryugu sample. We are pleased to report that no sample was lost during transfer into and out of both rotors and the sample was returned to Japan intact and unperturbed by the analysis. Thus the sample handling protocols adopted were sufficient.

Results: As expected the ¹H NMR signal is dominated by ¹H in the aromatic polymer, Torlon (Fig.1), at 7.1 ppm. We do detect a ¹H NMR signal at 1.3 ppm that arises from the Ryugu particle. In previous ¹H studies of pure IOM, aliphatic H appears at 1.3 ppm, so it may be that we are detecting Ryugu's aliphatic H. Note that IOM's aromatic H peak lies exactly at 7.1 ppm so it coincides with the background signal. It is now known that Ryugu mineralogy contains considerable amounts of saponitic clays, with two ¹H peaks at 4 and 0.35 ppm (Levin et al. 2004), thus the H from this clay is expected to be ~ 10 X that in IOM. However we don't see any H's from saponitic clay (Fig. 1). The most likely explanation is that the iron content of clays in the Ryugu sample are high enough that paramagnetic Fe "spoils" the signal from saponite H's and as IOM largely exists in the matrix as discrete organic grains, IOM signal persists. ¹H NMR of natural montmorillonite exhibits no signal due to Fe cations in its structure (Levin et al. 2004).

It is tempting to subtract the background signal from the bkgd+Ryugu particle, when one does this one finds that the line width of the Torlon is slightly greater than that of Torlon+Ryugu signal such that obvious spectra subtraction artifacts eventually arise and place a maximum constraint on how much

background subtraction can be performed, without this constraint one could range from majority aromatic-H to nearly 100 % aliphatic-H, neither case having been observed in any previous studies of type 1 and 2 chondritic IOM. Previous ¹H NMR analyses of IOM (Cody and Alexander, 2005; Herd et al. 2011) have been shown that there is a strong linear correlation between the Fraction of either aliphatic or aromatic H (F_{ARO-H}) with atomic H/C (*100) (see Fig.2) and with the fraction of aromatic carbon (F_{ARO-C}). Thus, using the restriction of maximum background subtraction we can place a minimum constraint on F_{ARO-H} of 0.5 (there is no restriction on how large F_{ARO-H} could be beyond assuming that there was no Torlon background). This places a maximum constraint of H/C*100 being 58 (there is no constraint on how low H/C*100 could be). Similarly, we can constrain a minimum as to how low F_{ARO-C} could be at 0.64 (the only constraint as to how high it could be is controlled by the 1.3 ppm feature). These values would suggest that Ryugu's IOM has slightly greater molecular evolution than what has been observed in CM and CI derived IOM (Cody and Alexander 2005), but much less than observed for the most molecularly evolved Tagish Lake IOM (Fig. 2).



This study demonstrates that it is possible to obtains ¹H NMR spectra of Ryugu samples. In the future, if it were possible to obtain 100 mg of Ryugu particles, 1 mg of pure IOM could be isolated. This would increase the ¹H signal by 100 X vastly reducing the background signal. We have obtained fairly high quality ¹³C NMR spectra on mg quantities of IOM, so additional molecular information would be obtained directly. Alternatively, if 20 mg of HCL extracted Ryugu particles were available (our 2.5 mm rotors can only handle 20 mg) these could be analyzed directly where the ¹H signal would be ~ 20 X that observed in Fig. 1. The advantage to this later approach would be that NMR is non-destructive and the sample would be available for other analyses by other researchers. **References:**

Cody, G.D. and Alexander, C.M.O.D. (2005) NMR studies of chemical structural variation of insoluble organic matter from different carbonaceous chondrite groups. Geochimica et Cosmochimica Acta 69, 1085-1097.

Herd, C.D.K., et al. (2011) Origin and evolution of prebiotic organic matter as inferred from the Tagish Lake meteorite. Science-SOM 332.

Levin et al. (2004) J. Applied Physics, 96, 5685

Oxygen isotope analyses of magnetite in Ryugu

Noriko T. Kita¹, Kouki Kitajima¹, Kazuhide Nagashima², Noriyuki Kawasaki³, Naoya Sakamoto³, Hisayoshi Yurimoto³,

The Hayabusa2-initial-analysis chemistry team, The Hayabusa2-initial-analysis core.

¹Department of Geoscience, University of Wisconsin-Madison, USA ²University of Hawaii, USA and ³Hokkaido University, Japan

Samples from the CI-like asteroid Ryugu consist mainly of minerals that were produced by aqueous alteration in its parent asteroid, such as phyllosilicates, dolomite, magnetite, and pyrrhotite [1]. A secondary ion mass spectrometer (SIMS) has been used to analyze in-situ oxygen 3-isotope ratios (δ^{17} O and δ^{18} O) of these alteration minerals in order to understand the aqueous activity that Ryugu parent body had experienced. Yokoyama et al. [1] reported δ^{17} O, δ^{18} O, and Δ^{17} O (= δ^{17} O – 0.52× δ^{18} O) of dolomite and magnetite in the polished section A0058-C1001 of Ryugu along with those in the Ivuna CI chondrite. Nagashima et al. [2] reported δ^{17} O, δ^{18} O, and Δ^{17} O of dolomite, calcite, and magnetite in the Ryugu polished section C0002-C1001. In A0058-C1001, a pair of magnetite and dolomite grains were found within 100 µm of each other and with indistinguishable Δ^{17} O values of ~ 0‰. By applying oxygen isotope thermometry between dolomite and magnetite, [1] estimated the temperature of co-precipitation of the Ryugu dolomite and magnetite, $37\pm10^{\circ}$ C. Oxygen isotope analyses from another magnetite grains in Ryugu and Ivuna show a significant range of δ^{18} O and Δ^{17} O [1-2], suggesting magnetite might have recorded multiple stages of aqueous activity on the Ryugu and Ivuna parent asteroid(s).

SIMS oxygen isotope analyses of magnetite are known to produce analytical artifacts due to crystal orientation that can degrade the analytical reproducibility of δ^{18} O (2–3‰ in 2SD [3]), though the effect is mass-dependent and would not affect Δ^{17} O. Huberty et al. [3] used lower primary ion acceleration voltage in the Cameca IMS 1280 (changed from 10 kV to 3 kV) and improved the analytical reproducibility (0.7‰; 2SD), likely related to lower total impact energy and smaller incident angle of primary ions to sample surface. Here, we report a new set of SIMS oxygen 3-isotope analyses of magnetite in the Ryugu samples using the IMS 1280 at the University of Wisconsin-Madison under 3 kV primary acceleration voltage in order to obtain higher accuracy in δ^{18} O analyses.

We analyzed magnetite grains (typically $\leq 10 \ \mu$ m) from two polished sections of Ryugu, A0058-C1002 and C0002-C1001. The primary Cs⁺ ion beam was accelerated by +3 kV at the Cs ion source and focused to sample surface (at -10 kV) resulting in an impact energy of 13 keV. The primary beam was focused to 3 μ m with 14 pA intensity and rastered over 2 μ m squares, which resulted in 3×4 μ m SIMS pits after 10 min of analysis (Fig. 1). The ¹⁶O⁻ intensity was typically 1.7×10⁷ cps for magnetite. Other conditions were similar to those in [4]. The external reproducibility of δ^{18} O from 30 randomly oriented magnetite standard 5830 [3] was 1.0‰ (2SD), similar to both internal and external errors of a single grain (0.7–0.9‰). The external reproducibility of δ^{17} O and Δ^{17} O were ~1.5‰. After the analyses, SIMS pits were examined using a Hitachi S-3400 scanning electron microscope (SEM).



Figure 1. Two types of SIMS pit textures for magnetite grains in Ryugu after SIMS oxygen isotope analyses. Magnetite grains showing smooth SIMS pit textures (A) often show well-defined crystal faces, indicating slow growth. Magnetite grains showing porous SIMS pit textures (B) often show fibrous textures, suggesting rapid growth.

SEM observations show that all SIMS spots were within magnetite grains analyzed and none of the analyses were rejected. There are two types of pit textures, smooth and porous, which often correspond to magnetite with defined crystal faces and fibrous grains, respectively (Fig. 1). Results of analyses are shown in Fig. 2. and compared to magnetite analyses reported by [1] using 20 keV impact energy. Both datasets are very similar to each other, though new data show two groups of magnetite analyses according to the range of δ^{18} O values, from -4‰ to -1‰ and from +3‰ to +7‰, which correspond to magnetite grains with smooth and porous pit textures, respectively. The Δ^{17} O values of the lower δ^{18} O group vary from 0‰ to +2‰, while the higher δ^{18} O group shows consistently higher Δ^{17} O values (2–3‰). Some of the smooth magnetite analyses in

A0058-C1002 are very similar to those equilibrated with dolomite in A0058-C1001 ($\delta^{18}O \sim -3\%$ and $\Delta^{17}O \sim 0\%$). Assuming that ¹⁶O-poor H₂O ice accreted to the Ryugu parent asteroid, melted, and interacted with relatively ¹⁶O-rich anhydrous silicates [2], these results suggest that porous (fibrous) magnetite with high $\Delta^{17}O$ values formed during an early stage of aqueous activity, while other magnetite without porosity mostly formed later stages and likely in oxygen isotope equilibrium with other minerals. However, small variations in $\Delta^{17}O$ values among magnetite with lower $\delta^{18}O$ may suggest that fluid activity in the Ryugu parent asteroid could have been localized and the oxygen isotope ratios of the fluid might have been variable.



Figure 2. SIMS oxygen 3-isotope analyses of minerals in Ryugu. (A, B) Analyses of magnetite and dolomite in A0058-C1001 and Ivuna CI chondrite [1]. (C, D) Analyses of magnetite using 13 keV impact energy (This work). TF and CCAM are terrestrial mass fractionation and Carbonaceous chondrite anhydrous mineral lines [5], respectively.

References

[1] Yokoyama T. et al. Science, 10.1126/science.abn7850 (2022). [2] Nagashima K. et al. this volume. [3] Huberty J. M. et al. Chemical Geology, 276, 269–283 (2010). [4] Ushikubo T. et al. Geochim. Cosmochim. Acta 90, 242–264 (2012). [5] Clayton R. N. et al. Earth Planet. Sci. Lett. 34, 209–224 (1977).

The Hayabusa2-initial-analysis chemistry team: T. Yokoyama, K. Nagashima, Y. Abe, J. Aléon, C.M.O'D. Alexander, S. Amari, Y. Amelin, K. Bajo, M. Bizzarro, A. Bouvier, R. W. Carlson, M. Chaussidon, B.-G. Choi, N. Dauphas, A.M. Davis, T. Di Rocco, W. Fujiya, R. Fukai, I. Gautam, M.K. Haba, Y. Hibiya, H. Hidaka, H. Homma, P. Hoppe, G.R. Huss, K. Ichida, T. Iizuka, T.R. Ireland, A. Ishikawa, M. Ito, S. Itoh, N. Kawasaki, N.T. Kita, K. Kitajima, T. Kleine, S. Komatani, A.N. Krot, M.-C. Liu, Yuki Masuda, K.D. McKeegan, M. Morita, K. Motomura, F. Moynier, I. Nakai, A. Nguyen, L. Nittler, M. Onose, A. Pack, C. Park, L. Piani, L. Qin, S.S. Russell, N. Sakamoto, M. Schönbächler, L. Tafla, H. Tang, K. Terada, Y. Terada, T. Usui, S. Wada, M. Wadhwa, R.J. Walker, K. Yamashita, Q.-Z. Yin, S. Yoneda, E.D. Young, H. Yui, A.-C. Zhang, H. Yurimoto.

The Hayabusa2-initial-analysis core: S. Tachibana, T. Nakamura, H. Naraoka, T. Noguchi, R. Okazaki, K. Sakamoto, H. Yabuta, H. Yurimoto, Y. Tsuda, S. Watanabe.

Magnetite and non-magnetite framboids in Ryugu sample

Yuki Kimura¹, Takeharu Kato², Satoshi Anada², Ryuji Yoshida², Kazuo Yamamoto², Toshiaki Tanigaki³, Tetsuya Akashi³, Hiroto Kasai³, Tomoki Nakamura⁴, Toru Matsumoto⁵, Takaaki Noguchi⁵, Masahiko Sato⁶, Tomoyo Morita⁴, Mizuha Kikuiri⁴, Kana Amano⁴, Eiichi Kagawa⁴, Hisayoshi Yurimoto⁷, Ryuji Okazaki⁸, Hikaru Yabuta⁹, Hiroshi Naraoka⁸, Kanako Sakamoto¹⁰,

Sei-ichiro Watanabe¹¹, Yuichi Tsuda¹⁰, and Shogo Tachibana^{5,10}

¹Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan

²Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan

³Research & Development Group, Hitachi, Ltd., Hatoyama, Saitama, 350-0395, Japan

⁴Department of Earth Sciences, Tohoku University, Sendai 980-8578, Japan

⁵Division of Earth and Planetary Sciences, Kyoto University; Kyoto 606-8502, Japan

⁶Department of Earth and Planetary Science, The University of Tokyo, Tokyo 113-0033, Japan

⁷Department of Natural History Sciences, Hokkaido University, Sapporo 060-0810, Japan

⁸Department of Earth and Planetary Sciences, Kyushu University, Fukuoka 819-0395, Japan

⁹Graduate School of Advanced Science and Engineering, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

¹⁰Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, Sagamihara 252-5210, Japan

¹¹Department of Earth and Environmental Sciences, Nagoya University, Nagoya 464-8601, Japan

There are many magnetite (Fe₃O₄) particles found in chondrites together with clay minerals [1,2] suggesting that they were formed by aqueous alteration [3]. Magnetite can record magnetic field environment at the time of its formation as natural remanent magnetization [4]. Therefore, it is important to know when and how magnetite particles formed in order to estimate the magnetic field environment of the early solar system and to understand the physical evolutionary processes that have a relationship with the magnetic field. A large amount of magnetite is also found in Ryugu samples [5] and it has been confirmend that submicron-scale magnetite is a main carrier of the natural remanent magnetization [6]. We conducted electron holography to visualize the magnetic field (vortex structure) and an external leakage of the magnetic field that could be a carrier of remanent magnetization [5,6]. In addition to the typical framboidal magnetite, here we report the discovery of a flamboidal magnetite-like mineral that does not exhibit a magnetic field in a sample.

Figure 1 shows a part of a typical flamboidal magnetite in an ultrathin section extracted from a Ryugu sample A0064-FO007 using a cryo-focused ion beam (FIB; NB5000, Hitachi High-Tech) under -90°C at Japan Fine Ceramics Center (JFCC). The bright-field transmission electron microscope (TEM) image shows at least eight magnetite particles of ~1 µm in diameter surrounded by phyllosilicates at the bottom part. The upper side of the image corresponds to the surface of the parent sample before they were extracted. The strong contrast area marked with W on the upper side is tungsten that was deposited before processing to prevent damage by FIB machining. Figures 1 i and ii show magnetic flux distribution images corresponding to two boxes observed by electron holography using a specially designed TEM (HF-3300, Hitachi High-Tech) at JFCC. The concentric stripes inside the particles represent the phase change due to magnetization, because the internal potential has been subtracted by taking images from the back and front. Namely, magnetite particles have a vortex magnetic domain structure. In addition, an external magnetic field can be seen on the outside of the particle. Magnetite particles are thought to have formed by aqueous alteration between 3.1-6.8 million years after the formation of first mineral, calcium–aluminium-rich inclusion, at the beginning of the Solar system [7]. The external magnetic field is a result of the magnetic field environment that existed when magnetite formed by aqueous alteration in the parent body of Ryugu [6].

Figure 2 shows a high-angle annular dark field scanning TEM (STEM-HAADF) image of an ultrathin section of a portion of a flamboid from a different fragment in the Ryugu sample A0064-FO007, which was broken into several pieces when fixed to the indium plate for easier handling, extracted using the cryo-FIB. Similar to the Fig. 1, several spherical particles of ~ 1 µm can be seen. Corresponding magnetic flux distribution image has been shown in Fig. 2B. Unlike i and ii in Fig. 1, the contrast within the particles is flat and there is no magnetic domain structure characteristic of magnetite. Elemental composition analysis using an energy dispersive X-ray spectroscopy (EDS) confirms that the particles are iron oxide (Fig. 2C). Although it looks like typical framboidal magnetitee, electron energy-loss spectroscopy analysis indicated that the bonding states of oxygen and iron were clearly different from that of magnetite. The observed bonding state was consistent with

wüstite ($Fe_{1-y}O$), which is antiferromagnetic and does not acquire remanent magnetization. Although particles appeared to be framboidal magnetite based on a micrograph, these particles were actually wüstite. We refer to this particle as framboidal pseudo-magnetite.

The framboidal pseudo-magnetite is present on the top surface of the host sample, and the bottom is a matrix composed mainly of phyllosilicates. TEM-EDS mapping showed iron-rich region that may be leached from the pseudo-magnetite into the matrix. Magnetite with porous surface texture and metallic iron has been found in the analysis by Sand team [8]. Sample analysis in the first Hayabusa mission has reported the formation of iron particles on a silicate grain by space weathering [9]. In case of our pseudo-magnetite, although the presence of metallic iron particulates was also confirmed, they appear to be coarser than those found in previous studies and are We expect that framboidal pseudo-magnetite may also have formed by space weathering of magnetite, but different mechanisms from other two samples. Similar pseudo-magnetite particles have also been found in other FIB thin sections. We will discuss the formation process of framboidal pseudo-magnetite at the symposium.



Figure 1. TEM image of a thin section of a typical magnetic framboid extracted from the sample A0064-FO007 and its characteristic magnetic structure observed by electron holography. Arrows show the direction of the magnetic flux.



Figure 2. Framboidal pseudo-magnetite. A. STEM-HAADF image of a thin section of a fragment from the sample A0064-FO007 prepared by FIB. B. Magnetic flux distribution image obtained from the reconstruction of remanent magnetic state of magnetites observed by electron holography. Uniform contrast indicate that the particles are not magnetic minerals. C. Corresponding elemental mapping of iron.

The authors acknowledge the Ministry of Education, Culture, Sports, Science and Technology (MEXT) (grants JPMXS0450200421, JPMXS0450200521).

References

[1] Brown, P. G. et al. 2000. Science 290:320. [2] Zolensky, M. E. et al. 2002. Meteoritics & Planetary Science 37:737. [3] Kerridge, J. F., Mackay, A. L. & Boynton, W. V. 1979. Science 205:395. [4] Dunlop, D. J., and Özdemir, Ö. 1997. Rock Magnetism: Fundamentals and Frontiers, Cambridge University Press, 573 pp. [5] Nakamura, T. et al. 2022. Science doi.10.1126/science.abn8671. [6] Sato, M. et al 2022. Journal of Geophysical Research under review. [7] Yokoyama T. et al. 2022. Science doi.10.1126/science.abn7850. [8] Matsumoto, T. et al. 2022. LPSC 1693. [9] Noguchi, T. et al. 2011. Science 333:1121.

Nitrization of magnetite on the surface of C-type asteroid Ryugu.

T. Matsumoto^{1,2}, T. Noguchi², A. Miyake², Y. Igami², M. Haruta³, Y. Seto⁴, M. Miyahara⁵, N. Tomioka⁶, D. Harries⁷,

the Min-Pet Fine sub-team and the Hayabusa 2 initial analysis core.

¹The Hakubi Center for Advanced Research, Kyoto University, ²Division of Earth and Planetary Sciences, Kyoto University,

³Institute for Chemical Research, Kyoto University. ⁴Department of Geoscience, Osaka Metropolitan University, ⁵Graduate

School of Advanced Science and Engineering, Hiroshima University, ⁶Japan Agency for Marine-Earth Science and Technology, ⁷Luxembourg Institute of Science and Technology, European Space Resources Innovation Centre.

(E-mail: matsumoto.toru.2z@kyoto-u.ac.jp)

L-man. maisumoto.toru.22@kyoto-u.ac.jp

Introductions: JAXA's Hayabusa2 spacecraft recovered samples from the C-type carbonaceous asteroid Ryugu [1]. The initial analysis of the Ryugu samples showed that they correspond to CI carbonaceous chondrite meteorites [2, 3]. Because the Ryugu samples were collected from the surface of Ryugu, they provide us with the first opportunity to understand phenomena occurring at the surface of the carbonaceous asteroid. Materials on airless bodies are gradually modified by exposure to solar wind and micrometeorite impacts. This process is called space weathering [4]. The evidence of space weathering has been found in Ryugu samples through the initial analysis. Dehydration of the phyllosilicate surface is the major modification by space weathering on Ryugu [5]. In addition, loss of volatile elements including hydrogen, carbon, oxygen, and sulfur have been identified in space-weathered anhydrous minerals [6]. In this study, we focused on the surface modifications of Ryugu samples related to nitrogen. It has been suggested that the nitrogen isotopes in Ryugu samples are affected by surface processes [7]. Thus far, there is no mineralogical observation related to the behavior of nitrogen on Ryugu's surface. The goal of this study is to understand how nitrogen is involved in the chemical evolution of regolith on Ryugu. Here, we describe nitrogen concentration on the surfaces of space-weathered magnetites in Ryugu samples.

Methods: We investigated three fine Ryugu grains, A104-021012, A104-028098, and A104-026006. These three grains were preserved in a glove-box filled with purified nitrogen gas. The grains are attached on gold plates using epoxy resin, and were observed by scanning electron microscopy (SEM) to analyze their surface morphologies. After the surface observation, electron-transparent sections were extracted from the grain surface using a focused ion beam system. The extracted sections were observed by scanning transmission electron microscopy (TEM/STEM). We applied 4D-STEM imaging (electron diffraction mapping using nano-beam) to identify nanometer-sized inclusions.

Results: FIB sections from A104-021012 and A104-028098 include assemblages of framboidal magnetites with 0.5 to 1 μ m in diameter. An FIB section from A104-026006 contains a spherulitic magnetite with 10 μ m in diameter. These magnetite grains are embedded in the fine-grained matrix composed mainly of phyllosilicates. Their exposed surfaces show porous textures that suggest surface modifications. STEM-EDS analysis showed that magnetites in A104-0210012 have the uppermost layers showing high Fe/O ratio. Electron diffraction patterns corresponding to body-centered cubic (bcc) iron were obtained from the iron-rich layer. Magnetite grains in A104-026006 and A104-028098 also have iron-rich layers at the surface. In addition, the iron-rich layers are also rich in sulfur and nitrogen (Fig.1). Electron diffraction patterns from the iron-rich layer in A104-026006 indicate the appearance of bcc-iron metal and troilite. Additionally, we obtained electron diffraction patterns showing a cubic crystal that has the lattice parameter corresponding to roaldite (Fe4N). Thin coatings of silicon and magnetium were identified on the modified magnetites in A104-021012, A104-028098, and A104-026006.

Discussion: The increase of Fe/O ratio and the formation of iron metals at the magnetite surface is likely due to selective loss of oxygen from magnetite caused by solar wind implantation and micrometeorite bombardments [6]. Because sulfur and nitrogen are not included in bulk magnetite, these elements would have been supplied to the exposed surfaces of magnetite. Impact vapors produced from carbonaceous chondrite likely have high sulfur fugacity enough to form iron sulfides [8]. Therefore, the sulfur enrichment and troilite formation at the magnetite surface in Ryugu samples may have been caused by sulfization of iron metals, when the space-weathered magnetite is exposed to vapors formed by micro-impacts. Iron nitrides have been identified in carbonaceous chondrites as the products formed by gas-metal interaction in the NH₃-rich nebular gas [9], and in iron meteorites as metamorphic products under high pressure [10]. In contrast, iron nitrides we observed are likely associated with space weathering of magnetite and may have been formed thorough surface processes on Ryugu. One possible mechanism for the concentration of nitrogen is implantation of solar wind nitrogen as suggested in lunar regolith samples from the Moon [11]. Another possible mechanism is the chemical reaction between space-weathered magnetites and nitrogen compounds included in impact vapors on Ryugu. Because iron metal is highly reactive with ammonia gas that leads to the formation of iron nitrides [12], nitrization of iron metals on space weathered magnetites may have occurred when the surfaces

are exposed to ammonia-beaning gases. Ammonia may be included in impact vapors from CI chondrite materials [13]. In addition. ammonia-rich vapors can be produced from nitrogen-rich organic materials, and/or ammonium compounds, such as NH₄⁺ salts and NH₄⁺ phyllosilicates, that could be supplied to the Ryugu's surface as interplanetary dust. Our observation will shed light on the migration of nitrogen and/or influx of nitrogen on the carbonaceous asteroid.



Figure 1. Elemental maps of magnetite surface (A104-026006) obtained by STEM-EDS analysis. Left, center, and right figures show the distributions of nitrogen, sulfur, and iron, respectively. SW-rim indicates the space-weathered rim enriched in iron, sulfur, and nitrogen. Mgt indicates magnetite.

References

- [1] Sugita S. et al. 2019. Science 364, 252.
- [2] Yokoyama T. et al. 2022. Science eabn7850.
- [3] Nakamura T. et al. 2022. Science eabn8671.
- [4] Pieters C. and Noble S. K. 2016. J. Geophys. Res. Planet 121, 1865-1884.
- [5] Noguchi T. et al. 2022. LPS LIII. Abstract #1747.
- [6] Matsumoto T. et al. 2022. LPS LIII, Abstract #1693.
- [7] Okazaki R. et al. 2022. LPS LIII, Abstract #. 1348
- [8] Thompson M. S. et al. 2019. Icarus 319, 499-511.
- [9] Harries D. et al. 2018. 81st Annual Meeting of The Meteoritical Society. Abstract #2067.
- [10] Buchwald V. F. and Nielsen H. P. 1981. LPS XII. pp. 112-114.
- [11] Hashizume K. et al. 2001. Science 290. 1142-1145.
- [12] Mittemeijer, E. J. & Slycke, J. T. 1996. Surf. Eng. 12, 152-162
- [13] Kuwahara H. and Sugita. S. 2015. Icarus 257. 290-301.

Neutron Capture ³⁶Cl in Ryugu Samples

Kunihiko Nishiizumi¹, Marc W. Caffee², Jozef Masarik³, Keisuke Nagao⁴, Ryuji Okazaki⁵, Hisayoshi Yurimoto⁶, Tomoki Nakamura⁷ Takaaki Noguchi⁸, Hiroshi Naraoka⁵, Hikaru Yabuta⁹, Kanako Sakamoto¹⁰, Shogo Tachibana^{11, 12}, Sei-ichiro Watanabe^{10, 12}, Yuichi Tsuda¹⁰

¹Space Sci. Lab., Univ. of California, Berkeley, CA 94720-7450, USA., ²Dept. of Phys. & Astro., Purdue Univ., West Lafayette, IN 47907-2036, USA., ³Comenius Univ., Batislava, Slovakia, ⁴KOPRI, Incheon 21990, Korea, ⁵Kyushu Univ., Fukuoka 819-0395, Japan, ⁶Hokkaido Univ., ⁷Tohoku Univ., ⁸Kyoto Univ., ⁹Hiroshima Univ., ¹⁰ISAS/JAXA, ¹¹Univ. of Tokyo, ¹²Nagoya 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. The 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]. The 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 (SCR) and galactic cosmic rays (GCR). 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. With this information we hope to better understand 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 TD 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 6 particles from Chamber C (C0106-09, -10, -11, -12, C0002-V01, and -V02) for measurements of cosmogenic radionuclides and noble gases. Each sample is several hundred µm in size.

As a part of initial analysis of Ryugu we have measured cosmogenic ¹⁰Be ($t_{1/2} = 1.36 \times 10^6 \text{ yr}$) [3], ²⁶Al (7.05 x 10⁵ yr) [4], and stable noble gases [5] in above samples. The Table 1 summarizes ²⁶Al, ¹⁰Be, and cosmogenic ²¹Ne concentrations in each sample. Based on those measurements, we found that sampling depth of A0105-19 was 10-15 g/cm² and A0105-20 was ~5 g/cm². The exposure ages of both A0105 samples were 6.4-7.5 Myr. The chamber A samples were exposed to cosmic rays at Ryugu's near surface (~10 cm), as expected, and had similar exposure ages of ~7 Myr. On the other hand, the four C0106 particles were exposed at depth of ~50, 110, 130, and 145 g/cm² respectively and had exposure ages of ~1.6, 3.2, 4.5, and 5.8 Myr respectively. Our results indicate that Chamber C samples are mixture of particles ejected from various depths on Ryugu by the SCI impact. It is noteworthy that all four particles had different exposure ages on Ryugu. Exposure depths of each sample are also shown in Table 1.

To further study of the exposure condition of Ryugu surface materials, we analyzed cosmogenic 36 Cl (3.01 x 10⁵ yr). After dissolution of each sample with a few drops of HF-HNO₃ mixture, Cl was separated as AgCl prior to Be and Al separation [3, 4]. After chemically purified AgCl, the concentration of 36 Cl was measured by accelerator mass spectrometry (AMS) at Purdue University [6], using a 36 Cl AMS standard [7] for normalization. The concentrations of 36 Cl (dpm/kg) in each Ryugu sample are shown in Table 1 along with that of Nogoya CM2 chondrite for validation. The 36 Cl concentrations in all Ryugu samples are more than an order of magnitude higher than that of Nogoya. The dominant production pathway for 10 Be and 26 Al is by high-energy neutron spallation reactions. Although 36 Cl can be produced by both thermal neutron capture reaction, 35 Cl (n, γ) 36 Cl, and high-energy neutron spallation on K, Ca, and Fe, the thermal neutron production of 36 Cl is dominant owing to the high H and Cl concentrations in Ryugu. Using the MCNP Code System [8], we calculated GCR production rate of 36 Cl by spallation reactions for a body having a 2 π geometry with Ryugu's chemical compositions [9]. The obtained production rates are 5.4 36 Cl atom/min/kg at surface to 3.3 at ~150 g/cm². The thermal neutron production of 36 Cl is calculated by subtracting spallation contribution from measured value and normalized to Cl concentrations in Ryugu are extraordinarily high. Among carbonaceous chondrites, only the CI chondrite Orgueil is higher, having 160 ± 1 dpm/kg (unpublished), assuming exposure in a 4π geometry. This corresponds to 220 ± 3 dpm 36 Cl /g Cl assuming 700 ppm Cl in Orgueil.

Assuming a chemical compositions for each particle the same as the bulk analysis of Ryugu [9], the thermal neutron produced ³⁶Cl in Ryugu is maximum at slightly below 100 g/cm² or between depth of C0106-10 and -11. The depth of maximum production for the low-energy neutron capture reaction on Ryugu is shifted toward surface compared to that of the Moon (~150
g/cm²). This occurs because Ryugu contains high H (0.94 %) and C (4.6 %) [9] which are effective moderators of neutrons. Since we don't have exact Cl concentration in each particle, it is hard to compare observed ³⁶Cl concentration to model calculation such as MCNP code system at present. Although we are planning measurements of thermal neutron capture ⁴¹Ca ($t_{1/2} = 0.10$ Myr) in Ryugu, it requires larger sample size than this work because low thermal neutron capture cross section on ⁴⁰Ca compared to that of ³⁵Cl (0.43 b vs. 43.6 b) and lower AMS sensitivity of ⁴¹Ca measurements.

| Table 1. Cosmog | enic nuclic | le ³⁶ Cl, ²⁶ Al, | ¹⁰ Be, and ²¹ Ne c | oncentrations in | Ryugu samples a | and Nogoya CM2 | chondrite. |
|-----------------|-------------|--|--|---------------------------------|-------------------------------|------------------------|--------------------------------|
| Sample | Mass | Depth ^a | ³⁶ Cl ^b | ³⁶ Clth ^c | ²⁶ Al ^d | $^{10}\mathrm{Be^{e}}$ | ²¹ Nec ^f |
| | (µg) | (g/cm^2) | (dpm/kg) | (dpm/g Cl) | (dpm/kg) | (dpm/kg) | (10^{-9} cm^3) |
| | | | | | | | STP/g) |
| A0105-19 | 242.9 | 5 | 31.1±2.3 | 33±3 | 27.1±1.1 | 12.76 ± 0.37 | 7.55 |
| A0105-20 | 206.1 | 10-15 | 28.9±1.9 | 30±2 | 33.3±1.8 | 12.75±0.29 | 7.75 |
| C0106-09 | 122.8 | 50 | 72.0±6.2 | 86 ± 8 | 23.3±1.4 | $7.10{\pm}0.30$ | 1.79 |
| C0106-10 | 154.3 | 110 | 116.5±6.9 | 144±9 | 25.7±1.3 | 7.48 ± 0.26 | 3.58 |
| C0106-11 | 189.8 | 130 | 23.4±2.5 | 26±3 | 25.5±1.2 | 7.21±0.43 | 5.07 |
| C0106-12 | 959.8 | 145 | 24.2 ± 0.9 | 27±1 | 23.8 ± 0.7 | 7.36 ± 0.33 | 6.54 |
| C0002-V01 | 45.3 | 125 | 30.1±4.3 | 34±6 | 24.9 ± 1.9 | 8.29 ± 0.95 | - |
| C0002-V02 | 11.1 | 125 | 11±13 | - | 21.9±5.1 | 7.87 ± 1.80 | - |
| Nogoya CM2 | 459.4 | - | 2.2 ± 0.5 | - | - | 2.09 ± 0.13 | - |
| Nogoya CM2 | 343.7 | - | 2.2 ± 0.6 | - | $7.7{\pm}0.5$ | 2.12 ± 0.09 | - |
| Nogoya CM2 | 204.9 | - | 0.6 ± 1.0 | - | 9.1±0.6 | 2.00±0.13 | - |

^aEstimated depth based on ¹⁰Be and ²⁶Al [4]; ^bThis work; ^cAfter subtraction of spallation component (see text); ^d[4]; ^e[3]; ^f[5].

Acknowledgments: We thank Hayabusa2 project and initial analysis team, especially Hayabusa2 curation members. Z. Nett and K. C. Welten helped a part of laboratory works. Nogoya was obtained from Field Museum of Natural History. This work was supported by NASA's LARS program.

References

[1] Arakawa M. et al. 2020. Science 368, 67-71. [2] Tsuda Y. et al. 2020. Acta Astronautica 171, 42-54. [3] Nishiizumi K. et al. 2021. Hayabusa Symposium 2021 S3-1. [4] Nishiizumi K. et al. 2022. Lunar Planet. Sci. 53, #1777. [5] Nagao K. et al. 2022. Meteor. Planet. Sci. 57, A337 #6320. [6] Sharma P. et al. 2000. Nucl. Instrum. Methods Phys. Res. B 172, 112-123. [7] Sharma P. et al. 1990. Nucl. Instrum. Methods Phys. Res. B52, 410-415. [8] Masarik J. and Reedy R. C. 1994. Geochim. Cosmochim. Acta 58, 5307-5317. [9] Yokoyama T. et al. 2022. Science 10.1126/science.abn7850.

Lithological variation of asteroid Ryugu samples returned by the Hayabusa2 spacecraft: Assessment from the 18 particles distributed to the initial analysis "Stone" team

T. Mikouchi¹, H. Yoshida¹, T. Nakamura², M. Matsumoto², A. Tsuchiyama^{3,4}, J. Matsuno³, K. Tsutsui², M. E. Zolensky⁵,

D. Nakashima², M. Masuda¹, K. Hagiya⁶, M. Kikuiri², T. Morita², K. Amano², E. Kagawa², H. Yurimoto⁷, T. Noguchi⁸,

R. Okazaki⁹, H. Yabuta¹⁰, H. Naraoka⁹, K. Sakamoto¹¹, S. Tachibaba^{1,11}, S. Watanabe¹² and Y. Tsuda¹¹

¹University of Tokyo, Japan (mikouchi@um.u-tokyo.ac.jp), ²Tohoku University, Japan, ³Ritsumeikan University, Japan,
 ⁴Guangzhou Inst. of Geochemistry, Chinese Academy of Sciences, China, ⁵NASA John Space Center, USA, ⁶University of Hyogo, Japan, ⁷Hokkaido University, Japan, ⁸Kyoto University, Japan, ⁹Kyushu University, Japan, ¹⁰Hiroshima University, Japan, ¹¹ISAS/JAXA, Japan, ¹²Nagoya University, Japan

Introduction: JAXA's Hayabusa2 spacecraft successfully returned ~5.4 g of C-type asteroid Ryugu materials on Dec. 2020 [e.g., 1] and the recovered samples were extensively analyzed by initial analysis teams and Phase2 curation teams. The reported results show that Ryugu samples are similar to CI chondrites in chemistry and mineralogy, showing evidence for aqueous alteration in the parent body [e.g., 2,3]. As a "stone" team of the initial analysis, we received 18 coarse particles (>1 mm) of Ryugu samples to characterize their mineralogy and petrology. We found that the samples were breccias of mm-to-sub mm size clasts. All of the clasts are mainly composed of Mg-Fe phyllosilicates, but the alteration degree appears slightly different from one clast to another [3]. Here we report a lithological variation of Ryugu samples to propose their reasonable lithological classification based upon different mineral assemblages and associated mineralogy, which will provide important information to elucidate the formation and evolution of the Ryugu parent body.

Samples and Methods: We analyzed 18 coarse particles that are 7 Chamber A particles (A0026, A0055, A0063, A0064, A0067, A0094 and A0106) and 11 Chamber C particles (C0002, C0023, C0025, C0033, C0040, C0046, C0055, C0061, C0076, C0103 and C0107), respectively. Chamber A particles are from the first touchdown site while Chamber C particles are from the second touchdown site where the SCI impact experiment was carried out to attempt to collect subsurface materials [4]. In total 52 polished sections were prepared from all particles. The JEOL JXA-8530F field emission electron microprobe (FE-EPMA) at Univ. of Tokyo was employed for both WDS X-ray mapping and quantitative analyses of constituent minerals using well-characterized natural and synthetic standards after observation using back-scattered electron (BSE) images. X-ray mapping was carried out with

a 1-3 μ m interval to understand distribution of constituent minerals.

Results: Most of the analyzed polished sections show brecciated textures on a scale of mm to μ m (Fig. 1). In spite of such brecciation, all clasts are mainly composed of Mg-Fe phyllosilicates that are TEM-scale mixtures of serpentine and saponite [3]. Other minor phases include carbonates (Cacarbonates, magnesite ("breunnerite") and dolomite), magnetite, Fe,Ni sulfides (pyrrhotite and pentlandite), Ca phosphate, olivine, pyroxene, Mg,Na phosphate, Mn-rich ilmenite, spinel, chromite, Fe,Ni phosphide and Fe,Ni metal.

Among these accessory phases, carbonates exhibit the most remarkable mineralogy because they are present as different mineral species in each clast, which appears to be related to the degree of aqueous alteration [3]. When Ca carbonates are present, olivine and pyroxene are also associated, suggesting that



Fig. 1. Mg and Fe X-ray maps (above) and MgCaSi and FeNiS composite RGB maps (below) of the A0055-01 polished section. In this section lithologies III, V and VI were found (noted in the Fe map (upper right)). Yellow~green phases in the MgCaSi map are dolomites. The same analysis was done for all other polished sections.

such clasts are less altered compared to the others. In fact, the modeling calculation of progressive aqueous alteration of chondritic anhydrous minerals predicts that only Ca carbonates form when the water to rock ratio is low [3], resulting in less aqueous altera-

tion. Such modeling is in accordance with the Ryugu sample observation that olivine and pyroxene are absent in clasts when Ca carbonates are absent and only dolomite and/or magnesite are present. This observation indicates that olivine and pyroxene are unaltered phases that survived aqueous alteration in the parent body. The more water-rich alteration condition forms dolomite and subsequently magnesite [3]. Rimming of magnesite on dolomite is observed, further supporting this proposal (Fig. 2). Similarly, Mg,Na phosphate is absent when Ca carbonates are absent. The presence of Fe,Ni phosphide and Fe,Ni metal is associated with the presence of olivine and pyroxene. In clasts with these phases, Ca phosphate is rare, suggesting that Ca phosphate formed by aqueous alteration of Fe,Ni phosphide and Ca-bearing phases. As noted in [3], there is the rare presence of olivine-rich clasts that appears to be the least altered clasts in Ryugu samples. In these clasts, dolomite and magnesite are rare and GEMS-like material is present [3].



Fig. 2. BSE image of carbonates in A0067-02. Magnesite surrounds the dolomite core, suggesting formation of magnesite after dolomite.

Discussion and Conclusion: In summarizing the above observations, we tried to classify lithological variations of our coarse Ryugu particles based upon mineral assemblages and associated mineralogy, mostly using X-ray mapping results of FE-EPMA. The key mineral phases for this classification are olivine and carbonates. The presence/absence of olivine can broadly divide the clasts into two lithologies: olivine-bearing and olivine-free lithologies, corresponding to less altered and altered lithologies, respectively. Because olivine-bearing lithologies are rarer, olivine-free lithologies are major lithologies of Ryugu samples [3]. We assigned rare olivine-rich clasts as "lithology I" and the other olivine-bearing clasts as "lithology II". For olivine-free lithologies, the carbonate mineralogy can further divide them into four: dolomite-bearing ("lithology III"), dolomite+magnesite-bearing ("lithology IV" (Fig. 2)), carbonate aggregates ("lithology V") and carbonate-poor ("lithology VI"). We assigned lithology V clasts when carbonates show aggregate textures that are larger than 100 µm in size. Because we frequently found carbonate-poor clasts, we assigned lithology VI when carbonates are only ~<1 vol.% in abundance and small in size ($\sim <10 \ \mu m$). Except for these six types of different lithologies, there are exceptional lithologies such as coarse isolated mineral grains. The lithologies I to IV appear related to the degree of aqueous alteration by this order since the calculation of progressive aqueous alteration by increasing water to rock ratios predicts different carbonate species (Ca carbonate \rightarrow dolomite \rightarrow magnesite) matching with the observed carbonate mineralogy in these lithologies [3]. The lithologies V and VI would have been formed at somewhat different conditions other than lithologies III and IV, respectively. We checked the phyllosilicate compositions of different lithologies and found that phyllosilicates in olivine-bearing lithologies (I and II) were more Fe and Na-rich compared to those in olivine-free lithologies (III-VI). There are no clear compositional differences among phyllosilicates in lithologies III-VI, except that phyllosilicates in lithology VI are slightly poorer in Fe and Na compared to those in lithologies III-V.

Thus, we propose that the lithology of Ryugu samples can be divided into 7 types (lithology I, II, III, IV, V, VI and others) based upon mineralogy of constituent minerals in different clasts due to the brecciated nature of Ryugu samples. When we looked at 18 coarse Ryugu particles that we analyzed, we found that olivine and pyroxene are absent in our Chamber A particles, namely Chamber A particles include only lithologies III, IV, V, VI and others. In contrast, most of Chamber C particles contain olivine and pyroxene, which is lithology II in many cases. The largest section in our sample (C0002 plate 5) contains rare type lithology I clasts although they are small (~100 μ m). Therefore, we clearly see that there is a mineralogical difference between Chamber A and C particles. This observation may suggest heterogeneous distributions of materials with different degrees of aqueous alteration at the two different sampling sites. However, we cannot rule out the possibility of sampling bias because the samples analyzed are small. Also, it is unclear whether such lithological differences are related to the subsurface sampling at the second touchdown site by artificial crater formation.

References: [1] Yada T. et al. (2021) *Nat. Astron.* 6:214. [2] Yokoyama T. et al. (2022) *Science* 10.1126/science.abn7850. [3] Nakamura T. et al. (2022) *Science* 10.1126/science.abn8671. [4] Kadono T. et al. (2020) *Astrophys. Jour. Lett.*, 899, L22.

Non-destructive analysis of C-type asteroid Ryugu using negative Muon: Determination of bulk chemistry of Ryugu samples

*K. Terada¹, T. Nakamura², K. Ninomiya¹, T. Osawa³, T. Takahashi⁴, Y. Miyake⁵, S. Takeshita⁵, I. Umegaki⁵, I. Chiu¹, M. K. Kubo⁶, A. Taniguchi⁷, T. Wada², S. Watanabe⁸, H. Yurimoto⁹, T. Noguchi⁷, R. Okazaki¹⁰, H. Yabuta¹¹, H. Naraoka¹⁰, K. Sakamoto⁸, S. Tachibana⁴, S. Watanabe¹², Y. Tsuda⁸ and J-PARC Muon Team¹³

¹Osaka University, ²Tohoku University, ³Japan Atomic Energy Agency, ⁴The University of Tokyo, ⁵High Energy Accelerator

Research Organization, ⁶International Christian University, ⁷Kyoto University, ⁸Japan Aerospace Exploration Agency, ⁹Hokkaido University, ¹⁰Kyushu University, ¹¹Hiroshima University, ¹²Nagoya University and ¹³Japan Proton Accelerator

Research Complex

We have been developing a non-destructive Muonic X-ray analysis for extraterrestrial materials [1, 2, 3, Figure-1(a)]. Since muon has a mass about 200 times greater than that of an electron, negative muon behaves as a heavy electron in the sample. In the classical Bohr model, orbital radii of negative leptons (electron and/or muon) around an atomic nucleus are inversely proportional to the lepton mass, and therefore a muon trapped by an atom has an orbit closer to the atomic nucleus than electrons due to its ~200 times heavier mass (Figure-1(b)). As a result, muon-induced characteristic X-rays have about 200 times higher energies than those associated with the orbital transition of electrons. For instance, electron-induced K α -X-ray of C has an energy of 0.3 keV, whereas muonic K α -X-ray of C has an energy of 75 keV, which is large enough to penetrate a rock sample of about 1 cm in size without significant self-absorption. Another advantage is that the position at which the characteristic Xrays are generated (i.e. the depth of penetration from the sample surface) can be controlled by controlling the momentum of the incident muons, making it possible to non-destructively analyse the chemical composition inside a material from light elements to heavy elements.



Figure 1. (a) Muon beam line at J-PARC, (b) Schematic view of muon-induced characteristic X-ray.

Ten coarse Ryugu samples (A0026, A0064, A0067, A0094, C0002, C0025, C0033, C0061, C0076, and C0103), which were allocated to the initial analysis STONE team, have been investigated at J-PARC MUSE (Japan Proton Accelerator Research Complex, MUon Science Establishment) [4]. Because of the muon beam size (more than 3 cm in diameter), we obtained a bulk elemental abundance of total 122.86 mg (17.72 mg from chamber-A and 105.14 mg from chamber-C). For comparison, pellets of the meteorites Murray (CM2; 306.5 mg) and Orgueil (CI; 195 mg) were also measured. In order to avoid the contamination from atmosphere (N and O), during the analysis, samples were set in the chamber which was filled with helium [3]. Figure-3 shows the muonic X-ray spectra from Ryugu and Orgueil. Significant Muonic X-rays of C, N, O, Na, Mg, Si, S and Fe were detected from Ryugu and Orgueil. Signals of Cu and Be, originated from the inside shield of vacuum chamber, the sample holder and the detector windows, were also detected.



Figure 2. Muonic X-ray spectra of Ryugu and Orgueil (CI)

We calculated elemental mass ratios X/Si (X=C, N, O, Na, Mg, S, and Fe) of Ryugu samples from relative intensity ratios of muonic X-rays using Murray with known X/Si ratios. The obtained mass ratios of C, N, O, Na, Mg, S and Fe relative to Si are 0.338±0.008, 0.019±0.009, 3.152±0.099, 0.039±0.006, 0.890±0.021, 0.510±0.019, and 1.620±0.040, respectively. These elemental ratios are in a good agreement with the reported values for CI chondrites [5] and the conventional solar abundance [6],

except for the 25% lower O/Si for Ryugu relative to CI (Figure-3). This means that Ryugu is depleted in oxygen by 11.3 % by mass compared to CI, assuming similar Si concentration for Ryugu to CI chondrites. The Ryugu samples were prepared and analyzed in low oxygen conditions (< 0.1%) and at low dew points (< -50° C), thus the very low oxygen concentration is indigenous feature. This result is consistent with [7], which was obtained from a chamber-A grain (~1 mg). Lesser water content in Ryugu samples relative to CI chondrites [7] is likely the main factor for the low oxygen concentration.

Thus, we have succeeded in a non-destructive Muonic Xray analysis for Ryugu sample, including light elements such C, N and O. This innovative technique will also be powerful for sample returns from the C-type asteroid Bennu and/or from the Martian satellite Phobos, which are expected to be enriched in organic matter.

normalized to observed Orgueil normalized to CI chondrite (Lodders 2021) 2.0 (X/Si)_{Ryugu} / (X/Si)_{Cl} 1.5 1.0 0.5 0.0 Fe С Ν 0 Na Mg Si S Figure3. Elemental ratios of Ryugu to

normalized to Orgueil and CI chondrite

References

- [1] K. Terada et al. (2014) Sci. Rep. 4, 5072
- [2] K. Terada et al. (2017) Sci. Rep. 7, 15478
- [3] T. Osaka et al. (2022) Analytical Chemistry submitted
- [4] T. Nakamura et al. (2022) Science 10.1126/science.abn8671.
- [5] K. Lodders (2021) Space Science Reviews 217, 44
- [6] M. Asplund, A. M. Amarsi, N. Grevesse (2021) Astronomy & Astrophysics 653, A141.
- [7] T. Yokoyama et al. (2022) Science 10.1126/science.abn7850.

Chondrule-like objects and CAIs in asteroid Ryugu: Earlier generations of chondrules

D. Nakashima¹, T. Nakamura¹, M. Zhang², N. T. Kita², T. Mikouchi³, H. Yoshida³, Y. Enokido¹, T. Morita¹, M. Kikuiri¹, K. Amano¹, E. Kagawa¹, T. Yada⁴, M. Nishimura⁴, A. Nakato⁴, A. Miyazaki⁴, K. Yogata⁴, M. Abe⁴, T. Okada⁴, T. Usui⁴, M. Yoshikawa⁴, T. Saiki⁴, S. Tanaka⁴, S. Nakazawa⁴, F. Terui⁵, H. Yurimoto⁶, T. Noguchi⁷, H. Yabuta⁸, H. Naraoka⁹, R. Okazaki⁹, K. Sakamoto⁴, S. Watanabe¹⁰, S. Tachibana³, and Y. Tsuda⁴

¹Tohoku University, Japan (dnaka@tohoku.ac.jp), ²University of Wisconsin-Madison, USA, ³University of Tokyo, Japan, ⁴ISAS/JAXA, Japan, ⁵Kanagawa Institute of Technology, Japan, ⁶Hokkaido University, Japan, ⁷Kyoto University, Japan, ⁸Hiroshima University, Japan, ⁹Kyushu University, Japan, ¹⁰Nagoya University, Japan.

Introduction: The Hayabusa2 spacecraft returned samples from C-type asteroid Ryugu [1]. The "stone" team, one of the six initial analysis teams, received 16 stone samples from the ISAS curation facility and conducted analyses for elucidation of early evolution of asteroid Ryugu [2]. The Ryugu samples mineralogically and chemically resemble CI chondrites [2-5]. It was suggested that the Ryugu original parent body formed beyond the H₂O and CO₂ snow lines (> 3 - 4 au) in the solar nebula at 1.8 - 2.9 Myr after CAI formation [2]. Here we report oxygen isotope analyses (~ $1 \mu m$ spots; IMS-1280 at UW-Madison) of chondrule-like objects and CAIs observed in the Ryugu samples [2] and discuss the significance of the presence of chondrule-like objects and CAIs in asteroid Ryugu and their origins.

Results: Small chondrule-like objects and CAIs (< 30 µm; Fig. 1) occur with isolated olivine, pyroxene, and spinel in lessaltered clasts in the polished section C0002-P5 and in polished sections of C0040-02 and C0076-10. The three chondrule-like objects have rounded-to-spherical shapes and consist of olivine with Mg# of ~ 99, FeNi metal, sulfide, and Al-Ti-free diopside but free from glass or glass-altered phase. Two of the three chondrule-like objects contain low-iron, manganese-enriched (LIME) olivine [6], and one of them shows sub-µm-sized 120° triple junctions, which is evidence of annealing [7]. The two CAIs consist of spinel and hibonite along with tiny perovskite inclusions. The oxygen isotope ratios show a bimodal distribution at peaks of ~ – 43‰ and ~ 0‰ in δ^{18} O along the CCAM and the PCM lines [8,9] (Fig. 2). Oxygen isotope ratios of the individual objects are indistinguishable within the uncertainty. Two out of the three chondrule-like objects are ¹⁶O-rich with Δ^{17} O of ~ –23‰ (C0002-P5-C2-Chd and C0040-02-Chd), while the other is ¹⁶O-poor with Δ^{17} O of ~ –3‰ (C0002-P5-C1-Chd). The two CAIs are ¹⁶O-rich with Δ^{17} O of ~ –23‰ (C0040-02-CAI and C0076-10-CAI).

Discussion: Mg# of ~ 99 and the Δ^{17} O value of ~ -3‰ for C0002-P5-C1-Chd are characteristic for type I chondrules in carbonaceous chondrites [10]. The two ¹⁶O-rich chondrule-like objects with Mg-rich olivine share characteristics with AOAs [11] and are likely to have been originally AOAs (or fragments) and melted (and annealed) by a heating event in the ¹⁶O-rich environment possibly near the Sun. The three chondrule-like objects, which are dominated by Mg-rich olivine and free from glass, resemble what has been proposed as earlier generations of chondrules [12]. If the three objects are earlier generations of chondrules, the two distinct oxygen isotope ratios of ¹⁶O-rich and -poor are evidence for the argument that ¹⁶O-rich and -poor isotope reservoirs existed in the early stage of the chondrule formation [10].

Spinel-rich CAIs accompanied by altered phases like the two Ryugu CAIs are observed in CM chondrites [e.g., 13]. However, the two Ryugu CAIs are smaller than the CM-CAIs and as small as CAI-like Wild2 particles [14]. Spinel in the CM-CAIs contain Cr_2O_3 mostly less than 0.6 wt% [13], while that in cometary CAIs contains more Cr_2O_3 than 1.7 wt% [15]. The relatively high Cr_2O_3 contents are explained by addition of Cr from Cr-bearing gas or dust during the remelting events at few Myr after CAI formation [15,16]. Spinel in the two Ryugu CAIs contain Cr_2O_3 less than 0.2 wt%. It is possible that the two Ryugu CAIs escaped from remelting events that supplied Cr. If this is the case, the two Ryugu CAIs are possibly as old as the CM-CAIs.

The Ryugu original parent body formed at > 3 - 4 au from the Sun [2], while CAIs formed near the Sun [11]. Radial transport of the CAIs and the two ¹⁶O-rich chondrule-like objects to the region where the Ryugu original parent body formed is required. Likewise, it has been suggested from the observations of chondrule-like and CAI-like Wild2 particles that chondrules and CAIs were transported from the inner regions to the Kuiper belt in the solar nebula [14,17]. Given the smaller sizes of the cometary chondrules and CAIs than those in chondrites, radial transport favoring smaller objects to farther locations may have occurred in the solar nebula; e.g., a combination of advection and turbulent diffusion [18]. If this is the case, the occurrence of chondrule-like objects, CAIs, isolated anhydrous grains that are likely to be fragments of chondrules and CAIs, and AOA-like porous olivine [2,19,20], which are as small as the Wild2 particles, suggests that the Ryugu parent body formed at farther location than any other chondrite parent bodies and acquired these anhydrous objects transported from the inner regions of the solar nebula.

Chondrules in different chondrite groups have distinct chemical, isotopic, and physical properties, suggesting chondrule formation in local disk regions and subsequent accretion to their respective parent bodies without significant inward/outward migration [10]. The rarity of chondrules (and chondrule-like objects) in the Ryugu samples suggests the Ryugu parent body formation in a region scarce in chondrules. Instead, small chondrules and fragments may have been transported with CAIs from the inner regions of the solar nebula. Since the formation age of the Ryugu parent body is as early as those of major types of carbonaceous chondrite chondrules [2,21], chondrules typically observed in chondrites (~ 1 mm) should have presented in the inner regions of the solar nebula when forming the Ryugu parent body. Considering radial outward transport favoring smaller objects, small fragments of relatively large chondrules may have also been provided and observed as isolated anhydrous grains in the Ryugu samples. CAIs in the Ryugu samples are much less abundant (~ 20 ppm) than those in the Wild2 particles (~ 0.5%; [15]), suggesting destruction of the CAIs and chondrules in the Ryugu parent body during the extensive aqueous alteration. The observed chondrulelike objects and CAIs may have survived along with isolated anhydrous grains in less-altered regions in the Ryugu parent body.

References: [1] Yada T. et al. (2021) *Nat. Astron.* 6:214. [2] Nakamura T. et al. (2022) *Science* 10.1126/science.abn8671. [3] Ito M. et al. (2022) *Nat. Astron.* 10.1038/s41550-022-01745-5. [4] Nakamura E. et al. (2022) *Proc. Jpn. Acad. Ser. B* 98:227. [5] Yokoyama T. et al. (2022) *Science* 10.1126/science.abn7850. [6] Klöck W. et al. (1989) *Nature* 339:126. [7] Han J. & Brearley A.J. (2015) *M&PS* 50:904. [8] Clayton R.N. et al. (1977) *EPSL* 34:209. [9] Ushikubo T. et al. (2012) *GCA* 90:242. [10] Tenner T.J. et al. (2018) *in Chondrules: Records of Protoplanetary Disk Processes* 196. [11] Krot A.N. (2019) *M&PS* 54:1647. [12] Libourel G. & Krot A.N. (2007) *EPSL* 254:1. [13] Rubin A.E. (2007) *M&PS* 42:1711. [14] Zolensky M.E. et al. (2006) *Science* 314:1735. [15] Joswiak D.J. et al. (2017) *M&PS* 52:1612. [16] Matzel J.E.P. et al. (2010) *Science* 332:1528. [17] Nakamura T. et al. (2008) *Science* 321:1664. [18] Hughes A.L.H. & Armitage P.J. (2010) *ApJ* 719:1633. [19] Liu M.-C. et al. (2022) *Nat. Astron.* 10.1038/s41550-022-01762-4. [20] Kawasaki N. et al. (2022) *Sci. Adv.* Submitted. [21] Fukuda K. et al. (2022) *GCA* 322:194.





Fig. 2: Oxygen three-isotope ratios of three chondrule-like objects and two CAIs in the Ryugu samples. TF, PCM, and CCAM represent the Terrestrial Fractionation line, the Primitive Chondrule Mineral line, and the Carbonaceous Chondrite Anhydrous Mineral line.

Fig. 1: BSE images of three chondrule-like objects and two CAIs in the Ryugu samples analyzed for oxygen isotopes. SIMS analysis spots are shown by the vertex of an open triangle. The rectangle area drown by the dashed line in panel c corresponds to the region extracted by the FIB sectioning. Abbreviations: Ol, olivine; Mt, Fe-Ni metal; Sul, Fe-sulfide; Ox, oxide; Diop, diopside; Sp, spinel; Hib, hibonite; Pv, perovskite; Phyl, phyllosilicates.

GEMS-like material from asteroid Ryugu regolith

Hope A. Ishii¹, John P. Bradley¹, Elena Dobrică¹, Kenta Ohtaki¹, Takaaki Noguchi^{2,3}, Toru Matsumoto⁴, the Min-Pet Fine Sub-

team and the Hayabusa2 initial analysis core

¹Hawai'i Institute of Geophysics and Planetology, University of Hawai'i at Mānoa, Honolulu, HI 96822, USA

²Division of Earth & Planetary Science, Kyoto University, Kyoto, Japan

³Department of Geology and Mineralogy, Kyushu University, Kyoto, Japan

⁴Hakubi Center for Advanced Research, Kyoto University, Kyoto, Japan

Introduction: Because GEMS, glass with embedded metal (kamacite) and sulfides (pyrrhotite) are found in primitive cometary particles and likely accreted at extremely low temperatures, their presence is often taken as an indicator of cosmic primitivity and lack of alteration in meteoritic parent bodies [1]. GEMS are found in anhydrous, carbon-rich interplanetary dust particles (IDPs) and have also been confirmed in Antarctic micrometeorites (MMs) [2]. GEMS-like materials, having similar texture and morphology (glass with embedded opaques) have been reported in several chondrites, e.g. [3,4]. Close study in some chondrites shows key differences to GEMS in cometary-type particles, for example, in size range, glassy matrix composition and mineralogy of opaques [5,6]. JAXA's Hayabusa2 mission returned regolith from near-Earth Cb-type asteroid 162173 Ryugu, and GEMS-like material has recently been reported in Ryugu regolith grains within less-altered lithologies [7].

Samples and Methods: Two Ryugu grains with high porosity, A0104-029025 and C0105-039023, were identified late in the initial analysis period and analyzed to determine if they contain GEMS. Initial characterization was performed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) on a JEOL JSM-7001F FE_SEM at Kyoto U. a ThermoFisher Scios FIB-SEM at Kyushu U., and a ThermoFisher Helios Nanolab 660 FIB-SEM at U. Hawaii. SEM-EDS characterization shows that grain A0104-029025 is ~50 μ m in length and has a silica-rich matrix holding remnant olivine up to ~5 μ m across, pyrrhotite, pentlandite, magnetite, Mg-rich Cr-spinel, calcite, and a Fe-Ni-P-bearing phase. Grain C0105-039023 is ~75 μ m in length and its silica-rich matrix contains smaller remnant olivine and pyroxene grains, pyrrhotite, pentlandite, magnetite, calcite, phosphates, and a submicron-sized fragment of the Ta projectile. Using Focused Ion Beam (FIB) methods, regions of both samples were extracted as blocks (e.g., Fig. 1), embedded in epoxy, and ultramicrotomed to produce electron-transparent sections for analysis by scanning transmission electron microscopy (STEM). STEM analyses were performed using a ThermoFisher TitanX 60-300 with 4-quadrant windowless EDS detector at the Molecular Foundry, Lawrence Berkeley National Laboratory.

Figure 1. Preparation of FIB-extracted block from grain C0105-039023. Clockwise from top left: SE image of grain; view with sample tilted and protective Pt layer deposited; FIB milling to free block from grain; and final block mounted on a Cu TEM half-grid, ready for embedding and ultramicrotomy [after 8].

Results: Observed at modest TEM magnifications, C0105-039023 and A0104-029025 both contain regions of abundant fine-grained layer silicate with Fe-rich inclusions that has a GEMS-like appearance. Anhydrous silicates were not observed in either of the FIB-sections analyzed, although they were observed by SEM. C0105-039023 is dominated by compact, well-ordered layer silicates and with



abundant pentlandite and pyrrhotite, minor Fe-oxides, and Mg,Ca-rich carbonates. High porosity in this grain is due to many cracks in the interior. Some GEMS-like objects with rounded shapes were identified in C0105-039023. Closer investigations revealed that, unlike in GEMS in cometary-type interplanetary dust particles and Antarctic micrometeorites, ultra-fine-grained inclusions are absent; no kamacite was detected; both pyrrhotite and pentlandite are present; and the "matrix" is layer silicate. We found that even in regions of the samples where imaging contrast appears uniform and suggestive of amorphous structure, poorly ordered fine fibers of layer silicate, a few basal spacings thick, are observed at high magnifications. Figure 2 shows a

few GEMS-like objects in C0105-039023. Compositions of these GEMS-like objects are approximately chondritic in major elements, like GEMS and other primitive objects. Higher carbon content in one GEMS-like object, relative to the surrounding matrix, is somewhat suggestive of *bona fide* GEMS that might have altered in place. The presence of co-located Na and Cl, presumably salt, in the same field of view as the GEMS-like objects underscores the significant role of aqueous processing in these grains.



Figure 2. GEMS-like objects in Ryugu grain C0105-039023. Left: HAADF STEM image showing 3 GEMS-like objects located in upper right, lower right and lower left quadrants of image. Middle: EDS map of Mg (blue), Fe (green), C (red), S (yellow), Ni (magenta) of same region. One GEMS-like object is outlined in yellow and shown at higher magnification in an overlaid EDS map of Fe (red), S (blue) and Ni (green) showing presence of both pentlandite and pyrrhotite. The top right GEMS-like object has higher carbon content than surrounding layer silicate matrix. Right: HAAF STEM image overlaid by Cl (blue) and Na (red) EDS maps showing presence of NaCl (bottom, middle), indicative of aqueous processing.

A0104-029025 has two texturally distinct regions, one with high porosity and the other with lower porosity. The more porous region consists of poorly ordered, hydrated silicate and fine-grained pyrrhotite. Pentlandite was not observed in the high porosity region. The less porous region contains finer-grained pyrrhotite, pentlandite, and a platy S-rich phase thought to be proto-tochilinite. These mineralogical differences are evident in EDS maps over the boundary. No metal was observed in either of these two grains.

Discussion and Conclusions: Based on our observations, GEMS-like objects in porous Ryugu grains are not GEMS, as defined according to their characteristics in cometary-type IDPs and MMs. We observed one GEMS-like object with higher carbon content than its surroundings, suggestive of possible alteration in place of GEMS; however, the majority of GEMS-like objects contain pentlandite and pyrrhotite, no kamacite (metal) and have matrices that consist of poorly ordered hydrated silicate. Instead, we conclude that the GEMS-like objects in the porous Ryugu grains we studied are sulfide clusters that co-deposited with hydrated silicate. This interpretation of a likely role of aqueous processing is supported by the presence of NaCl near the GEMS-like objects in C0105-039023. For A0104-029025, we hypothesize that the observed boundary between high and lower porosities represents a leach front. The lower porosity region shows evidence of more extensive aqueous alteration in the form of pentlandite, reduced pyrrhotite grain size, and the platy sulfide that may result from oxidation of pyrrhotite. The observation of anhydrous silicates by FE-SEM demonstrates that aqueous alteration in incomplete, and larger anhydrous silicates in A0104-029025 support less heavy modification of that grain relative to C0105-039023. High porosity in both grains may reflect a sufficiently low degree of compaction and remnant porosity to allow aqueous alteration products to form in void spaces.

References

[1] Ishii H.A. et al. (2018) Proc. National Academy Sci. 115:6608-6613. [2] Noguchi T. et al. (2015) Earth Planet. Sci. Lett.
410:1-11. [3] Leroux H. et al (2015) Geochimica et Cosmochimica Acta 170:247-265. [4] Nittler L. R. et al. (2019) Nature Astronomy 3:659-666. [5] Ohtaki K. et al. (2021) Geochimica et Cosmochimica Acta 310:320-345. [6] Villalon K. R. et al. (2021) ibid, 346-362. [7] oral presentation, Nakamura T. et al. (2022) LPS LIII, Abstract #1753. [8] Ohtaki K. et al. (2020) Microscopy & Microanalysis 26:120-125.

Zinc, copper and calcium isotopic composition of Ryugu's samples

Frédéric Moynier¹, Marine Paquet¹, Wei Dai¹, Tetsuya Yokoyama², Yan Hu¹, The Hayabusa2-initialanalysis chemistry team, The Hayabusa2-initial-analysis core. ¹Université Paris Cité, Institut de physique du globe de Paris, CNRS; 75005 Paris, France

Onversite 1 unis Cite, institut de physique du globe de l'unis, Chillis, 75005 l'unis, 1 l'une

²Department of Earth and Planetary Sciences, Tokyo Institute of Technology; Tokyo 152-8551, Japan.

In December 2020, the JAXA Hayabusa2 spacecraft returned to Earth with the first samples collected from a Cb-type asteroid, (162173) Ryugu [1,2]. Initial analyses showed that Ryugu's composition is close to that of the CI (Ivunalike) carbonaceous chondrite group [3,4], the chemically most primitive meteorites characterized by near-solar abundances for most elements. Some isotopic signatures (Ti, Cr) of Ryugu overlap, however, with other carbonaceous chondrite (CC) groups. Zinc (Zn) and copper (Cu) are moderately volatile elements (MVE) that display variable isotopic compositions across the different chondrite groups and could be used to further test the Ryugu/CI connection. Furthermore, one notable chemical difference between Ryugu and CI chondrites is an apparent excess of over 50% Ca in the former that may be related to a heterogeneous distribution of carbonates (dolomite and calcite) [3,5]. Given that calcium in carbonates can be isotopically fractionated during aqueous alteration and carbonate precipitation, leading to more than 1‰ variations in the $^{44}Ca/^{40}Ca$ ratio in terrestrial carbonates, it could be a useful tool for investigating the origin of the Ca excesses in the Ryugu samples compared to CI. In addition, Ca exhibits large isotopic variations among bulk carbonaceous chondrites (CC), with the $^{44}Ca/^{40}Ca$ ratio range also spanning a range of 1 ‰, and therefore, Ca stable isotopes could be used to further test the Ryugu/CI connection.

Here we will present the first stable isotopic composition of Zn, Cu, [6] and Ca [7] from two Ryugu sampling sites. We show that Ryugu and CI chondrites have identical Zn and Cu isotopic compositions, demonstrating their common genetic heritage and ruling out any affinity with other groups of CC. Since Ryugu's pristine samples match the solar elemental composition for many elements, their Zn and Cu isotopic compositions likely represent the best estimates of the proto-solar composition. Earth's mass-independent Zn isotopic composition is intermediate between Ryugu/CC and non-carbonaceous chondrites, suggesting a contribution of Ryugu-like material to Earth's budgets of Zn and other MVE. We also show that both Ryugu samples have similar Ca isotopic composition that falls within the range defined by CIs, notwithstanding their higher Ca contents. This similarity likely indicates that the Ca isotopic composition and the Ca budget of CIs and Ryugu samples are dominated by carbonates and consistent with a major event involving precipitation of carbonates in the Ryugu samples that has been dated by ⁵³Mn-⁵³Cr chronology to have occurred ~5Ma after Solar System formation.

The Hayabusa2-initial-analysis chemistry team: K. Nagashima, I. Nakai, E.D. Young, Y. Abe, J. Aléon, C.M.O'D. Alexander, S. Amari, Y. Amelin, K. Bajo, M. Bizzarro, A. Bouvier, R. W. Carlson, M. Chaussidon, B.-G. Choi, N. Dauphas, A. M. Davis, T. Di Rocco, W. Fujiya, R. Fukai, I. Gautam, M. K. Haba, Y. Hibiya, H. Hidaka, H. Homma, P. Hoppe, G.R. Huss, K. Ichida, T. Iizuka, T.R. Ireland, A. Ishikawa, M. Ito, S. Itoh, N. Kawasaki, N. T. Kita, K. Kitajima, T. Kleine, S. Komatani, A. N. Krot, M.-C. Liu, Yuki Masuda, K.D. McKeegan, M. Morita, K. Motomura, A. Nguyen, L. Nittler, M. Onose, A. Pack, C. Park, L. Piani, L. Qin, S.S. Russell, N. Sakamoto, M. Schönbächler, L. Tafla, H. Tang, K. Terada, Y. Terada, T. Usui, S. Wada, M. Wadhwa, R.J. Walker, K. Yamashita, Q.-Z. Yin, S. Yoneda, H. Yui, A.-C. Zhang, H. Yurimoto.

The Hayabusa2-initial-analysis core: S. Tachibana, T. Nakamura, H. Naraoka, T. Noguchi, R. Okazaki, K. Sakamoto, H. Yabuta, H. Yurimoto, Y. Tsuda, S. Watanabe.

References

^[1] Tachibana, S. *et al.* Pebbles and sand on asteroid (162173) Ryugu: In situ observation and particles returned to Earth. *Science* **375**, 1011-1016, doi:10.1126/science.abj8624 (2022). [2] Yada, T. *et al.* Preliminary analysis of the Hayabusa2 samples returned from C-type asteroid Ryugu. *Nature Astronomy* **6**, 214-220, doi:10.1038/s41550-021-

01550-6 (2022). [3] Yokoyama, T. *et al.* The first returned samples from a C-type asteroid show kinship to the chemically most primitive meteorites. *Science* 10.1126/science.abn7850 (2022). [4] Nakamura, E., K., K., Tanaka, R., Kunihiro, T. & Kitagawa, H. On the origin and evolution of the asteroid Ryugu: A comprehensive geochemical perspective. *Proc. Jpn. Acad., Ser. B* **6**, 227-282 (2022). [5] Nakamura, T. et al. *Science* (accepted).[6] Paquet et al. Copper and Zinc Isotopic Fingerprints of the Contribution of Ryugu-like Material to Earth's Volatile Inventory. *Nature Astronomy* (in revision). [7] Moynier et al. The Solar System calcium isotopic composition inferred from Ryugu samples. *Geochemical Perspective Letters* (accepted).

Molybdenum and Osmium isotopic compositions of Ryugu sample

Nao Nakanishi^{1,2}, Akira Ishikawa², Tetsuya Yokoyama², and Richard J. Walker¹,

The Hayabusa2-initial-analysis chemistry team, The Hayabusa2-initial-analysis core.

¹Dept. of Geology, University of Maryland, USA

²Dept. of Earth & Planetary Sciences, Tokyo Institute of Technology, Japan

The Hayabusa2 mission conducted two sampling sequences on the Cb-type asteroid Ryugu and brought 5.4 g of the asteroidal materials back to Earth. The initial analyses found that Ryugu samples are dominated by minerals that experienced extensive aqueous alteration in the parent body and are related to CI (Ivuna-like) carbonaceous chondrites [1]. To further investigate the origin of the materials that accreted to form Ryugu and chemical processes that affected these materials after accretion we examined the isotopic compositions of the siderophile elements Os and Mo. Eleven ¹⁸⁷Os/¹⁸⁸Os ratios were obtained from bulk Ryugu samples (A0106-A0107, and C0108 from both sampling locations) using N-TIMS (*Triton Plus*) at Tokyo Tech. A composite sample of four bulk Ryugu samples that were combined (A0106-A0107, A0106, C0108, and C0107 from both sampling locations) was dedicated for the determination of the Mo isotopic composition of the composite using MC-ICP-MS (*Neptune Plus*) at UMd.

The bulk Ryugu samples have uniform ¹⁸⁷Os/¹⁸⁸Os ratios, averaging 0.1264 \pm 0.0005 (2SD, n = 11) (Fig. 1), which is consistent with the ¹⁸⁷Os/¹⁸⁸Os ratio of bulk CI chondrites (0.1265 \pm 0.0001, 2SD; [2]). This observation supports the main conclusion of previous studies that Ryugu is mainly composed of materials related to CI chondrites [3]. The uniform ¹⁸⁷Os/¹⁸⁸Os ratio implies homogeneous distribution of elemental Re/Os ratios of the Ryugu materials. This is likely to reflect the redistribution of Re and Os by aqueous alteration that occurred on the Ryugu parent body. Given the sample size for one analysis (0.4–1.1 mg), the Re/Os homogenization would be achieved even on a small scale.

The composite bulk Ryugu sample analyzed for Mo is characterized by positive ε^{i} Mo values (ε^{i} Mo = [(iMo/ 96 Mo)_{sample}/(iMo/ 96 Mo)_{standard} - 1] ×10⁴) for 92 Mo, 94 Mo, 95 Mo, and 97 Mo, consistent with a deficit of *s*-process Mo isotopes (Fig. 2). Previous studies have shown that Mo isotopic data for carbonaceous (CC) and non-carbonaceous (NC) meteorites define two separate linear trends on the ε^{95} Mo– ε^{94} Mo diagram (e.g., [4]). The Ryugu sample plots on the CC line (Fig. 3), which is consistent with the observation that Ryugu samples are also characterized by CC-type ε^{50} Ti– ε^{54} Cr isotopic systematics [3]. The ε^{94} Mo and ε^{95} Mo values for the comparise Ryugu sample are larger than these of any linear bulk comparison.



Figure 1. Os isotopic composition of Ryugu materials and chondrites. Reference data are from [2]. The error bars reflect the range of isotopic compositions measured for each category (Ryugu: 2SD; Chondrites: 1SD).

composite Ryugu sample are larger than those of any known bulk carbonaceous chondrites including CIs (Fig. 3).

There are at least three possible explanations for the large *s*-process deficits in the Ryugu sample. First, the measured Mo isotopic composition might accurately reflect the composition of the bulk asteroid. In this case, it would suggest that Ryugu formed from a nebular region with a Mo isotopic composition that differed from that of the limited number of CI chondrites analyzed for Mo to date. This would be in conflict with the evidence from the lithophile Ti and Cr isotopic compositions. Second, Mo isotopes might have been heterogeneously distributed on the asteroid Ryugu. In this case, the Mo isotopic composition obtained from the ~70 mg of Ryugu material analyzed may not represent the bulk composition of the asteroid, and may instead reflect the redistribution and concentration of strongly *s*-process depleted Mo by aqueous processes. Third is incomplete dissolution of presolar SiC grains during the acid digestion steps, given that SiC grains are resistant to dissolution by the acid digestion techniques applied for this measurement. SiC is characterized by *s*-process-enriched compositions [e.g., 5]. A leachate study on Orgueil found that incomplete digestion creates anomalies in Mo isotopic composition [6]. Thus, the *s*-process deficit may reflect an absence of the SiC component contribution to the bulk composition.



Figure 2. Mo isotopic composition of Ryugu and Allende analyzed in this study. The reference bulk meteorite data are from [6-8]

Figure 3. ϵ^{95} Mo- ϵ^{94} Mo diagram of Ryugu material and bulk Allende. The reference bulk meteorite data are from [8].

References

[1] Yada T. et al. 2022. Nature Astronomy 6:214. [2] Walker R. J. et al. 2002. GCA 66:4187. [3] Yokoyama T. et al. 2022 Science abn7850. [4] Kleine, T. et al. 2020. Space Sci. Rev. 216:1. [5] Stephan T. et al. 2019. ApJ 877:101. [6] Dauphas N. et al. 2002 ApJ 569:139. [7] Burkhardt C. et al. 2011. EPSL 312:390. [8] Yokoyama, T. et al. 2019. ApJ 883:62.

The Hayabusa2-initial-analysis chemistry team: T. Yokoyama, K. Nagashima, I. Nakai, E.D. Young, Y. Abe, J. Aléon, C.M.O'D. Alexander, S. Amari, Y. Amelin, K. Bajo, M. Bizzarro, A. Bouvier, R. W. Carlson, M. Chaussidon, B.-G. Choi, N. Dauphas, A. M. Davis, T. Di Rocco, W. Fujiya, R. Fukai, I. Gautam, M. K. Haba, Y. Hibiya, H. Hidaka, H. Homma, P. Hoppe, G.R. Huss, K. Ichida, T. Iizuka, T.R. Ireland, A. Ishikawa, M. Ito, S. Itoh, N. Kawasaki, N. T. Kita, K. Kitajima, T. Kleine, S. Komatani, A. N. Krot, M.-C. Liu, Yuki Masuda, K.D. McKeegan, M. Morita, K. Motomura, F. Moynier, A. Nguyen, L. Nittler, M. Onose, A. Pack, C. Park, L. Piani, L. Qin, S.S. Russell, N. Sakamoto, M. Schönbächler, L. Tafla, H. Tang, K. Terada, Y. Terada, T. Usui, S. Wada, M. Wadhwa, R.J. Walker, K. Yamashita, Q.-Z. Yin, S. Yoneda, H. Yui, A.-C. Zhang, H. Yurimoto.

The Hayabusa2-initial-analysis core: S. Tachibana, T. Nakamura, H. Naraoka, T. Noguchi, R. Okazaki, K. Sakamoto, H. Yabuta, H. Yurimoto, Y. Tsuda, S. Watanabe.

Ryugu's volatiles investigated using stepped combustion and EGA methods

A.B. Verchovsky¹, F. A. J. Abernethy¹, M. Anand¹, I. A. Franchi¹, M. M. Grady¹, R. C. Greenwood¹ and M. Suttle¹, M. Ito², N. Tomioka², M. Uesugi³, A. Yamaguchi⁴, M. Kimura⁴, N. Imae⁴, N. Shirai⁵, T. Ohigashi^{6,7}, M-C. Liu⁸, M. Abe⁹, T. Usui⁹.
¹The Open University, Milton Keynes, MK7 6AA, UK. ²KOCHI JAMSTEC, ³JASRI/SPring-8, ⁴NIPR, ⁵ Kanagawa Univ., ⁶UVSOR IMS, ⁷PF/KEK ⁸LLNL, ⁹ISAS/JAXA, the Ph2K team, the MicrOmega team.

Samples of the asteroid Ryugu collected by the Hayabusa 2 mission [e.g., 1-4] provide an excellent opportunity to undertake a comparative study for volatiles (e.g., H, C. N, S) measured in meteorites of similar type. This allows for a better understanding of the evolution of the meteoritic material during their transition through the atmosphere and residence on the surface of the Earth. In this study, we present the abundances and isotopic compositions of C, N and some noble gases in a Hayabusa 2 sample A0219 (as collaborative research under the Phase2 Kochi curation activity) and three CI meteorites (Orgueil, Ivuna and Alais). These measurements were performed using stepped combustion QEGA (Quantitative Evolved Gas Analysis) methods. It is important to note that utmost care has been taken to avoid any exposure of Hayabusa 2 material to the terrestrial atmosphere, from the time of the recovery of the sample capsule in Australia to sample allocation and preparation (in gloves box filled with pure N_2) and loading (with portable gate valve) for analysis by the Finesse instrument [5, 6] at the Open University. The sample aliquots used for the stepped combustion and QEGA were 2 and 0.5 mg respectively.

1. **Hydrogen.** Release of H_2 from A0219 during EGA occurs over a broad temperature range (400-1000 °C) with the major peak at 730 °C, similar to what is observed for the three CIs and seems to be associated with decomposition/oxidation of the organic macromolecular material. The total concentration (0.3 wt.%) of the molecular hydrogen in A0219 is also similar to that found in other CIs.

2. Water. In contrast to all other CIs analysed, the release of H_2O in A0219 has a single peak with maximum at ~550 °C: for Orgueil, Ivuna and Alais, the H_2O release is bimodal with an additional (apart from that at 530-570 °C) peak at low (~250 °C) temperature (Fig.1). The peak at 530-570 °C is thought to be associated with structural transformation of phyllosilicates at which their hydroxyl groups are released in the form of water. The low temperature peaks in CIs can be related to the adsorbed and/or hydroxide decomposition water release, associated with terrestrial weathering. In another study, the Hyabusa 2 sample analysed by TG-MS [7] showed a small peak of water at 100 °C, which was taken as evidence of heating on the surface of the asteroid to be limited to below 100 °C. However, the results here (Fig. 1) show no measurable water release below ~300 °C; the quadrupole MS signal at these temperatures is at the background level (<100) cps. As saponite can readily resorb water from atmosphere, it is

possible that the release at 100 °C reported by Yokoyama et al. [6] is terrestrial contamination, and that the samples have been heated on the Ryugu's surface to temperatures of up to 300 °C. The total water content determined in A0219 (7.6 \pm 1.5 wt. %) is

similar to that published for other Hayabusa 2 samples [6]. 3. **Carbon.** Stepped combustion results clearly indicate that most of carbon in Hayabusa 2 (as in other CIs [8]) is associated with the macromolecular organic material and carbonates (Fig. 2). CO_2 from the latter is released at ~600 °C, characterised by a relatively high δ^{13} C values (up to 80‰) and present in CIs in variable amounts. In that sense, A0219 is not different from other CIs, though its carbonate concentration is relatively high. The petrographic studies of the Hayabusa 2 samples [6, 8] confirm the presence of Ca, Ma and Fe carbonates. Clearly, A0219 contains very little, if any, presolar SiC, signature of which (~1200 ‰ in its pure form) is often seen in CIs as arbaneod $\delta^{13}C$ (up to four hundred near mile) at 1100.1200°C. ECA

in CIs as enhanced δ^{13} C (up to few hundred per mile) at 1100-1300°C. EGA data show that carbon is released as both CO₂ at relatively low T and CO at higher T. Apart from decomposition of carbonates, these gases appear to be a result of oxidation of organic material in chemical reaction of the latter with the oxygen-bearing minerals. The total range of the carbon release is similar

to that observed for molecular hydrogen confirming that all the species are associated with the macromolecular organics. The

total concentration of carbon determined by stepped combustion and QEGA are 6.3 and 4.6 wt. %, respectively that are within the range observed for CIs.

4. **Nitrogen.** During stepped combustion, nitrogen release is correlated with that of carbon indicating that it is one of the major constituents (along with C and H) of the macromolecular material. This is observed for the Hayabusa 2 and all CI samples. The variations in δ^{15} N in the temperature steps are also similar to those seen in other CIs (Fig. 3). In particular a characteristic feature of the variations (along with the presence of the relatively isotopically heavy organic component) is the excursion of the δ^{15} N to the isotopically light values at ~400 °C that could be explained by contribution from presolar nanodiamonds, pure separates of which have δ^{15} N ~-350 ‰. However, the calculated concentration of the nanodiamonds in the Hayabusa 2 sample using two-component mixing model with the isotopically heavy N shown by the dashed line (Fig. 3) and δ^{15} N = -350 ‰ assuming 1 % of the N in the nanodiamonds is significantly higher (by a factor of 2-3) than in fact observed in the most primitive meteorites. The same is true for Orgueil and Tagish Lake [8]. Therefore, there must be another more significant

Figure 3. Release of N and δ^{15} N variations during stepped combustion.

source of the isotopically light N component (possibly phase Q) with isotopic composition of N as light as the solar values (δ^{15} N ~-400 ‰), and which is oxidised in the same temperature range as nanodiamonds [5]. Nitrogen could not be identified by EGA because of the dominant presence of CO at m/z=28.

5. **Sulphur.** Compared to all Cis, A0219 contains almost no sulphur. It is released at 300 °C and its estimated concentration is ~1.2 ppm, while CIs contain a few wt. % of sulphur. It is a surprising result and the reason for such a low concentration is not completely clear but may reflect sample heterogeneity. Further analyses need to confirm it. Only a part of sulphur in CIs is associated with terrestrial contamination. It follows from multicomponent sources of its release observed over a wide temperature range including elemental, organic, sulphite and sulphide sulphur as well as from its isotopic composition [10]. Investigation of other Hayabusa 2 samples by TG-MS [7] also indicated that the SO₂ signal is very low though petrographic data showed the presence of different sulphide minerals [7, 8]. On the other hand, in some works [11] it was suggested that most of sulphur in the meteorites is due to terrestrial contamination. Therefore, the low S concentration in the Hayabusa 2 samples is arguably as a result of the absence of any terrestrial contamination.

6. **Noble gases.** The ⁴He, ²⁰Ne and ³⁶Ar relative abundances in A0219 correspond to a mixture of solar and planetary (Q) components. The isotopic composition of Ne shows a very small contribution of the cosmogenic component: most of the experimental points plots on the solar Ne fractionation line which is also a mixture of the solar and Q Ne, so that a contribution of the latter cannot be excluded. The data for other Hayabusa 2 grains [9] show Ne isotopic composition both without and with some contribution of the cosmogenic component. The A0219 material and other Hayabusa 2 grains with very little cosmogenic Ne contribution appear to have been exposed to solar wind radiation for a relatively short time being buried at a depth where galactic cosmic rays cannot penetrate for a longer time.

Conclusions. The EGA indicates that the A019 sample does not contain a low-temperature water release suggesting that its presence in all other CIs is due to terrestrial contamination. The very low sulphur content in the sample may also be an indication that sulphur in other CIs is also mostly due to terrestrial contamination. The A0219 Hayabusa 2 sample shows many features in C, N and noble gases abundance and isotopic compositions similar to those observed in CI chondrites. Carbonates concentration in A0219 is relatively high compared to other CIs. Hayabusa 2 definitely belong to the CI meteorite clan.

References

[1] Ito M. at al., 2022. *Nat Astron* (2022). <u>https://doi.org/10.1038/s41550-022-01745-5</u>. [2] Liu, MC., et al., 2022. *Nat Astron* (2022). <u>https://doi.org/10.1038/s41550-022-01762-4</u>. [3] Greenwood R. C. et al., 2022. Nat Astron. 2022 (Accepted).
[4] Nakamura T. et al., 2022. Science 10.1126/science.abn8671. [5] Verchovsky A. B., 2017. Geochemistry International 55: 957. [6] Verchovsky et al. 2020. Planetary and Space Science 181, 104830. [7] Yokoyama T. et al., 2022. Science 7850. [8] Grady M. M. et al., 2002. Meteoritics & Planetary Science 37: 713. [9] Nakamura E. et al., 2022. Proc. Jpn. Acad. Ser. B 98: 227. [10] Airieaus S. A. et al., 2005. Geochim. at Cosmochim. Acta 69: 4166. [11] Velbel M. A. and Palmer E. E., 2011. Clays and Clay Minerals 59: 416.

Defect microstructure of pyrrhotite in regolith material returned from C-type asteroid 162173 Ryugu – evidence for shock metamorphism

Falko Langenhorst¹, Dennis Harries², Takaaki Noguchi³, Toru Matsumoto^{3,4}, Akira Miyake³, Yohei Igami³, the Min-Pet "Sand" Team, and the Hayabusa2 Initial Analysis Core.

¹Institute of Geoscience, Friedrich Schiller University Jena; Carl-Zeiss-Promenade 10, D-07745 Jena, Germany; ²Luxembourg Institute of Science and Technology, European Space Resources Innovation Centre; Belvaux, Luxembourg; ³Division of Earth and Planetary Sciences, Kyoto University; Kitashirakawaoiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan; ⁴The Hakubi Center for Advanced Research, Kyoto University; Kitashirakawaoiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan

Introduction. The Hayabusa2 mission successfully returned regolith materials from two sampling sites of the C-type Near-Earth Object (NEO) 162173 Ryugu [1]. Mineralogical characterization of samples revealed that aqueous alteration was an omnipresent process, which resulted mainly in the formation of phyllosilicates, carbonates, phosphates, and other phases forming under hydrous conditions [2]. Since Ryugu is an airless body whose surface is directly exposed to interplanetary space, it was also expected that regolith samples contain traces of space weathering (effects due to solar wind particle and micrometeoroid bombardments). Effects of solar wind bombardment were discovered in several samples [3,4], while traces of shock metamorphism are scarce [5], which is unusual considering the rubble pile nature of asteroid Ryugu.

Samples and methods. Ryugu samples from the two sampling sites were collected in separate chambers A and C of the sample catcher [2]. Within the activities of the Min-Pet "Sand" team, we have examined three samples from chamber A (A0058-T4, AP002-g03, AP007-g06), which probed the uppermost surface material of Ryugu. The three samples were first investigated by field emission scanning electron microscope (FE-SEM: JSM-7001F at Kyoto University). We then extracted electron-transparent sections of regions of interest on the Ryugu grains, using a focused ion beam (FIB) system (Helios NanoLab G3 CX at Kyoto University). The FIB sections were finally observed using analytical transmission electron microscopy (TEM, Tecnai G2 FEG at Univ. of Jena). Bright-field and dark-field TEM imaging techniques combined with selected area electron diffraction (SAED) were employed to characterize the defect microstructures.

Results. Among all the mineral grains in the three FIB sections, only a relatively large (9 x 4 μ m dimensions) pyrrhotite grain from sample AP007-g06 turned out to exhibit a rich defect microstructure. This grain is only partially surrounded by phyllosilicates, where it displays well-developed faces parallel to (001), (010), and (011). At the free surface, the grain is however irregularly shaped and pitted. Our previous investigation revealed a systematic variation in the superstructure type towards the free surface with N values ranging from 4.0 (4C-pyrrhotite, x \approx 0.125) in the grain interior to 5.9 (close to 6C-pyrrhotite, x=0.083) at the surface [4].

Additionally, we observe a high density of dislocations in various geometric configurations pervading the entire grain. Straight, up to 1 μ m long dislocations with dislocation lines parallel to [001] are most abundant (density up to 2 x 10¹³ m⁻²), while dislocations reorganized in sub-grain boundaries and dislocation loops occur subordinately. The straight elongated dislocations are apparently glissile with 1/3[110](001) acting as slip system. Bright-field TEM images and SAED patterns indicate also the presence of multiple microtwins on the (001) plane throughout the entire grain. Sub-grain boundaries and dislocation loops occur in the vicinity of internal voids that might have been once filled with fluid.

Discussion. This overall rich defect microstructure of pyrrhotite implies that the grain was affected by various processes. The variation in the superstructure type below the irregular pitted surface was attributed to incipient space weathering, causing a loss of sulfur on the free surface and an inward diffusion of Fe into the grain interior [4]. Internal voids and dislocation loops are, however, likely defects produced during aqueous alteration. The activation of a large number of perfect dislocations and microtwins on the basal plane are a typical response of monosulfides to dynamic loading [7]. Although no crater is observed on the surface, we interpret these defects as clue to shock metamorphism affecting the entire grain.

References

al. 2019. Science 364, 268-272. [2] Nakamura al. Science [1] Watanabe S. et Т. et 2022. 377. https://doi.org/10.1126/science.abn8671. [3] Noguchi T. et al. 2022. Abstract #1747, 53rd LPSC, [4] Harries et al. 2022. Meteoritics & Planetary Science 57: 6073. [5] Kikuiri M. et al. 2022. Meteoritics & Planetary Science 57: 6199. [6] Yada T. et al. 2021. Abstract #2008, 52nd LPSC. [7] Langenhorst F. et al. 2014, Earth, Planets and Space 66: 118.

Chemical heterogeneity of insoluble organic matter in Ryugu grains

E. Quirico¹, L. Bonal¹, Y. Kebukawa², K. Amano³, H. Yabuta⁴, E. Dartois⁵, C. Engrand⁶, J. Mathurin⁷, J. Duprat⁸,

H. Yurimoto⁹, T. Nakamura³, T. Noguchi⁶, R. Okazaki¹⁰, H. Naraoka¹⁰, K. Sakamoto¹¹, S. Tachibana¹², S. Watanabe¹³, Y.

Tsuda³ and the Hayabusa2-initial-analysis IOM team

¹Université Grenoble Alpes, CNRS, Institut de Planétologie et Astrophysique de Grenoble (IPAG), UMR 5274, Grenoble F-38041, France. ²Yokohama National Univ., Yokohama 240-8501, Japan. ³Department of Earth Sciences. Tohoku University, Senda 980-8578, Japan. ⁴Hiroshima University (Japan), ⁵ISMO, Université Paris-Saclay (France). ⁶IJCLab Université Paris-Saclay/IN2P3 (France). ⁷Institut de Chimie Physique, Université Paris-Saclay (France). ⁸Museum National d'Histoire Naturelle, Paris (France). ⁹Hokkaido University (Japan), ¹⁰Kyushu University (Japan), ¹¹JAXA Sagamihara (Japan), ¹²Univ. of Tokyo (Japan), ¹³Nagoya University (Japan).

Introduction: The Hayabusa2 mission has returned to Earth 5.42 g of samples collected at the surface of asteroid Ryugu (Yada et al., 2022). Two touchdowns were operated: the first on February 21 2019 to collect material from the top surface, and the second on July 11 2019, ~20 m north from the artificial crater generated by the impact experiment a few months ago, for probing ejecta coming from deeper in the subsurface (Tsuda et al., 2020). The bulk and multi-instrumental mineralogical and isotopic characterization of Ryugu samples show that they are related to CI chondrites, but experienced a lower stage of hydrothermalism resulting in a more reduced mineralogy (e.g. Nakamura et al., 2022). Insoluble organic matter (hereafter IOM) has been extracted from Ryugu's samples, and infrared spectroscopic analyses have revealed differences with respect to IOMs extracted from historical falls as Alais, Ivuna and Orgueil (Yabuta et al., 2022; Kebukawa et al., 2022). Here, we investigate the chemical heterogeneity of IOM in a series of Ryugu grains selected from the A and C chambers, corresponding to the first and second touchdowns, respectively. Small grains (100-500 μ m) were processed with an HF/HCl extraction protocol and characterized by micro-FTIR. Some of these grains were also analyzed by Raman micro-spectroscopy (Bonal et al. 2022).

Experimental: IOM samples were extracted with the HF/HCl protocol (Durand and Nicaise 1980), adapted to microsized grains. Infrared transmission spectra were collected with a Bruker HYPERION 3000 micro-FTIR, equipped with a MCTdetector. The spot size at the sample was ~50 μ m x 50 μ m and the spectral resolution was 4 cm⁻¹. Measurements were run with an environmental cell maintained under secondary vacuum (~ 10⁻⁶ mbar) and the sample was heated at 80°C to remove adsorbed terrestrial water.

Results and discussion: The samples are presented in Tab. 1 and some infrared spectra in Fig. 1. The spectra collected from the series of samples show significant chemical variations, which can have different origins : (1) Terrestrial weathering versus sample freshness; (2) Analytical artefacts; (3) Accretion of distinct organic precursors and (4) Post-accretional processes. Ryugu samples are extremely fresh and have experienced little interactions with the terrestrial atmosphere. In contrast, the historical falls Alais, Orgueil and Ivuna fell in 1804, 1864 and 1938, respectively, and storage conditions in old times were not optimized. However, systematic measurements on finds and falls covering a long period of time, including recent falls (e.g. Tagish Lake, Mukundupura), do not support an IOM evolution controlled by terrestrial weathering (Alexander et al. 2007; Cody et al. 2005; Kebukawa et al., 2011; Orthous-Daunay et al., 2013; Quirico et al. 2018). The HF/HCl digestion protocol could be subjected to analytical artifacts, such as oxidation and contamination (e.g. viton particles from the wires). However, we crosschecked the extraction quality by extracting IOM from well known chondrites (e.g. Orgueil), and in some cases in parallel with two reactors filled from the same solvents and reagents. In the past, comparison with IOM samples obtained independently with the CsF-technique developed at Carnegie Institute showed little difference with HF/HCl IOMs (Cody and Alexander 2005; Quirico et al., 2018). Artifact measurements are known to arise with infrared micro-FTIR because IOM samples contain insoluble minerals with varying sizes that generate scattering, which can blur the absorption signal. We have suspicions for C109-12, as the baseline correction was uncertain in the region 1700-1600 cm⁻¹. The accretion of different organic precursors is difficult to address here as no insights into petrography was available for our samples, and we cannot infer the presence of xenolithic clasts. Last, post-accretional processes are a potential source of heterogeneity, as observed in recent falls like Tagish Lake and Sutter's Mills (e.g. Herd et a., 2011; Quirico et al., 2018). Mineralogy, bulk and isotopic compositions of Ryugu samples are consistent with a CI chondrite, more reduced than the least altered CI Alais, and which experienced a hydrothermal event of lower intensity. Therefore, we do not expect a significant impact of fluid circulation, regarding the similarities of IOM composition across CM and CI chondrites when covering a broad range of petrologic subtypes. Last, a possible source of heterogeneity is short-duration thermal metamorphism, rated as stages from I to IV (Nakamura, 2005). According to systematics on a broad array of C1 and C2 chondrites, I_{CH2}/I_{CH3} appears as a suitable tracer of this process, while the aliphatic and carbonyl abundances are less accurate. In this respect, C0109-12, A0108-6, A0108-10 and A0106-23,24,25 appear inconsistent with the CI chondrites Alais, Ivuna and Orgueil. C0109-12 displays a high I_{CH2}/I_{CH3}, a low intensity aliphatic band and a low intensity carbonyl band (Fig. 2). However, short-duration metamorphism is not confirmed by Raman spectroscopy and the baseline correction of the spectra of this sample are questionable. A0108-6 and A0108-10 display a high I_{CH2}/I_{CH3}, but they were very thin and translucent samples, optically very different than other IOMs. In addition, they display a strong OH band, which does not appear in other IOMs as well. Regarding A0106-23,24,25, it looks similar to IOM from heated stage II C1 and C2 chondrites, but once again Raman spectroscopy does not report short-duration heating for A0108-10, A0106-23,24,25. Accordingly, the spectral heterogeneity cannot be firmly interpreted as the result of short duration heating. Last, the sample C0109-9 seems to depart from other samples in terms of Raman characteristics. However, its infrared spectrum is similar to that of unheated C2s, and the Raman data likely suffer from a statistical bias.

Conclusion: Our data reveal chemical heterogeneity across the IOM samples extracted from a series of Ryugu grains and aggregates. No clear differences are observed between the two chambers A and C. 6 samples are consistent with the IOMs of the three historical CI falls Alais, Ivuna and Orgueil, and strengthens the link with this chondrite class. 4 samples show substantial differences, which cannot be firmly interpreted as the evidence of short duration heating.

Table 1

Samples investigated.

Figure 1: Micro-FTIR of IOM from Ryugu grains and CI chondrites

References

Alexander C.M.O.'D et al. Geochimica Cosmochimica Acta, 7 4380-4403, 2007.

Bonal B. et al., 53rd Lunar and Planetary Science Conference, held 7-11 March, 2022 at The Woodlands, Texas. LPI Contribution No. 2678, 2022, id.1331

Cody G. and C.M.O.'D Alexander. Geochimica Cosmochimica Acta, 69, 1085, 2005.

Kebukawa Y. et al. Geochimica Cosmochimica Acta, 75, 3530-3541, 2005.

Kebukawa Y. et al. 53rd Lunar and Planetary Science Conference, held 7-11 March, 2022 at The Woodlands, Texas. LPI Contribution No. 2678, 2022, id.1271

Nakamura T. et al., 10.1126/science.abn8671, 2022.

Orthous-Daunay F.-R. et al. Icarus, 223, 534-543, 2013.

Quirico et al. Geochimica Cosmochimica Acta, 241, 17-37, 2018.

Tsuda, Y. et al. Hayabusa2 mission status: Landing, roving and cratering on asteroid Ryugu. Acta Astronautica 171, 42–54, 2020 Yabuta et al. 53rd Lunar and Planetary Science Conference, held 7-11 March, 2022 at The Woodlands, Texas. LPI Contribution No. 2678, 2022, id.2241

Yada T. et al. Preliminary analysis of the Hayabusa2 samples returned from C-type asteroid Ryugu. Nat Astron 6, 214-220.

Properties of the asteroid Bennu's surface based on contact measurements and their implications

D.J. Scheeres¹, G. Brown¹, R.-L. Ballouz², E.B. Bierhaus³, E.R. Jawin⁴, P. Sánchez¹, and K.J. Walsh⁵ ¹University of Colorado, Boulder, CO, USA ²Johns Hopkins University Applied Physics Laboratory, Laurel, MD, USA ³Lockheed Martin Space, Littleton, CO, USA ⁴National Air and Space Museum, Smithsonian Institution, Washington, DC, USA ⁵Southwest Research Institute, Boulder, CO, USA

When the OSIRIS-REx S/C touched the surface of Bennu to carry out its sampling operations, it opened a new view into the mechanical properties of rubble pile asteroids. The OREX S/C was able to take measurements of its deceleration as it penetrated the surface, in advance of initiating its sampling process. Based on these measurements, optical observations of surface deformations during its penetration, and detailed granular mechanics modeling of the interaction, it was determined that the surface regolith covering was highly porous and had a very low level of cohesion [1]. Figure 1 (from [1]) shows the main data used in determining the Bennu surface mechanical properties. Figure 2 shows granular mechanics simulations in a micro-gravity environment. The simulations capture the total spacecraft mass properties, the constant force spring in the sampling arm, and the geometry of the sampling head. The simulations show that for sufficiently low cohesion, the spacecraft head penetrates the regolith and displaces it, without activating the constant force spring. This is the scenario that was seen in the actual sampling event. Simulating regolith with stronger cohesive strength forces the spacecraft to stop and rebound, engaging the constant force spring.

Based on these measurements and modeling the surface packing fraction was determined to be as low as 0.25, half the inferred bulk packing fraction of the asteroid, and the cohesive strength on the order of 1 Pa or less. These properties imply that the surface regolith may be significantly weaker than the sub-surface, potentially due to the lack of fines, which have the net effect of strengthening a rubble pile structure [2]. This is also consistent with other observations of the Bennu surface geology [3] and crater profiles [4].

The implications of these regolith properties can be explored relative to the larger-scale mass distributions detected on Bennu, which found that the equatorial bulge region had a lower overall density than other regions of the asteroid [5]. Migration of regolith into Bennu's equatorial region brings this material within the rotational Roche lobe of the body where it is energetically trapped, allowing for accumulation [5]. This process should have been accelerating over time, as the YORP effect causes Bennu to spin more rapidly [6], moving the Roche lobe down to lower latitudes. Current predictions are that the surface of Bennu should start to lose regolith directly in about 400 Ky, assuming the YORP effect stays constant. In this talk, we will consider the mechanics of this overall cycle of behavior, and note what likely outcomes should be found. These can then be interpreted in light of the asteroid Ryugu, which has also been hypothesized to have undergone a period of past rapid spin [7].

References

[1] K.J. Walsh, et al. Near-zero cohesion and loose packing of Bennu's near subsurface revealed by

spacecraft contact, Sci. Adv., 8 (27), eabm6229. • DOI: 10.1126/sciadv.abm6229

[2] P. Sánchez and D.J. Scheeres. 2014. "The Strength of Regolith and Rubble Pile Asteroids," Meteoritics and Planetary Science 49(5): 788-811

[3] E. R. Jawin, et al. 2020. Global Patterns of Recent Mass Movement on Asteroid (101955) Bennu, JGR Planets 10.1029/2020JE006475

[4] E.B. Bierhaus, et al. Crater population on asteroid (101955) Bennu indicates impact armouring and a young surface, Nature Geoscience 15, pages 440–446 (2022)

[5] D.J. Scheeres, et al. Heterogeneous mass distribution of the rubble-pile asteroid (101955) Bennu, Science Advances 6, eabc3350 (2020)

[6] C. Hergenrother, et al. (2019). The Operational Environment and Rotational Acceleration of Asteroid (101955) Bennu from OSIRIS-REx Observations, Nature Communications 10: 1291

[7] M. Hirabayashi, et al. (2019). The western bulge of 162173 Ryugu formed as a result of a rotationally driven deformation process, ApJ Letters 874(1): L10

Figure 1: From Reference [1], these figures show the acceleration and surface imaging data used to constrain the mechanical properties of the regolith surface.

Figure 2: Granular mechanics simulations of the OSIRIS-REx TAGSAM sampling in a micro-gravity environment. Weakly cohesive regolith (top) allow the sampler head to penetrate and push the regolith. Stronger cohesion will stop the spacecraft and cause a small rebound. The actual sampling event mimics the weakly cohesive case.

Formation of Moons and Equatorial Ridge around Top-shaped Asteroids after Surface Landslide: Applications to asteroids Ryugu, Bennu, Didymos, and more

Ryuki Hyodo¹ and Keisuke Sugiura² ¹ISAS/JAXA ²ELSI

Top-shaped asteroids have been observed among near-Earth asteroids. About half of them are reported to have moons (on the order of ~ 1 wt.% of the top-shaped primary) and many of them have an equatorial ridge. A recent study has shown that the enigmatic top-shaped figure of asteroids (e.g., Ryugu, Bennu, and Didymos) could result from an axisymmetric landslide of the primary during a fast spin-up near the breakup rotation period. Such a landslide would inevitably form a particulate disk around an asteroid with a short timescale (~ 3 hr). However, the long-term full dynamical evolution is not investigated. Here, we perform a continuous simulation (~ 700 hr) that investigates the sequence of events from the surface landslide that forms a top-shaped asteroid and a particulate disk to disk evolution. We show that the disk quickly spreads and produces moons (within ~ 300 hr). The mass of the formed moon is consistent with what is observed around the top-shaped asteroids. We also demonstrate that an equatorial ridge is naturally formed because a fraction of the disk particles re-accretes selectively onto the equatorial region of the primary. We envision that Ryugu and Bennu could once have an ancient moon that was later lost due to a successive moon's orbital evolution. Alternatively, at a top-shaped asteroid that has a moon, such as Didymos, no significant orbital evolution of the moon has occurred that would result in its loss. Our study would also be qualitatively applicable to any rubble-pile asteroids near the breakup rotation period.

The above abstract is obtained from Hyodo R. and Sugiura, K. (2022). "Formation of moons and equatorial ridge around top-shaped asteroids after surface landslide". ApJL, 937, L36. https://doi.org/10.3847/2041-8213/ac922d

Schematic summary of our paper (a figure from Hyodo & Sugiura 2022, ApJL). Panel (a): a rubble-pile asteroid spins up due to, for example, the YORP effect, small impacts, a close encounter with a planet, or re-accumulation after a catastrophic impact. Panel (b): a surface landslide occurs when a critical spin state is realized and a top-shaped figure is formed (Sugiura et al. 2021). Panel (c): a particulate disk spreads due to inelastic collisions and gravitational interactions among particles. Panel (d): a moon is gravitationally accreted outside the Roche limit of the central top-shaped body, and an axisymmetric equatorial ridge is formed due to the re-accretion of disk particles. Panels (e) and (f): the formed moon is lost or remains, depending on the long-term orbital evolution between the moon and the primary.

Yarkovsky-Driven Orbital Migration of Asteroid Ryugu: Implications for its Collisional History and Source Family

Masanori Kanamaru¹, Seiji Sugita¹ and Tomokatsu Morota¹ ¹The University of Tokyo

With the ongoing analysis of samples brought back from the asteroid Ryugu, there is a growing need to understand their geological/dynamical context. It is essential to identify the asteroid family from which the asteroid Ryugu originated and to clarify the orbital evolution path from the main belt to the near-Earth region.

In this study, we estimate the time scale of Ryugu's orbital evolution in the inner main belt based on a thermophysical simulation. We simulated the temperature distribution on the surface of Ryugu over an orbit cycle using the current orbit, spin, and thermophysical properties (Watanabe et al. 2019; Okada et al. 2020), and calculated secular change in semi-major axis that induced by anisotropic thermal radiation, i.e., the Yarkovsky effect. A Yarkovsky drift rate was obtained by scaling that for the near-Earth orbit to the inner main belt. The thermophysical simulation was performed by a dynamical simulator for asteroids, Astrohsaper (Kanamaru et al. 2021).

As a result, it was estimated that Ryugu will take approximately 700 million years to migrate through the inner main belt from 2.1 to 2.5 au. The right panel of Figure 1 shows the time scales for Ryugu to reach the v_6 resonance by Yarkovsky as a function of initial orbital elements. v_6 is the secular resonance with Saturn and one of the most powerful resonances as an escape hatch to provide near-Earth asteroids.

In this region, there are two asteroid families that are possible candidates for the origin of Ryugu: Eulalia and New Polana as shown in the left panel of Figure 1. The formation ages of these families are estimated as ~830 million years and ~1.4 billion years, respectively (Bottke et al. 2015). The Yarkovsky time scale estimated in this study is comparable with the formation age of Eulalia family, while it is shorter than that of New Polana family. If Ryugu originated from Eulalia family, Ryugu was formed at the same time with the family formation and was transported to the v_6 resonance. On the other hand, if Ryugu originated from New Polana, a parent body of Ryugu was formed during the family formation. It is likely that Ryugu is a rubble pile of the second- or later generation that experienced multiple times of catastrophic disruption. Because the Yarkovsky drift is less effective for a massive body, Ryugu would have spent several hundred million years as the larger parent body.

In the future, we will attempt to shed light on the evolutionary history of Ryugu by comparing the results of analysis of returned samples.

Figure 1. Potential source family of asteroid Ryugu and time scales to reach v_6 resonance.

References

- Bottke, William F., David Vokrouhlický, Kevin J. Walsh, Marco Delbo, Patrick Michel, Dante S. Lauretta, Humberto Campins, Harold C. Connolly, Daniel J. Scheeres, and Steven R. Chelsey. 2015. "In Search of the Source of Asteroid (101955) Bennu: Applications of the Stochastic YORP Model." *Icarus* 247 (February): 191–217.
- Kanamaru, Masanori, Sho Sasaki, Tomokatsu Morota, Yuichiro Cho, Eri Tatsumi, Masatoshi Hirabayashi, Naru Hirata, et al. 2021. "YORP Effect on Asteroid 162173 Ryugu: Implications for the Dynamical History." *Journal of Geophysical Research. Planets* 126 (12). https://doi.org/10.1029/2021je006863.
- Okada, Tatsuaki, Tetsuya Fukuhara, Satoshi Tanaka, Makoto Taguchi, Takehiko Arai, Hiroki Senshu, Naoya Sakatani, et al. 2020. "Highly Porous Nature of a Primitive Asteroid Revealed by Thermal Imaging." *Nature* 579 (7800): 518–22.
- Watanabe, S., M. Hirabayashi, N. Hirata, Na Hirata, R. Noguchi, Y. Shimaki, H. Ikeda, et al. 2019. "Hayabusa2 Arrives at the Carbonaceous Asteroid 162173 Ryugu-A Spinning Top-Shaped Rubble Pile." https://doi.org/10.1126/science.aav8032.

The ESA Hera mission: detailed investigation of the NASA DART impact outcome and characterization of the binary asteroid Didymos

Patrick Michel¹, for the Hera Science Team

¹Université Côte d'Azur, Observatoire de la Côte d'Azur, CNRS, Lagrange Laboratory, Nice, France

The Hera mission is in development in the Space Safety Program of the European Space Agency (ESA) for launch in October 2024 [1]. It will perform a rendezvous with the binary asteroid (65803) Didymos in early 2027 and over 6 months, it will investigate it as well as the outcome of the successful impact of the NASA DART probe on the small moon called Dimorphos of the Didymos system.

DART was launched on 24 November 2021 at 06:21 UTC and successfully performed an impact at about 6.1 km/s on the 160 meter-size Dimorphos on 26 September 2022 at 23:14 UTC. Two weeks before impact, it deployed the Italian LICIACube that provided images of the few minutes following the impact. A campaign of observations from Earth and space allowed obtaining distant images of the event and is aimed at measuring the change of the orbital period of Dimorphos around Didymos resulting from the impact.

The great success of the DART impact will be left with many questions. In particular, we need to know the outcome of the impact on Dimorphos' surface, e.g., whether it produced a crater and its size and/or whether it led to a global reshaping of Dimorphos. We also need an accurate measurement of the mass of Dimorphos, which will allow quantifying the momentum enhancement factor, which is a crucial parameter to validate the kinetic impactor technique. We also need to determine in detail the physical, thermal and compositional properties of the asteroid, including for the first time internal properties, which have a great influence on the impact outcome. These are the objectives of the Hera mission, which will allow, with the knowledge provided by DART, having a fully documented deflection test and impact experiment to check our numerical impact models, to be able to extrapolate this deflection test to other scenarios and to improve our understanding of the complex geological properties and response of small asteroids.

To accomplish these objectives, with its mother spacecraft, which includes a JAXA contribution with the Thermal Infrared Imager, and its two cubesats, Hera will perform the first rendez-vous with a binary asteroid, arriving at Didymos about 4 years after DART. Hera will not only contribute greatly to the planetary defense effort by documenting entirely the DART impact, so that numerical impact models can be validated at the real asteroid scale and so that this knowledge can be extrapolated to other scenarios. It will also contribute greatly to our understanding of asteroid processes in the very low gravity regime of a very small asteroid (Dimorphos) as well as to our knowledge of binary asteroids and asteroid geophysics. The mission development is ongoing nominally and the various working groups of the Hera Science Team are working intensively to support this development and be best prepared to the surprises that Hera will offer during its visit to Didymos in 2027.

References

[1] Michel P. et al. 2022. Planetary Science Journal 3:160.

Acknowledgments

We acknowledge funding support from the European Union's Horizon 2020 research and innovation program under grant agreement No. 870377 (project NEO-MAPP), the CNRS through the MITI interdisciplinary programs, CNES and ESA.

The ANIME mission and beyond: SmallSat exploration of near-Earth asteroids

Davide Perna¹ ¹INAF – Rome Observatory (INAF-OAR)

Interest in near-Earth asteroids (NEAs) has rapidly grown in recent decades. The motivation is threefold: first, their proximity allows us to discover and investigate small bodies down to the metre-size, thus enhancing our understanding of the mechanisms underlying planetary formation; second, such information is also critical to mitigate their threat of collision with the Earth; third, their near-future exploitation can exponentially expand the natural resources available to humankind.

Ground-based observations of thousands of NEAs have revealed the striking diversity existing within this population in terms of physical properties. So far, only a handful of NEAs have been visited by space missions: each of them provided unexpected discoveries and huge steps forward in our understanding of planetary sciences. Deep-space SmallSats represent a new frontier for the solar system exploration. After the success of the NASA/JPL MarCO mission in 2018 and of the ASI LICIACube mission which testified the impact of the NASA DART spacecraft onto asteroid Dimorphos in September 2022, several further deep-space SmallSat missions will take place in the next few years, e.g. in the framework of ESA HERA and NASA Artemis projects.

The "Asteroid Nodal Intersection Multiple Encounters" (ANIME) mission has been proposed by an Italian consortium led by INAF – Rome Observatory, and selected in 2021 by the Italian Space Agency (ASI) in the framework of a call for future CubeSat missions. ANIME aims to explore three near-Earth asteroids, selected by virtue of their peculiar and yet unexplored size and physical regimes, as well as their relevance in terms of planetary protection. The rationale behind the ANIME target selection and interplanetary trajectory design lies in encountering asteroids that have a nodal passage in the proximity of the Earth, considering their relative positions and velocities (Fig. 1). With a launch envisaged in the 2026-2028 timeframe, the 20-kg, 12U CubeSat ANIME will flyby two Potentially Hazardous Asteroids, and then rendezvous with asteroid 2000 SG344. The study of such 40-m-sized object will allow constraining the latest theories about planetary system formation scenarios, addressing questions about the monolithic vs. cohesive vs. rubble pile aggregation structure of small asteroids. Moreover, 2000 SG344 presents a very high impact risk, with multiple potential collision solutions with our planet during the course of the next century. It is also considered an excellent target for future human exploration thanks to its accessibility.

Multiple similar/identical SmallSats (to maximize mission return while minimizing costs and risks) could be launched profiting of the same or separate mission opportunities, and then reach their respective targets using electric propulsion and optimized interplanetary trajectories. Each SmallSat would flyby and/or rendezvous multiple NEAs, with encounters at the nodal points, to explore the diversity of such population. E.g., assuming an ANIME-like platform and mission durations capped at 3 years, many mission scenarios with similar performances can be identified with total $\Delta V < 3$ km/s. This outlines the strong implementation flexibility of such mission concept, as the definitive choice of target NEAs can be easily updated even at relatively late project phases, also considering the current exponential growth of NEA discoveries. This provides a huge flexibility in terms of mission scenarios, which can be adapted to varying constraints. The strategic relevance of ANIME and further SmallSat missions to NEAs also lies in the step forwards that will be taken in validating critical small spacecraft technologies for deep space exploration.

Figure 1. Reference ANIME trajectory for a launch in late 2026. Alternative flyby targets can be identified for different launch windows.

The Physical Properties of Carbonaceous Asteroids

Daniel Britt University of Central Florida

The rendezvous and sampling of asteroids 162173 Ryugu and 101955 Bennu have opened a new window on carbonaceous asteroid physical properties. Both objects have the structure of low-density rubble piles [1], with surfaces that are extremely rough, covered in starkly angular blocks and boulders, and depleted in fine particle sizes and dust [2]. The returned Ryugu material is similar to CI carbonaceous chondrites [3] and Bennu is likely either CI or CM-like materials. The surface of Ryugu exhibits very low thermal conductivity and high porosity [4]. What does this imply for the link between the physical properties of carbonaceous asteroids and hydrated carbonaceous meteorites?

The mineralogy these objects are dominated by phyllosilicates, primarily serpentines and saponite [3]. For Ryugu the serpentines are the magnesium-rich endmember similar to CI mineralogies. For Bennu the serpentine mineralogy is still unknown but may be the iron-rich endmember Cronstedtite. One major characteristic of serpentines is a strong negative excursion in the coefficient of linear thermal expansion in the range of 200°-250° K [5]. This effect is shown in Figure 1 for five CM carbonaceous chondrites. Since the carbonaceous materials are basically conglomerates that include some very dissimilar minerals, this negative thermal expansion excursion in serpentines may be key to understanding their surface properties as they evolve in the inner solar system. Cobbles and boulders exposed on the surfaces of carbonaceous asteroids will undergo extreme temperature excursions as they rotate into the Sun and then are exposed to deep space. All the minerals in the conglomerates will expand and contract according to their thermal expansion coefficients. For most minerals the expansion is a linear, positive function of temperature. However, for carbonaceous chondrites the serpentines and other phyllosilicates will expand, contract, and then expand again in a course of their heating and subsequent cooling. This will produce an extreme energetic effect on the mineral grain boundaries, essentially pushing them apart, contracting to open space, and then pushing apart again. The overall effect will be to weaken the conglomerate and induce increasing porosity into what appear to be coherent cobbles/boulders. This will leave the surface covered with boulders and cobbles that are extremely friable, porous, and weak. Because the effect is limited to the penetration depth of the rotational thermal pulse, it may be that only the surface materials are significantly weakened by this process. Cobbles buried at some modest depth and do not undergo temperature excursions may retain significantly more coherence and strength than the surface material.

One important observation is the lack of small particle size and dusty materials in the surface regolith. With the stresses induced by the thermal excursions, it would be expected that at least some of the boulder and cobble material would

disaggregate to form a dusty regolith. However, the surface appears much like a "desert pavement" where active processes extract the fine materials from the surface and armor it with particle sizes too large to be moved by the active processes. Active ejection processes have been observed on Bennu with rocks as large as 10 cm being ejected. Because of the low gravity, fine particle sizes are likely to be entrained in the solar wind once ejected, resulting in a depletion of fines on the surface. Below the surface on both Ryugu and Bennu sampling activities revealed horizons more enriched in fine materials [1].

Figure 1. Thermal Expansion Coefficient for CM carbonaceous chondrites

References

[1] Sugita S. et al 2019. Science 364: 252 [2] Michikami T. et al. 2019. Icarus 331: 179. [3] Yokoyama T. et al. 2022. Science 10.1126/science.abn7850 [4] Gott M. et al. 2019 Nature Astronomy 3(11): 971. [5] Opeil C. et al. 2020. MAPS

10.1111/maps.13556. [6] Lauretta D. et al. 2019 Science 366:6470.

New theoretical results on asteroid regolith specific heat, cohesion and heat transfer, and a revisit of comet 67P surface strength

J. Biele¹, M. Grott², S. Ulamec¹, J. Knollenberg², J.-B. Vincent² ¹German Aerospace Center, DLR-RB/MUSC Cologne, Germany ²German Aerospace Center, DLR-PF, Berlin, Germany

We report and discuss on some of our recent theoretical advances on asteroid regolith specific heat c_P , van der Waals-force between regolith particles, and heat transfer in the regolith. We also report on the strength of comet surface material, including a refined model of its size dependence and wide variability depending on the degree of "cementation" (sintering) and a reappraisal of some particularly low and high strength values for comet 67P reported earlier in the literature. Thermal and mechanical properties are correlated.

Specific heat

Surface temperature models could be impacted by the drastic decrease in $c_P(T)$ values toward low temperatures; thermal models generally assume lunar basalt calorimetric properties, which are not well known outside the data range 90 K to 350 K. Indeed, 'knowledge of specific heat variability as a function of temperature and bulk material composition remains largely

under-constrained for the need of planetary thermal modelers'[1]. In particular, the specific heat capacity of geological materials relevant to solar system body surfaces below room temperature is not particularly well constrained and the thermal modeling community only has a limited set of adequate ready-to-use $c_P(T)$ trends for planetary surface temperature modeling. - We provide the means to calculate synthetic $c_P(T)$ from a known bulk composition, for almost any solar system material from 10 K to 1000 K, and additionally a method to predict the specific heat curve beyond the temperature range measured, even if the composition is not (well) known. [2]

Van-der-Waals force

[3] have calculated the pull-of force due to van der Waals interaction, and due to capillary bridges, between particles with <u>self-affine fractal (random) roughness</u>, which is realistic. They have shown that surface roughness, if big enough, results in an interaction (VdW) force which is independent of the size of the particles, in contrast to the linear size dependency expected for particles with smooth surfaces (simple JKR, DMT). For fractured rock particles a realistic surface roughness reduces the pull-of force between micrometer sized particles by a factor of ~ 100 , and even more for larger particles, it is of the order of 0.1 - 1

The smallest particles form a "glue" or "cement" for the bigger particles

Force to break the bond between a small particle (diameter d ~ 6 μ m) and another particle = F₁ Yield stress in tension $\sigma_{Y} = \kappa F_{1} / d^{2}$ where $\kappa \sim 1$ If $\sigma_{Y} = 25$ Pa then F₁ ~ 1 nN nN. This means that the dependence of cohesive strength (or tensile strength, in N/m²) of the granular medium on particle size is due to the increase in the number of particle-particle contacts (per unit area) alone. A decrease in particle size only increases the number of contacts without changing the strength of the particle-particle adhesive bond. The small-particle glue idea, figure 1, of [4] is a good one! This results also affects the predicted (high) porosity of granular media in micro-gravity, since the granular Bond number is very different now.

Figure 1. The big particles (fragments) in an asteroid could be kept together by a matrix of smaller particles. Effective yield stress of rubble pile asteroids of order (or less than) $\sigma_{\rm Y} \approx 25$ Pa.

Heat transfer

Thermal conductivity k of granular media and porous rocks seemed well explained by classical theories (Maxwell equations, Stefan-Boltzmann radiative transfer, contact mechanics like Hertz or JKR theory). All those classical thermal conductivity theories operate with models from the 19th century (Maxwell, Fourier, Stefan-Boltzmann law, Hertz) and completely neglect phonons and quantum mechanics! We are revising the underlying assumptions, and find that most are doubtful.

Rough irregular rock (silicate) particles do not form strong contacts when granular, not much phonon conduction across point contacts, JKR not applicable at all, heat transfer by near-field evanescent EM waves at least equally important, (NFRHT) $\sim 1/R^{0.8}$ -dependence. Radiative conduction is not $\propto T^3$ either, if grains are not well conducting (non-isothermality); different regime if void scale <= thermal wavelength $\lambda_T \approx 3000/T \ \mu m$ K (radiative transfer, dense media scattering and transmission, Planck not valid if particle size < λ_T); Most assumptions on porosity dependence, in particular of k_{rad} , were wrong [5, 6]. Porous rock effective conductivity (meteorites) as function of porosity in not Maxwell "swiss cheese", much lower values at medium porosities \rightarrow rather weakly cemented/sintered ex granular matter. Cracks, percolating and close pores, ... no theory is available! We are working both theoretically and experimentally to understand this better [7, 8].

Revisit of Comet Surface Strength

For comet 67P, we have re-analyzed the data for the apparently exceptional 67P Abydos site, where originally a *lower* limit of several MPa for compressive strength was suggested. We use a correlation going back to Digby [9, 10] between strength, Young's module and thermal conductivity for weakly sintered porous media; our revised value for compressive strength is 28–690 kPa on the 5–30 cm scale, still representing the probably most competent material on the comet, potentially with a reduced porosity compared to the average 70–80%. The size effect law [11] for quasi-brittle failures bridging the small-size asymptotic strength (compressive or tensile) and the power law $\sim 1/d^{1/2}$ of LEFM seems to apply for cometary and meteoritic material: the strength of very small lab samples cannot be simply extrapolated to larger sizes!

References

[1] Piqueux, S., et al., Journal of Geophysical Research: Planets, 2021. 126(11): p. e2021JE007003. [2] Biele, J., et al., International Journal of Thermophysics, 2022. 43(9): p. 144, DOI: 10.1007/s10765-022-03046-5. [3] Persson, B.N.J. and J. Biele, Tribology Letters, 2022. 70(2): p. 34, DOI: 10.1007/s11249-022-01570-x. [4] Scheeres, D.J., C.M. Hartzell, and P. Sanchez, Icarus, 2010. 210, DOI: 10.1016/j.icarus.2010.07.009. [5] Ryan, A.J., et al., Journal of Geophysical Research: Planets, 2020. 125(2): p. e2019JE006100, DOI: 10.1029/2019je006100. [6] Ryan, A.J., et al., JGR Planets, 2022: p. e2022JE007191. [7] Persson, B.N.J. and J. Biele Applied Physics Letters, 2022, submitted. [8] Biele, J., et al., 44th COSPAR Scientific Assembly. Held 16-24 July, 2022. 44: p. 186. [9] Digby, P., Journal of Applied Mechanics, 1981. 48(4): p. 803-808. [10] Grott, M., et al., Nature Astronomy, 2019. 3(11): p. 971-976. [11] Bažant, Z.P., Archive of Applied Mechanics, 1999. 69(9-10): p. 703-725, DOI: 10.1007/s004190050252.

Comparison of Thermal Inertia between Ryugu Sample and Carbonaceous Chondrites

Takuya Ishizaki¹, Hosei Nagano², Satoshi Tanaka¹, Tatsuaki Okada¹, Naoya Sakatani¹, Tomoki Nakamura³, Ryohei Fujita²,

Abdulkareem Alasli², Tomoyo Morita³, Mizuha Kikuiri³, Kana Amano³, Eiichi Kagawa³, Hisayoshi Yurimoto⁴, Takaaki

Noguchi⁵, Ryuji Okazaki⁶, Hikaru Yabuta⁷, Hiroshi Naraoka⁶, Kanako Sakamoto¹, Shogo Tachibana^{8, 1}, Sei-ichiro Watanabe²,

Yuichi Tsuda1

¹Japan Aerospace Exploration Agency, 3-1-1 Yoshinodai, Sagamihara, Kanagawa 252-5210, Japan

²Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi, 464-8603, Japan

³ Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai, Miyagi 980-8578, Japan

⁴ Hokkaido University, 5, Kitahachijonishi, Kita-ku, Sapporo, Hokkaido 060-0810, Japan

⁵ Kyoto University, Yoshidahonmachi, Sakyo-ku, Kyoto, Kyoto 060-0810, Japan

⁶ Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka, Fukuoka 812-8581, Japan

⁷ Hiroshima University, 1-3-2 Kagamiyama, Higashihiroshima, Hiroshima 739-8526, Japan

⁸ The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Introduction: According to the general planetary formation scenario, the Solar System bodies evolved over a long period of time through repeated collision, fragmentation, and aggregation of planetesimals formed in the solar nebula. Thermal evolution, which induces various physicochemical reactions such as aqueous alteration, thermal metamorphism, and volcanism, is important for the evolution of planets. The temperature history inside the planetesimals followed in thermal evolution can vary greatly depending on when and how large they agglomerate and effective thermal conductivity. Therefore, it is essential for the theory of planetary system formation to know the thermal conductivity of asteroids and meteorites, especially those that are thought to have existed since the early stages of planetary system formation.

The Ryugu sample brought back in 2020 by Hayabusa2 was found to be a primitive Ivuna-type carbonaceous chondrite, which is close to the average composition of the Solar System [1]. Although it is expected that the physical properties of Ryugu, including thermal conductivity, will be analyzed in detail, most of the measurements of physical properties of meteorites have been performed on relatively easily available ordinary chondrites [2–4], because they require more samples than chemical and petrological evaluations. Therefore, there has been no method that can evaluate thermal conductivity of limited amount of samples such as Ryugu samples. In this study, we developed a lock-in thermography (LIT) periodic heating method that can measure the thermal diffusivity of small sample of several mm scale without contact [5]. Then we measured the anisotropic distribution of thermal diffusivity for five types of Ryugu samples. Additionally, Thermal inertia was evaluated using reported density and specific heat and compared with values reported for other carbonaceous chondrites.

Samples and Methodology: In this study, six samples of C0002-plate 3, C0002-plate 4, C0025, C0033, A0026 and A0064 were evaluated. C0002-plate 3 and C0002-plate 4 are flat plates cut out from C0002, and the others have granular shape. A spot on the sample is periodically heated using a laser and the temperature response is measured by LIT to obtain the phase lag distribution on the sample surface. The thermal diffusivity is analyzed from the gradient of the phase lag according to this equation; $D = \pi f / (d\theta/dr)^2$. Here, *D* is thermal diffusivity, *f* is heating frequency, θ is phase lag and *r* is distance from heating point. Thermal inertia, which is expressed as the product of the square root of thermal diffusivity, density, and specific heat, was evaluated based on the reported density and specific heat. The heating frequency was selected according to the sample size to avoid the influence of reflected temperature waves at the sample edge, and then measurements were performed at 2, 1, 4, 4, 4, and 20 Hz for C0002-plate 3, C0002-plate 4, C0025, A0026, C0033, and A0064, respectively. C0002-plate 3, C0002-plate 4 and A0064 were measured under vacuum, and C0025, A0026, and C0033 were measured under atmospheric pressure because the vacuum environment was not available at that time yet. C0002-plate 4 was also measured under atmospheric pressure.

Results and Discussion: Figure 1 shows the phase lag distribution and the thermal diffusivity distribution of C0002-plate 3 as a representative of all samples. And the mean, maximum, minimum, and maximum to minimum ratio of the thermal diffusivity distribution for each sample are summarized in Table 1. C0002-plate 3 is known to have cracks in the evaluation region (in the direction of 105-195 deg), and it can be seen that the thermal diffusivity decreases significantly in the direction of the cracks. The other samples also show various thermal anisotropy. The results of C0002-plate 4 measured under both vacuum and atmospheric pressure show that the thermal diffusivity becomes larger, and the thermal anisotropy becomes smaller under atmospheric pressure. The thermal anisotropy seems to be caused by cracks inside the sample. Heterogeneity of mineral composition or microporosity may also affect. The returned Ryugu samples were found to have various mineral compositions and conglomerate-like structures [6].

Table 1. Measurement results of thermal diffusivity.

| Sample | Average, mm ² /s | Max/ Min, mm ² /s | Max/Min ratio |
|---------------------|--------------------------------|---------------------------------|------------------|
| C0002-3 | 0.28 ± 0.07 | 0.75/ 0.02 | 38.0 |
| C0002-4 (Vacuum) | 0.33 ± 0.08 | 1.05/ 0.07 | 15.0 |
| C0002-4 (1 atm) | 0.45 ± 0.12 | 0.60/ 0.31 | 1.94 |
| C0025 | 0.56 ± 0.10 | 1.12/ 0.36 | 3.11 |
| A0026 | 0.51 ± 0.02 | 0.60/ 0.34 | 1.76 |
| C0033 | 0.58 ± 0.11 | 0.82/ 0.27 | 2.96 |

Figure 1. Phase lag and thermal diffusivity distribution of C0002-plate 3.

The obtained thermal diffusivity was then converted to thermal inertia using specific heat and bulk density, and a plot of the relationship with bulk density is shown in Figure 2. Error bars for thermal inertia indicate maximum and minimum values. The bulk densities of these samples are 1820, 1740, 1650, 2260, and 1870 kg/m³ respectively, and the specific heat of 865 J/(kg · K) measured in the initial analysis was used as a representative value [6]. In addition, Figure 2 also shows plots of the thermal inertia of carbonaceous chondrites reported so far (Cold Bokkeveld (CM2), Jbilet Winselwan (CM2), Murchison (CM2), Murray (CM2), NWA 7309 (CM2), NWA 5515 (CK4), Allende (CV3), Kainsaz (CO3.2)) [4, 7]. The plots are shown in light blue for the measurements taken in vacuum and in purple for those taken at atmospheric pressure. The thermal inertia at atmospheric pressure becomes larger than that at vacuum pressure because the thermal diffusivity becomes larger due to the air-filled cracks.

The averaged values of the thermal inertia of 748-1475 $J/(s^{1/2}m^2K)$ obtained in this measurement is significantly larger than that observed value of $300\pm100 J/(s^{1/2}m^2K)$ [8] by the thermal infrared imager (TIR) onboard Hayabusa2. On the other hand, some of the minimum values corresponded to the observed values. This suggests that the value of thermal inertia may differ depending on the measurement scale. In this measurement, the thermal diffusivity was evaluated in the region of several hundreds of micrometers long as thermal diffusion length, but the TIR observations were made at depths down to several centimeters because the thermal inertia was analyzed using the diurnal variation of the surface temperature due to the 7.6-hour rotation period of asteroid Ryugu. Therefore, it is possible that large-scale cracks caused by meteor impacts and thermal stresses on a scale larger than several hundreds of micrometers are widely developed in the rocks and boulders of Ryugu

The Ryugu sample seems to be the lowest-density category when compared to carbonaceous meteorites, and the thermal inertia values appear to follow a correlation trend with the bulk density of carbonaceous chondrites. However, if the bulk density of the Ryugu sample were 2236 kg/m³, which is the average of the five CM2 densities, the average thermal inertia of the Ryugu sample would be 1132 J/(s^{1/2}m²K), which is almost identical to the average CM2 value of 1191 J/(s^{1/2}m²K). This means that the only substantial difference between Ryugu and CM2 is the bulk density, and the product of thermal conductivity and specific heat are almost the same. Since the thermal conductivity generally decreases when the bulk density decreases due to porosity, it is possible that the thermal conductivity of Ryugu's matrix is larger than that of CM2. Further validation will be conducted by evaluating additional carbonaceous chondrites including CI chondrites, which are closest to Ryugu.

Figure 2. Thermal inertia vs. bulk density of Ryugu samples and carbonaceous chondrites.

References

[1] T. Yokoyama et al., Science abn7850 (2022). [2] K. Yomogida et al., J Geophys Res. 88 (1983) 9513–9533. [3] M. Beech et al., Planet Space Sci. 57 (2009) 764–770. [4] A.J. Soini, et al., Meteorit Planet Sci. 55 (2020) 402–425. [5] T. Ishizaki et al., Int J Thermophys. 43 (2022). [6] T. Nakamura et al., Science abn8671 (2022). [7] C. Opeil et al., Meteor Planet Sci. 55(8) (2020) E1–E20. [8] T. Okada et al., Nature. 579 (2020) 518–522.

Thermal properties of asteroid Ryugu from global, local, and micro-scale observations and the possible formation and evolution scenario of Ryugu

Tatsuaki Okada^{1,2}, Satoshi Tanaka^{1,2}, Naoya Sakatani¹, Yuri Shimaki¹, Takehiko Arai³, Hiroki Senshu⁴, Hirohide Demura⁵, Tomohiko Sekiguchi⁶, Toru Kouyama⁷, Masanori Kanamaru², Takuya Ishizaki¹

¹Institute of Space and Astronautical Science, JAXA, Japan, ²University of Tokyo, Japan, ³Maebashi Institute of Technology, Japan, ⁴Chiba Institute of Technology, Japan, ⁵University of Aizu, Japan, ⁶Hokkaido University of Education, Asahikawa,

Japan, ⁷National Institute of Advanced Industrial Science and Technology, Japan..

Thermophysical properties of C-type asteroid 162173 Ryugu have been investigated through remote sensing using the Thermal Infrared Imager (TIR)[e.g., 1-3], on the surface using the radiometer MARA on MASCOT lander [4,5], and the analysis of return sample [e.g.,6,7]. The global average and the local distribution of thermal inertia were mapped by TIR, with the typical value of 200 to 400 J m⁻² kg⁻¹ s^{-0.5} (tiu, hereafter) [1], which is lower than that of typical chabonaceous chondrite meteorites of 600 to 1000 tiu [8]. Surface boulders and their surroudings have almost the same thermal inertia, indicating that most of boulders are consisted of materials with high porosity (pores and cracks in them) and not completely consolidated, and the surroundings are covered with boulders and rocks (not sandy regolith) [1], which was confirmed during the descent operations. The flat diurnal temperature profiles observed at the afternoon local time indicate the very rough surface [1]. Considering the thermal model with rough surface [9], the thermal inertia and roughness are derived simultaneously [2]. Upclose observations by TIR during the descent operations suggested that boulders have a variety of thermal inertia, with more than 80 % of them having 200 to 400 tiu, while some portions have very low (<100 tiu) or very high (>600 tiu) thermal inertias [3]. They are identified as "Hot Spots" and "Cold Spots", because they are observed exceptionally hotter or colder compared with their surroundings [1,3]. The surface experiment by MARA indicated the similar thermal inertia for a single boulder [4], so that the rough boulders should be the representative material on the asteroid. Multi-band radiometry by MARA indicates the similarity to aqueously altered carbonaceous chondrites (CI or CM) but not like heated carbonaceous chondrites [5].

The average thermal properties of returned samples show the thermal inerita almost similar to that of typical charbonaceous chondrites for $<100 \,\mu\text{m}$ scale [6,7], although the thermal inertia (or more directly the thermal diffusivity) in the direction where cracks exist indicate much lower, consistent with the thermal inertia by remote sensing by TIR or surface measurements by MARA. The return samples are not always representative as the intact surface on Ryugu regaring the physical properties, since fragile portions of them might have been broken during impact sampling as well as during the severe shock and vibration in the return capsule when entry to Earth. The return samples seem to be consisted of more consolidated parts of Ryugu surface materials with flatter surface, instead of fragile and porous features observed as cauliflower-like cramby boulders on Ryugu. The return sample are more like CI chondrites in mineralogy, chemistry, and textures but with darker, more porous and fragile characteristics [10,11]. The difference of thermal inertia between larger scale (> 1mm) and a smaller scale (<0.1 mm) might attribute to the existing cracks and pores inside of boulder materials. A formation scenario of Ryugu will be shown to explain the history of Ryugu formation and evolustion or even a planetary formation.

Our scenario is like this: 1) porous dust with ices of volatile species (water and CO₂) were accumulated to form a planetesimal in the outer solar system. 2) Aqueous alteration occurred by internal heating due to radioactivity of Al²⁶ but not heated to drive strong thermal metamorphism. Materials were more altered at the innermost region to consolidate almost equal to typical carbonaceous chondrites, but less altered at the outermost region to leave the materials so porous and fragile. 3) The parent body migrated to inner region of the Solar System, 4) Impact fragmentation of parent body, sometimes by S-type bodies [12]. 5) Degassing of volatiles by sublimation due to expose to space, to make freeze-dry porous materials. 6) Reaccretion of fragmented rocks and boulders with high porosity by low degree of consolidation and freeze-dry and formation of a rubble pile body. Most of surface boulders are occupied by those from the inner region of the parent body as the representative boulders, while relatively porous boulders originated from the outermost region are the "hot spots" and relatively consolidated boulders originated from the innermost region are the "hot spots" and relatively consolidated boulders originated from the innermost region are the "hot spots" and relatively consolidated boulders originated from the innermost region are the "hot spots" and relatively consolidated boulders originated from the innermost region are the "hot spots" and relatively consolidated boulders originated from the innermost region surface processes by spaceweathering.

References

[1] Okada T. et al, 2020. Nature 579, 518-522. [2] Shimaki Y. et al., 2020. Icarus 348, 113835. [3] Sakatani N. et al. 2021.
 Nature Astron. 5, 766-774. [4] Grott M. et al. 2019. Nature Astron. 3, 971-976. [5] Hamm M. et al. 2022. Nature Comm. 13, 364. [6] Nakamura T. et al. 2022 Science abn8671. [7] Ishizaki T. et al. This issue, [8] Flynn, GJ, 2018. Chem. Erde. 78, 269-298. [9] Senshu H. et al. 2022. Intl J. Thermophys. 43, 102. [10] Yada T. et al. 2022. Nature Astron. 6, 221-225. [12] Tatsumi E. et al. 2021. Nature Astron. 5, 39-45.

Evidence of Permafrost Processes in C-asteroid Regoliths

M. Zolensky¹, T. Nakamura², T. Mikouchi³, H. Yurimoto⁴, T. Noguchi⁵, R. Okazaki⁶, H. Yabuta⁷, H. Naraoka⁶, K. Sakamoto⁸, S. Tachibana³, S. Watanabe⁹, and Y. Tsuda⁸

¹ARES, NASA Johnson Space Center, Houston, TX 77058, USA (<u>michael.e.zolensky@nasa.gov</u>); ²Tohoku University, Miyagi 980-8578, Japan; ³The University of Tokyo, Tokyo 113-0033, Japan; ⁴Hokkaido University, Sapporo 060-0819, Japan; ⁵Kyoto University, Kyoto 606-8502, Japan; ⁶Kyushu University, Fukuoka 819-0395, Japan; ⁷Hiroshima University, Higashi-Hiroshima 739-8526, Japan; ⁸ISAS/JAXA, Sagamihara 252-5210, Japan; ⁹Nagoya University, Nagoya 467-8501, Japan.

Introduction: C-complex asteroids have suffered a wide variety of physical processing, some of which are not very obvious. Carbonaceous chondrites experienced and recorded a very wide range of chemical and physical processing in both nebular and asteroidal settings [1-7], resulting in the following textures: brecciation, flattened chondrules and foliation (CV and CM chondrites in particular), carbonate and phyllosilicate veins (CI, CM, CV3 dark inclusions), local alignment of matrix phyllosilicates (CR2, CI, CM), and shearing (mylonitization) around lithic fragments. Many of the extensively altered carbonaceous chondrites contain rounded to elliptical aggregates of phyllosilicates, carbonates, spinels (chromite and magnetite), Fe-Ni sulfides, and embayed olivines and pyroxenes, generally ascribed to impact shock or static burial pressures [6,7]. However, it is probable that even in the wettest regions of an asteroid dry periods were experienced during the periodic breaching of an icy surficial rind [8], which could have occurred during impacts or "volcanic" venting of gas and heat from the interior (this assumes internal heating). Thus, there should have been multiple wet-dry cycles experienced by these regolith or immediately subsurface materials. We have previously suggested that all the deformation features mentioned above would have arisen naturally from cycles of wet-dry and, more critically, freeze-thaw environmental conditions (permafrost) in asteroid regoliths [5]. Here we detail two related textures observed in CI chondrites, including asteroid Ryugu samples (essentially CI chondrite), consistent with permafrost processes.

Permafrost Processes in Regoliths: It is well-known to soil scientists that conditions of radically alternating humidity can have important morphologic and petrologic consequences [9]. Grains and lithic clasts can become rotated, crushed and drawn out into linear features (shearing). Porosity (including contraction and shearing cracks) and other bulk physical properties will vary in a dramatic manner. Easily altered materials will be dissolved while more resistant materials will be pulverized and mixed into matrix. These effects would be most pronounced for the C1-2 lithologies where the swelling clay saponite can be found in abundance, including the CI chondrite meteorites and asteroid Ryugu samples. Another important process to be considered is periodic growth and melting of ice crystals in the regolith [10-11]. The positive molal volume change during crystallization of water will induce oriented microfabrics to develop in the regolith, normal to the direction of ice crystal growth. Thus, masses of platy grains (in this case phyllosilicates, especially saponite flakes) will develop a pronounced compaction and preferred alignment. This process will recur for each freezing episode. Since the orientation of the growing ice mass will vary for each succeeding generation of growth, the eventual result will be to impart a particular, invasive, regolith fabric consisting of sheets of aligned clays for each generation, which will appear as anastomosing strings of phyllosilicates with roughly aligned basal directions in polished or thin sections (Figure 1). Our study has revealed that such textures are common in the CI chondrites.

Ice crystal growth could explain the preferred alignment of saponite observed in some Ryugu samples (see Figure 6b of [12]). However, a more likely explanation for this particular texture is mobilization of saponite flakes during wet, water saturated episodes, and deposition of these flakes onto the surface of underlying rock fragments under the force of gravity. These features are termed "silt caps", and these are a common feature of permafrost soils [11,13]. Of course, a major difference between permafrost processes on earth as compared to asteroids is the greatly reduced gravity on the latter. However, mass wasting is usually observed on small bodies including asteroids (including Ryugu and Bennu) and comet nuclei [14,15], so gravity-driven processes operated on the Ryugu parent body. Growth and collapse of subsurface asteroidal icicles would also impart cyclical changes in bulk regolith porosity, induce rotation and movement of crystals and lithic fragments through frost heaving, and consequent shearing [11]. This process could also account, to some degree, for the flattened chondrules observed in some carbonaceous chondrites (especially CMs).

Conclusions: We therefore suggest that cyclical, indigenous environmental processes, rather than impact gardening, could be responsible for some of the late-stage petrologic characteristics of wet carbonaceous chondrites, and Ryugu samples. We note that this suggestion has also recently been proposed by another group [16]. Bulk petrographic features of additional Ryugu samples and carbonaceous chondrites should be investigated more systematically in order to test this idea, especially samples rich in clays such as saponite.

References: [1] Moskovitz et al. (2013) *Icarus* **224**, 24; [2] Vilas (2008) *Ap. J.* **135**, 1101–1105; [3] Lazaro et al. (2012) *A&A* **549**, L2; [4] Zolensky et al. (2022) *MAPS* **57**, MAPS.13909; [5] Zolensky (1995) *Meteoritics* **30**, 606-607; [6] Sneyd et al. (1988) *Meteoritics* **23**, 139-149; [7] Scott et al. (1992) *GCA* **56**, 4281-4293; [8] DuFresne and Anders (1962) *GCA* **26**, 1085-1114; [9] Nahon (1991) *Introduction to the Petrology of Soils and Chemical Weathering*, pp. 122-133; [10] Van Vliet and Fox (2018) Frost Action. In *Interpretation of Micromorphological Features of Soils and Regoliths*, 2nd Ed., Elsevier; [11] Zhang et al. (2021) The Influence Mechanism of Freeze-Thaw on Soil Erosion: A Review. *Water* **13**, 1010; [12] Nakamura T. et al., (2022) *Science* **377**, 10.1126/science.abn8671; [13] Menzies and Ellwanger (2011) *Boreas* **40**, 271-288; [14] Jawin et al.

(2020) *JGR Planets* **125**, Issue 8; [15] Steckloff and Samarasinha (2018) *Icarus* **312**, 172-180; [16] Nakamura E. et al. (2022) *Proceedings of the Japan Academy, Series B* **98**, 227-282.

Figure 1. Ivuna CI chondrite, in cross polars. Two views of the same area in different rotation angles showing two distinct directions of phyllosilicate (yellow stringers) preferential orientations (arrows). Views measure 2 mm in longest dimension.

Modeling of aqueous alteration in the parent body of the asteroid Ryugu

A. Tsuchiyama^{1,2}, J. Matsuno¹ and M. Matsumoto³

¹ Research Organization of Science and Technology, ²CAS, Guangzhou Institute of Geochemistry, ³Tohoku University

The mineralogy, petrology and chemical properties of the samples collected from the asteroid 162173 Ryugu by the Hayabusa2 spacecraft show that the samples correspond to CI meteorites not affected by terrestrial weathering (e.g., [1-3]). The parent body of Ryugu were formed by accretion of minerals, organics, and ice, and aqueous alteration occurred by reaction of melted ice with the minerals and organics [1]. The major lithology of the Ryugu samples consists mostly of hydrous phyllosilicates (serpentine and saponite), carbonates, FeS and magnetite which precipitated from liquid (melted ice) during the aqueous alteration. Least- and less-altered lithologies, where some anhydrous minerals, such as olivine, remained unaltered or partially altered, were also observed [1]. Model chemical equilibrium of the aqueous alteration was calculated in an appropriate condition (*e.g.*, 40°C based on oxygen isotope equilibrium [2] and ice of H₂O + 0.08 CO₂ based on CO₂-bearing fluid inclusion[1]) as a function of the initial water/rock ratio (in mass), *W/R*, and found that the mineral assemblages are almost consistent with the least-altered, less-altered and altered major lithologies at *W/R* of 0.06 to 0.1, 0.1 to 0.2, and 0.2 to 0.9, respectively [1]. The order of precipitation of minerals in the major lithology was also estimated from the included and enclosed relations among these minerals [4].

We understood the outline of the aqueous alteration by the Ryugu sample initial analysis as mentioned above. However, we still do not know how the aqueous alteration occurred and ceased; for example, how liquid was present, and precipitation occurred from the liquid. Therefore, in this study, we performed a modeling of the aqueous alteration by reference to the minerals and their assemblages and the chemical composition of the Ryugu samples.

In the present model, we made the following assumptions to simplify the problem; (1) the system Mg-Fe-Si-Ca-O-S-C-H is taken into consideration with the bulk chemical composition of CI [5] that is unchanged during the alteration except for O (oxidation or reduction permitted). (2) The starting material is composed of anhydrous minerals, amorphous silicate, organics, and CO₂-H₂O ice. Olivine, metallic Fe, and FeS are considered for the anhydrous minerals. We adopted Mg# (Mg/(Mg+Fe) in mole) of 0.99 for olivine, which was observed in least- and less-altered lithologies [6]. Material similar to GEMS (glass embedded with metal and sulfide) is considered for amorphous silicate based on the observation in the least-altered lithology [1]. This GEMS-like material (GLM) is assumed to have the mean GEMS composition of [7]. We consider relatively oxidized GLM, where only nanoFeS particles (without nanoFe) are embedded in FeO-bearing amorphous silicate. Thus, the Mg# of the amorphous silicate becomes 0.612 to maintain the mean GEMS composition. The density of GLM is assumed to be 3 g/cm³. (3) We consider only IOM as organics. The chemical composition of IOM is adopted from [8] and its density is assumed to be 1.3 g/cm^3 . IOM is not changed by the alteration. (4) The ice CO₂/H₂O ratio is 0.08 as proposed by [1]. The ice melts to form CO₂bearing water. The temperature is 40°C proposed by [2] and the pressure is less than \sim 50 bar for a 50-km-radius parent body [1]. In these conditions, the melted ice is a liquid state (not fluid) and the densities of H_2O and CO_2 are almost constant (1 g/cm³ [9]) and 1.04 g/cm³ [10], respectively). (5) The aqueously altered products are serpentine, saponite, FeS, magnetite, and dolomite. The Mg#'s of serpentine and saponite are 0.85 based on the Ryugu sample analysis [1]. Dolomite is only considered as a carbonate although other carbonates (magnesite and calcite) are present in the Ryugu samples. (6) GLM stats to react with liquid to form serpentine and saponite first, and simultaneously the same proportion of Fe as that of altered GLM becomes magnetite. If the GLM is completely altered, olivine starts to react with liquid. (7) GLMs and the phyllosilicates (serpentine and saponite) have nano-sized pores (nanopores) based on the TEM observation of the Ryugu samples [1]. Any other pores are not present in the initial state, but the space that used be as ice acts as micron-sized pores (micropores). (8) The water/rock ratio, W/R, is defined as the mass ratio of water (or ice) to whole of the other materials including IOM.

The amounts of the formula weights of the phases (minerals, IOM and liquid) were calculated to have elemental balance among the chemical compositions of the phases and the bulk chemical compositions, and their volumes were obtained from the densities of the phases. This calculation is similar to the CIPW norm calculation, and chemical equilibrium was not considered. We made calculation for a case where the initial IOM volume is 10% with respect to solid phases and the porosities of the nanopores in both GLM and phyllosilicates are 40%.

In the initial state, the modes of olivine, Fe, FeS (nanoFeS in GLM not included), GLM with nanopores, and IOM are calculated to be 17.2, 2.5, 4.9, 67.4, and 8.1 vol.%, respectively, to have the elementary balance (Fig.1 at W/R = 0). We changed the initial water/rock ratio (in mass), W/R, as a parameter. The final mineral assemblages after the complete reaction with liquid were calculated with different W/R. Changes in the volumes of the phases are shown in Fig. 1. In the range of W/R = 0 to 0.10 (Stage-1 in Fig. 1), mainly saponite and minor amounts of serpentine and magnetite form from GLM and Fe, and H₂O in liquid

is completely consumed. CO₂ in liquid is also completely consumed to form dolomite, and therefore no liquid remains in this stage after the aqueous alteration. GLM and Fe are completely consumed at W/R = 0.10. With further increase in W/R, olivine starts to react with water, and serpentine forms by consuming some saponite together with olivine to accommodate their Mg/Si ratios (W/R = 0.10 to 0.12, Stage-2 in Fig. 1). Olivine is completely consumed at W/R = 0.12, and no liquid remains in this stage too. In W/R > 0.12, some liquid remains after complete reaction with GLM, Fe and olivine, and the volumes of magnetite, saponite, serpentine, and FeS are constant (W/R = 0.12 to 0.19, Stage-3 in Fig. 1). The volume of dolomite increases by consuming CO₂ in liquid, and no CO₂ remains in liquid in this stage. In W/R > 0.19 (Stage-4 in Fig. 1), some CO₂ remains in liquid because [C] > 2[Ca] and the volume of dolomite is constant. Stage-1, Stage-2 and Stages-3 and -4 roughly correspond the least-altered, less-altered, and altered major lithologies, respectively, in terms of their mineral assemblages. The modes of dolomite, magnetite, saponite with nanopores, serpentine with nanopore, FeS, and IOM in Stage-4 are 2.0, 4.3, 31.3, 48.1, 8.1, and 6.2 vol.%, respectively. These are similar to those of the main lithology [1]. The relation of W/R and stages are also roughly consistent with the chemical equilibrium calculation of [1]. The boundary between Stages-2 and -3 (W/R = 0.12) corresponds to W/R = 0.18 in [1]. This difference is derived from the rough calculation in the present model. The broad similarities suggest that the present model roughly reflects the equilibrium although the model itself does not consider equilibrium.

As a next step, we calculated the proportions of liquid filling pores. The total volume of the bulk material consisting of minerals, IOM, and pores (nanopore in GLM and/or phyllosilicates and micropore after ice) increases by the aqueous alteration from the initial volume (minerals, IOM, nanopore in GLM, and ice) by $\sim 10 - 20\%$. Because such volume increase would not occur for asteroids, we assumed that the initial bulk volume maintains constant by collapsing some of micropores. Liquid (if present) occupies the remaining pores. Fig. 2 shows the liquid proportion filling pores, f, and the total porosity including liquid, ϕ , as a function of W/R for the initial state before aqueous alteration. As we assumed liquid preferentially fills nanopores due to capillarity, with increasing W/R, f(nanopore) increases first, and then f(micropore) increases after f(nanopore) reaches 100 %. For the final state after aqueous alteration (Fig. 3), similar behavior of f's can be seen, but f(nanopore) and f(micropore) are 0 % in Stages-1, and -2. These results showed that liquid partially occupies only nanopores if W/R is small, and even if W/R is large, macropores are not fully filled with liquid, suggesting that pores are not fully filled with liquid during aqueous alteration. The bulk density of Ryugu samples was determined to be 1.79 g/cm³, indicating the porosity of 31 % if we compared with the grain density of CI meteorites [1]. If the porosity has not changed from the end of aqueous alteration to present, ϕ of 31 % corresponds to W/R of 0.19 (Fig. 3), where 100 % of nanopores and 61 % of micropores are filled with liquid, respectively, before the alteration (Fig. 2), and 55 % of nanopores and 0 % of micropores are filled with liquid, respectively, after the alteration (Fig. 3). These suggest that aqueous alteration in the Ryugu parent body should occur through dissolution and reprecipitation in conditions where not so much water present.

Figure 1. The volumes of phases after aqueous alteration at different water/rock ratio, W/R.

Figure 2. Liquid proportion filling pores and porosity before aqueous alteration.

Figure 3. Liquid proportion filling pores and porosity after aqueous alteration.

References

[1] Nakamura T. et al. 2022. Science. 10.1126/science.abn8671. [2] Yokoyama T. et al. 2022. Science
10.1126/science.abn7850. [3] Ito M. et al. 2022. Nature Astron. 10.1038/s41550-022-01745-5. [4] Tsuchiyama A. et al. 2022.
85th Annual Meeting of The Meteoritical Society 2022 6221.pdf. [5] Lodders K. et al. 2009. Landolt–Bornstein (Berlin:
Springer), 42. [6] Mikouchi T. et al. 2022. 85th Annual Meeting of The Meteoritical Society 2022 6180.pdf. [7] Keller L.P. and Messenger S. 2011. Geochim. Cosmochim. Acta 75:5336. [8] Alexander C.M.O'D. et al. 2007. Geochim. Cosmochim. Acta 71:4380. [9] Xiaoyan Ji. et al. 2005. Ind. Eng. Chem. Res. 44:8419. [10] Longhi J. et al. 2005. Geochim. Cosmochim. Acta 6: 529.

Chemical abundances in Ryugu, nugget effect, and cosmic composition

Nicolas Dauphas¹, Tetsuya Yokoyama², Ryota Fukai³, Tomohiro Usui³, Shogo Tachibana⁴, Maria Schönbächler⁵, Andrew M.

Davis¹, Hisayoshi Yurimoto⁶, The Hayabusa2-initial-analysis chemistry team, The Hayabusa2-initial-analysis core.

¹Origins Lab, Dept. of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, USA

²Dept. of Earth & Planetary Sciences, Tokyo Institute of Technology, Japan

³Dept. of Solar System Sciences, ISAS, JAXA

⁴Dept. of Earth and Planetary Science, University of Tokyo, Japan

⁵Inst. für Geochemie und Petrologie, ETH Zürich, Switzerland

⁶Dept. of Earth and Planetary Sciences, Hokkaido University, Japan

Approximately 99.86% of the mass of the solar system is locked up in the Sun, which is largely inaccessible and whose composition is only known through spectroscopy and analysis of solar wind. Much of our knowledge of the chemical and isotopic compositions of the bulk solar system comes from analysis of meteorites, and among those CI (Ivuna-type) carbonaceous chondrites, which contain most elements except the most volatile ones in proportions that match estimates from solar photosphere observations [1,2]. CI chondrites are rare and most of them have been in meteorite collections for many decades (the largest one, Orgueil, fell in 1864), where they have been exposed to moisture, airborne and handling contaminants. The Hayabusa2 mission sampled ~5.4 g of pristine material from Ryugu, a Cb-type asteroid [3]. Laboratory analyses of the returned sample show that Ryugu is related to CI chondrites and probably originated from the outskirts of the solar system [4-7]. The only known contaminant for Ryugu samples is Ta in the projectile used to liberate dust and fragments from Ryugu's surface [8]. Given their pristine nature, Ryugu samples are ideally suited to constrain the composition of outer-solar system material, which we take as a proxy for the solar composition. A caveat to estimating the solar composition using Ryugu or CI chondrites is that these may contain extraneous refractory dust compared to other inner solar system objects. This was most clearly demonstrated with rare earth elements (REEs), as carbonaceous chondrites all show Tm anomalies relative to non-carbonaceous chondrites [9,10], presumably due to the presence of refractory dust with a group II REE pattern characterized by large positive Tm anomalies produced by evaporation/condensation processes in the solar nebula [11]. At this stage, it is unclear if the Sun would contain the same complement of refractory dust as CI chondrites, or if inner solar system objects are more representative.

Fig. 1. Correlations between Mn/Cr, Fe/Mn, and Rb/Sr ratios. The yellow star is the CI composition. The red points are bulk fragment measurements for Ryugu [4,7]. The curves are calculated mixing curves between bulk CI and dolomite in CI chondrites [12,13].

Yokoyama *et al.* [4] and Nakamura E. *et al.* [7] reported high precision chemical composition analyses of Ryugu fragments by quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS), the gold standard for such analyses. Those measurements show that Ryugu has almost unfractionated chemical abundances relative to CI chondrites, strengthening the case for a link between Cb-asteroid and CI chondrites. The fragments analyzed are relatively small (from ~0.2 to ~30 mg) and show significant departures relative to CI chondrites that are unrelated to volatility. This is true even in the largest fragments analyzed, which show significant enrichments in REEs, Ca, Sr, Ba, P, and Mn [4]. Chemical abundance variations have been seen previously in chondrites that presumably reflect heterogeneous distribution (and unrepresentative sampling) of phases highly enriched in some elements [9]. This is known as a nugget effect and represents a limit in the precision that can be attained in bulk rock analyses. Carbonate and phosphate phases have been found in Ryugu samples [4,6,7] and could be responsible for the chemical variations seen in bulk fragment analyses.
A nugget effect for REEs associated with the presence of phosphate was identified in carbonaceous and ordinary chondrites [9]. There are several telltale signatures of such a nugget effect. The first one is that in elemental ratio plots, "bulk" analyses should define mixing curves between the true bulk and the mineral composition. In ordinary and carbonaceous chondrites, the presence of phosphate nuggets was identified as a negative correlation between La/Lu ratios and Eu/Eu* (=observed Eu/interpolated Eu) anomalies (phosphates in ordinary chondrites have high La/Lu and negative Eu/Eu* anomalies) [9]. The phosphates in Ryugu lack these characteristic features and are more difficult to detect [7]. Ryugu fragments are rich in dolomite, which has high Mn/Cr, low Rb/Sr, and low Fe/Mn. In Fig. 1, we plot CI-normalized Mn/Cr and Fe/Mn against Rb/Sr. As shown, the ratios are correlated, and the variations observed can be well explained by admixture or removal of dolomite at the percent level. Another telltale signature of a nugget effect is that the dispersion in elemental ratios should decrease as the inverse of the square root of the mass of sample homogenized [9]. As shown in Fig. 2, the dispersions in elemental ratios are consistent with a sampling problem associated with a nugget effect. The dispersion in elemental ratios can be calculated if the nugget size, abundance, and composition are known [9]. Because these are poorly constrained for carbonates, we calculated instead the dispersion for the smaller fragments digested and calculated the predicted dispersion for larger masses. Having established that unrepresentative sampling of carbonate is likely responsible for the dispersion in specific elemental ratios, we can predict the expected dispersion if large sample masses are digested. We thus estimate that for 1 g of Ryugu sample homogenized/digested, the dispersion (2σ) of the bulk Mn/Cr and Rb/Sr ratios will be better than ~±5%. Elements that are not concentrated in specific minerals will be much less affected by this uncertainty. Our analysis shows that much of the dispersion in chemical composition between Ryugu grains is a due to non-representative sampling of mineral phases highly enriched in some elements. This artifact can be remediated by homogenizing a larger sample mass (~ 1 g), which is important to constrain the "cosmic" composition, and test if previous estimates based on CI chondrites are reliable.



Fig. 2. Elemental ratios sensitive to carbonate nugget effects against mass homogenized/digested. If a nugget effect is present, we would expect the dispersion to decrease as the inverse of the square root of the mass of sample homogenized/digested (black envelope) [9]. As shown, this seems to be the case.

References. [1] Lodders, K., 2021. Space Science Reviews, 217, 1. [2] Asplund M. et al. 2021. Astronomy & Astrophysics 653, A141. [3] Yada T. et al. 2022. Nature Astronomy 6:214. [4] Yokoyama T. et al. 2022 Science eabn7850. [5] Ito, M et al. 2022. Nature Astronomy, 1, https://doi.org/10.1038/s41550-022-01745-5. [6] Nakamura T. et al., 2022. Science, eabn8671. [7] Nakamura E. et al. (2022) Proceedings of the Japan Academy, Series B 98, 227. [8] Sawada H. et al. 2017. Space Science Reviews, 208, 81. [9] Dauphas, N. and Pourmand, A., 2015. Geochimica et Cosmochimica Acta, 163, 234. [10] Barrat, J.A., Dauphas, N., et al., 2016. Geochimica et Cosmochimica Acta, 176, 1. [11] Hu, J. Y., et al. (2021). Science Advances, 7(2), eabc2962. [12] Endreß, M. and Bischoff, A., 1996. Geochimica et Cosmochimica Acta 60, 489. [13] Macdougall, J.D., et al. 1984. Nature, 307, 249.

The Hayabusa2-initial-analysis chemistry team: T. Yokoyama, K. Nagashima, I. Nakai, E.D. Young, Y. Abe, J. Aléon, C.M.O'D. Alexander, S. Amari, Y. Amelin, K. Bajo, M. Bizzarro, A. Bouvier, R. W. Carlson, M. Chaussidon, B.-G. Choi, N. Dauphas, A. M. Davis, T. Di Rocco, W. Fujiya, R. Fukai, I. Gautam, M. K. Haba, Y. Hibiya, H. Hidaka, H. Homma, P. Hoppe, G.R. Huss, K. Ichida, T. Iizuka, T.R. Ireland, A. Ishikawa, M. Ito, S. Itoh, N. Kawasaki, N. T. Kita, K. Kitajima, T. Kleine, S. Komatani, A. N. Krot, M.-C. Liu, Yuki Masuda, K.D. McKeegan, M. Morita, K. Motomura, F. Moynier, A. Nguyen, L. Nittler, M. Onose, A. Pack, C. Park, L. Piani, L. Qin, S.S. Russell, N. Sakamoto, M. Schönbächler, L. Tafla, H. Tang, K. Terada, Y. Terada, T. Usui, S. Wada, M. Wadhwa, R.J. Walker, K. Yamashita, Q.-Z. Yin, S. Yoneda, H. Yui, A.-C. Zhang, H. Yurimoto.

The Hayabusa2-initial-analysis core: S. Tachibana, T. Nakamura, H. Naraoka, T. Noguchi, R. Okazaki, K. Sakamoto, H. Yabuta, H. Yurimoto, Y. Tsuda, S. Watanabe.

Abundance and properties of Ryugu diffuse organic matter

Rhonda Stroud^{1,2}, Bradley De Gregorio², Jens Barosch³, Larry Nittler^{1,3}

The Hayabusa2-initial-analysis Organic Macromolecule Team and Core Team

¹School of Earth and Space Exploration, Arizona State University, USA,

²Materials Science and Technology Division, US Naval Research Laboratory, USA,

³Earth and Planets Laboratory, Carnegie Institution of Washington, USA

Initial Analysis studies have revealed that Ryugu regolith particles contain abundant organic carbon (3 wt%) [1,2], and that organic matter has the same range of morphologies as previously observed in primitive chondrites, including solid and hollow nanoglobules, nanodiamonds, dense, irregularly shaped particles, and diffuse materials with poorly-defined boundaries [3]. The diffuse organics form coatings on and fill the space between mineral grains, and intercalate into phyllosilicates. Because the diffuse carbon can be very thin (single nm) and intimately mixed with the nanoscale minerals, especially phyllosilicates, it is below the spatial limit for many techniques. Many analyses focus instead on globules or other organic particles > 200 nm. However, the diffuse carbon represents a substantial portion, possibly 50% or more, of the total organic carbon, and must be considered for a complete understanding of the Ryugu organics. To better understand the abundance and properties of diffuse carbon, we used correlated scanning transmission x-ray microscopy (STXM), scanning transmission electron microscopy (STEM) and nanoscale secondary ion mass spectrometry (NanoSIMS) to examine samples from Chambers A and B.

Figure 1A shows a bright-field STEM image montage of a focused ion beam (FIB) lift-out section from particle A108-?? pressed into a Au mount for NanoSIMS analysis. The BF STEM image shows a mixture sulfides and phyllosilicates with domain sizes of 10s to 100s of nm, but no discernable carbonaceous particles. However, STEM-based energy dispersive x-ray spectroscopy (EDS) mapping of the section Fig. 1B reveals carbon distributed throughout. Quantification of the C:Si molar ratio with Cliff-Lorimer routines for areas > $1\mu m^2$ for no visible nanoglobules indicate values of ~ 0.8 ± 0.3 . Similar STEM-EDS analysis of additional FIB sections shows comparable C:Si ratios, confirming that a large portion of the organic carbon is present as diffuse matter rather than globular carbon in general, not only in this specific particle. However, it is difficult to obtain a precise determination of fraction of the diffuse vs. particulate carbon because the ability to resolve individual organic carbon particles < 100 nm depends greatly on the sample preparation and analysis conditions. In 100-nm thick FIB sections such as this, amorphous carbon particles as large as 50 nm could be hidden in images by the greater intensity variation of the phyllosilicates and sulfides, and only revealed by spectroscopy.

Measurement of the carbon K edge x-ray absorption near edge structure (XANES) with STXM can provide the average functional chemistry distribution of the diffuse carbon (Fig. 1D, Fig. 1E). Notably, there are four prominent peaks in the diffuse carbon spectrum from regions across this FIB section, with the typical aromatic (C=C), ketone (C=O), carboxyl (COOH) groups commonly seen in chondritic IOM, plus the CO₃ carbonate peak. Although the carbonate peak is very intense, the additional x-ray absorption peaks associated with crystalline carbonates are absent. In addition, the STEM-EDS shows Ca is absent, and no signs of Fe or Mg carbonate nanocrystals are observed in the STEM images. XANES spectra extracted from smaller ROIs show variability in the relative intensity of the four functional groups and in some cases distinct aliphatic-rich regions can be found (Fig.1D blue box, 1E blue spectrum).

To better constrain the nature of the diffuse carbon, it is also helpful to analyze samples of particle prepared by ultramicrotome and as demineralized acid-insoluble organic matter (IOM) isolates. Those date are discussed but not shown here due to space constraints, but will be presented at the meeting. Some, but not all, of the diffuse organic matter is preserved in the IOM samples, and comprises the fine-grained porous material referred to as "fluffy", distinct from the nanoglobules. Notably, the prominent carbonate peak, easily observed in the FIB sections, is not present in the IOM XANES data. The CO₃ peak is present though difficult to measure in the XANES data from microtomed

particles. Electron energy loss spectroscopy in the STEM, coupled with EDS, shows the carbonate peak is associated with organic carbon in direct contact with phyllosilicates. This suggests that different portions of the diffuse IOM have distinct chemical origins, with the molecular carbonate signature possibly due to reaction of C-rich fluids with phyllosilicates.





Figure 1. A Bright field scanning transmission electron microscope image montage of a FIB section from particle 108xx. B. Energy dispersive x-ray spectroscopy composite elemental map of C, Si, Au and Ga. The Au is the substrate, and Ga from FIB carbon deposition. C. Extracted sum spectrum from the area outlined in white in (C). D. Scanning transmission x-ray absorption microcopy image of the FIB section at 288.9 eV. E. Extracted normalized spectrum in optical density units from representative regions, revealing pervasive molecular carbonate chemistry and localized enhancement in aliphatic content.

References

Yokoyama T et al. 2022. Science abn7850. [2] Yabuta H. et al. 2022. Abstract #2241. 53d LPSC. [3] Stroud R.
 M., et al. 2022. Abstract #2052. 53d LPSC.

The Hayabusa2-initial-analysis Organic Macromolecule Team and Core Team: H. Yabuta, G. D. Cody, C. Engrand, Y. Kebukawa, B. De Gregorio, L. Bonal, L. Remusat, R. Stroud, E. Quirico, L. R. Nittler, M. Hashiguchi, M. Komatsu, E. Dartois, J. Mathurin, J. Duprat, T. Okumura, Y. Takahashi, Y. Takeichi, D. Kilcoyne, S. Yamashita, A. Dazzi, A. Deniset-Besseau, S. Sandford, Z. Martins, Y. Tamenori, T. Ohigashi, H. Suga, D. Wakabayashi, M. Verdier-Paoletti, S. Mostefaoui, G. Montagnac, J. Barosch, K. Kamide, M. Shigenaka, L. Bejach, T. Noguchi, H. Yurimoto, T. Nakamura, R. Okazaki, H. Naraka, K. Sakamoto, S. Tachibana, S. Watanabe, and Y. Tsuda

Sulfur-XANES of intact Ryugu grains and the isolated IOM

H. Suga¹, Y. Tamenori¹, H. Yabuta², H. Yurimoto³, T. Nakamura⁴, T. Noguchi⁵, R. Okazaki⁶, H. Naraoka⁶, K. Sakamoto⁷, S. Tachibana⁸, S. Watanabe⁹, Y. Tsuda⁷, and the Hayabusa2-initial-analysis IOM team

¹Japan Synchrotron Radiation Research Institute (JASRI/SPring-8),1-1-1 Kouto, Sayo, Hyogo pref. 679-5198 Japan,

²Hiroshima University, Japan, ³Hokkaido University, Japan, ⁴Tohoku University, Japan, ⁵Kyoto University, Japan, ⁶Kyushu University, Japan, ⁷JAXA, Japan, ⁸Univ. of Tokyo, Japan, ⁹Nagoya University, Japan.

Introduction: The Hayabusa 2 spacecraft was launched on December 2014 to collect samples of the near-Earth C-type (carbonaceous) asteroid (162173) Ryugu [1]. This mission aims to investigate the origin and evolution of the early Solar System and life. In December 2020, the spacecraft returned 5.42 g of the Ryugu surface samples to the Earth [2]. The initial sample analysis team and the JAXA phase2 curation found that the elemental compositions, mineralogy, and organic chemistry of asteroid Ryugu were identical to those of CI chondrites [e.g., 3-6].

A variety of sulfur-bearing organic molecules have been identified from both soluble organic matter (SOM) and insoluble organic matter (IOM) in carbonaceous chondrites [e.g., 7-9]. Sulfur has a wide range in oxidation states from -2 to +6, so it can be used as a cosmochemical indicator of redox conditions; therefore, it contributes to elucidating the formation of organic molecules in the early Solar System. X-ray Absorption Near Edge Structure of Sulfur (S-XANES) can be used to estimate oxidation states of sulfur from a large chemical shift, and the chemical species can be discussed by the spectral profile. In this study, we conducted the S-XANES analysis on intact Ryugu grains and the isolated IOM to determine the sulfur composition.

Samples and Method: The Ryugu aggregate samples A0109-21 and C0057-1&2 were selected for S-XANES measurements. The acid treatment protocol of IOM isolation is described in [3] in detail. The intact Ryugu grains and the isolated IOM were analyzed by non-destructive bulk S K-edge XANES analysis at BL27SU in SPring-8.

Results and Discussion: Sulfur-XANES spectra were obtained from the intact Ryugu grains and the isolated IOM. The spectral profile of the intact grains is composed of the dominant peak around 2470.4 eV and broad spectra ranging from 2475.0 to 2484.0 eV. The peak of 2470.4 eV corresponds to the inorganic sulfide (S^{1-}) [8]. Compared with the spectral profile of standard materials in the previous study [e.g., 10], it corresponds to pyrrhotite, a common sulfide in Ryugu [5]. In addition, a peak derived from sulfate (S^{6+}) was observed at 2482.6 eV from A0109-21.

The S-XANES spectra of Ryugu IOM were entirely different from those of the intact grains. The peak around 2472.0 eV corresponding to organic sulfides (C-S-S-C, C-S-C) was the most prominent from the spectra of Ryugu IOM. The shoulder feature at 2474.3 eV is consistent with the presence of heterocyclic sulfur (S⁰) [9]. The broad profile ranging at 2477.0–2484.0 eV could be a mixture composed of oxidized organic sulfur species; such as sulfonate (R-SO₂O-R'), sulfone (R-SO₂-R'), and sulfites (R-SO₃) [8]. A moderate peak of sulfates was also observed, which is likely to be correspond to organic sulfate (R-O-SO₃) because inorganic sulfate compounds should have already been dissolved from the Ryugu samples during acid treatment to extract IOMs. No significant difference was found between IOMs extracted from A0109 and C0057.

The spectral shapes of the isolated Ryugu IOM were broadly similar to those of IOM from carbonaceous chondrites [8,9], except that the peak derived from inorganic sulfide was not detected from the Ryugu IOM. In particular, moderate abundances of heterocyclic sulfur and oxidized organic sulfur functional groups in Ryugu IOM were closer to those in IOM isolated from CM rather than that of CI. CI experienced a higher temperature (100–150 °C) than CM, and heterocyclic sulfur and oxidized organic sulfurs in them are the aqueous alteration products related to the alteration temperature [8]. Our study shows that Ryugu experienced as low temperature as CM chondrites during the parent body aqueous alteration, which is consistent with the discussion by [5].

Conclusion: In this study, organic sulfur functional groups were identified from the IOM isolated from Ryugu samples by S-XANES. Our results indicate that reductive organic sulfur components, i.e., organic sulfides (C-S-S-C, C-S-C), are dominant relative to oxidized organic sulfurs in Ryugu IOM. Ryugu IOM experienced low-temperature parent body aqueous alteration.

References

[1] Tachibana S. et al. 2014. Geochemical Journal 48:571–587. [2] Yada T. et al. 2022. Nature Astronomy 6:214–220. [3] Yabuta, H. et al. 2022, Science, under review. [4] Yokoyama T. et al. 2022. Science, eabn7850. [5] Nakamura T. et al. 2022.

Science, abn8671. [6] Ito M. et al. 2022. Nature Astronomy, https://doi.org/10.1038/s41550-022-01745-5. [7] Schmitt-Kopplin Ph. et al. 2010. PNAS 107:2763–2768. [8] Orthous-Daunay FR. et al. 2010. Earth and Planetary Science Letters 300:321–328. [9] Bose M. et al. 2017. Meteoritics & Planetary Science 52:546–559. [10] Suga H. et al. 2021. Minerals 11:514.

The Hayabusa2-initial-analysis Organic Macromolecule and Core Teams: H. Yabuta, G. D. Cody, C. Engrand, Y. Kebukawa, B. De Gregorio, L. Bonal, L. Remusat, R. Stroud, E. Quirico, L. R. Nittler, M. Hashiguchi, M. Komatsu, E. Dartois, J. Mathurin, J. Duprat, T. Okumura, Y. Takahashi, Y. Takeichi, D. Kilcoyne, S. Yamashita, A. Dazzi, A. Deniset-Besseau, S. Sandford, Z. Martins, Y. Tamenori, T. Ohigashi, H. Suga, D. Wakabayashi, M. Verdier-Paoletti, S. Mostefaoui, G. Montagnac, J. Barosch, K. Kamide, M. Shigenaka, L. Bejach, T. Noguchi, H. Yurimoto, T. Nakamura, R. Okazaki, H. Naraoka, K. Sakamoto, S. Tachibana, S. Watanabe, and Y. Tsuda

Investigating the noble gas and nitrogen relationship between Ryugu and other carbonaceous chondrites

M. W. Broadley¹, D. J. Byrne¹, E. Füri¹, L. Zimmerman¹, B. Marty¹ R. Okazaki², T. Yada³, F. Kitajima², S. Tachibana^{3,4}, K. Yogata³, K. Sakamoto³, H. Yurimoto⁵, T. Nakamura⁶, T. Noguchi⁷, H. Naraoka², H. Yabuta⁸, S. Watanabe⁹, Y. Tsuda³, and the Hayabusa2 Initial Analysis Volatile Team

¹Université de Lorraine, CNRS, CRPG, F-54000 Nancy France, ²Kyushu University, Japan. ³Institute of Space and Astronautical Science, JAXA, Japan, ⁴University of Tokyo, Japan, ⁵Hokkaido University, Japan, ⁶Tohoku University, Japan, ⁷Kyoto University, Japan, ⁸Hiroshima University, Japan, ⁹Nagoya University, Japan.

The Hayabusa2 mission of the Japan Aerospace Exploration Agency (JAXA) successfully returned surface material from the C-type asteroid (162173) Ryugu to Earth. This material has now been classified as closely resembling CI-type chondrites, which are the most chemically pristine meteorites. The analysis of material from the surface of Ryugu therefore provides a unique opportunity to analyze the volatile composition of material that originated from a CI-type asteroid [1] without complications arising from terrestrial contamination. Given their highly volatile nature, the noble gas and nitrogen inventories of chondrites are highly sensitive to different alteration processes on the asteroid parent body, and to terrestrial contamination.

We investigated at CRPG Nancy (France) the nitrogen and noble gas signature of two grains collected from the first and second touchdown sites [2] to provide an insight into the formation and alteration history of Ryugu. We find that the concentration of trapped noble gas in the Ryugu grains is greater than the average composition of previously measured CI chondrites. The trapped noble gases are primarily derived from phase Q, although a significant contribution of presolar nanodiamonds Xe-HL is noted. The large noble gas concentrations coupled with a significant contribution of presolar nanodiamonds suggests that the Ryugu grains may represent some of the most primitive unprocessed material from the early solar system.

In contrast to the noble gases, the abundance of nitrogen and $\delta^{15}N$ composition of the two Ryugu grains are lower than the average CI chondrite value. We attribute the lower nitrogen abundances and $\delta^{15}N$ measured in this study to the preferential loss of a ¹⁵N-rich phase from our grains during aqueous on a parent planetesimal. The analyses of other grains returned from Ryugu have shown large variations in nitrogen concentrations and $\delta^{15}N$ indicating that alteration fluids heterogeneously interacted with material now present on the surface of Ryugu. Finally, the ratio of trapped noble gases to nitrogen is higher than CI chondrites, and is closer to refractory phase Q and nanodiamonds. This may indicate that Ryugu experienced aqueous alteration that led to the significant loss of nitrogen likely from soluble organic matter hosted in our two grains without significant modification of the noble gas budget, which is primarily hosted in insoluble organic matter and presolar diamonds and is more resistant to aqueous alteration.

References

[1] Yokohama et al. 2022 Science DOI: 10.1126/science.abn7850. [2] Okazaki et al. Science, Accepted.

Nitrogen isotopes in Ryugu return samples revealed by the stepwise combustion analysis, in comparison with CI falls and Antarctic finds

Ko Hashizume¹, Akizumi Ishida², Ayano Chiba¹, Ryuji Okazaki³, Toru Yada⁴, Fumio Kitajima³,

Hisayoshi Yurimoto⁵, Tomoki Nakamura², Hiroshi Naraoka³, Takaaki Noguchi⁶, Hikaru Yabuta⁷, Shogo Tachibana⁸, Sei-ichiro Watanabe⁹, Kanako Sakamoto⁴ and Yuichi Tsuda⁴

¹Faculty of Science, Ibaraki University, ²Department of Earth Science, Tohoku University, ³Department of Earth and Planetary Sciences,

Kyushu University, ⁴Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, ⁵Department of Earth and Planetary Sciences, Hokkaido University, ⁶Division of Earth and Planetary Sciences, Kyoto University, ⁷Department of Earth and Planetary Systems Science, Hiroshima University, ⁸UTokyo Organization for Planetary and Space Science, The University of Tokyo, ⁹Department of Earth and Environmental Sciences, Nagova University

Nitrogen isotope ratio is a powerful tool in cosmochemistry to decipher the origin and evolution of planetary materials. The nitrogen isotope ratio ${}^{15}N/{}^{14}N$, usually expressed by the delta notation, $\delta^{15}N \equiv [({}^{15}N/{}^{14}N)/({}^{15}N/{}^{14}N)_{AIR} - 1] \times 1000$ (‰), exhibits large variations among different meteorites (Fig. 1). The isotope ratio of nitrogen, being a typical volatile element, is particularly useful to constrain the formation and evolution processes of planetary atmosphere for Earth and other rocky planets. Viable Earth formation models assume that CI/CM-like volatile-rich carbonaceous chondrites may have contributed as one of the important volatile sources for Earth, if not entirely on the source for the rocky body of this planet. CI chondrites, the most volatile-rich chondritic group known so far, exhibit $\delta^{15}N$ values typically around +40 ‰. The higher $\delta^{15}N$ values for the CI chondrites than for the present Earth atmosphere may impose important constraints on the formation and evolution history of the Earth atmosphere.

The texture and mineralogical composition of Ryugu samples are similar to CI chondrites. Three fall meteorites categorized as CI chondrites, Alais, Ivuna and Orgueil, have been studied so far for nitrogen isotopes. However, recent search on the vast stock of Antarctic meteorites has revealed that there exist several Antarctic meteorites which exhibit similar texture and mineralogical composition with the fall CI chondrites. Though similar, these potential CI Antarctic meteorites still exhibit marked difference from the CI falls, particularly from the volatile-element points of view: The majority of phyllosilicates are dehydrated in these Antarctic CI meteorites, while the phyllosilicates of CI falls mostly remain hydrated [4]. Fig. 2 compares bulk nitrogen isotope composition of Ryugu samples with those of CI chondrites, falls (Alais, Ivuna and Orgueil) and an Antarctic find (Y-980115). Interestingly, the $\delta^{15}N$ values are correlated with the nitrogen concentrations: lower the concentration, lower the $\delta^{15}N$ value. Note that this correlation is not compatible with the one we normally expect to occur by Rayleigh-distillation type devolatilization process, nor by addition of a terrestrial contamination at different degrees. Apparently, an unknown isotope fractionation (or mixing) effect in the nitrogen isotope composition has emerged among the CI-chondrite family.

The stepwise analyses may provide isotope "fingerprints" to compare the identities of planetary materials. By this method, we may distinguish possible endmembers co-existing in the samples. Fig. 3 demonstrates the usefulness of this method, for example, by the profiles obtained from a Ryugu bulk sample, compared with the one for CI chondrite Orgueil. These profiles provide information, not only the bulk δ^{15} N value and bulk N and C concentrations, but include points such as, (a) presence of a nitrogen component easily combustible at low (>200°C) temperatures with δ^{15} N <+10 ‰, (b) a component released



Fig 1. Bulk nitrogen isotope composition among different meteorites. Compilation by Hashizume (2015) [1]. Important isotope data beyond this range include protosolar composition (-380 ‰; Marty et al, 2011 [2]) or cometary range (+600 - +1000‰; Marty et al, 2016 [3])



Fig 2. Bulk nitrogen isotope composition of Ryugu samples and CI chondrites. Ryugu data labelled A0105-07 and C0106-07 are reported in [5] (Ibaraki data); A0105-05 and C0106-06 in [6] (Nancy data); A0106 in [7] (JAMSTEC data). The other solid marks are literature bulk data for CI chondrites from [8-13]. Open marks (Ivuna and Y-980115) are sums of unpublished stepwise combustion data recently acquired at Ibaraki Univ.

spike-wise at ~500°C with δ^{15} N « 0 ‰, which is inferred to be hosted by presolar nano-diamonds, (c) one released at 600-800°C exhibits a plateau δ^{15} N value of +17‰, and (d) finally the one released at 1100°C and above with a δ^{15} N value as low as -20%. Apparently, nitrogen in Ryugu consist of several components with distinct origins. The combustion profile of Orgueil, though shows partially similar isotope signature with Ryugu, for example the one presumably from presolar microdiamonds, exhibits generally δ^{15} N higher than Ryugu by several tens of ‰, and higher N concentrations. The differences are particularly prominent at low temperature range below 600°C, which is generally considered to be the range where N from the organic matter is released. Seemingly the organic matter with δ^{15} N values as high as +60% is missing in Ryugu, which could correspond to the "missing component" inferred by comparing the bulk composition for samples belonging to the CI chondrite family (Fig. 2). It is worth to note that, though the missing component could be inferred to be an organic component from the combustion temperature, it seems to be decoupled with the bulk of carbon, and could be a component with a peculiar chemical composition with much higher N/C ratios than the bulk composition.

In this presentation, we will compare the stepwise combustion profiles obtained for Ryugu, with those of Ivuna and Y-980115 recently obtained using the same facility equipped at Ibaraki University. Though part of the Ryugu data (A0105-07 and C0106-07) exhibit similar bulk nitrogen concentrations and δ^{15} N values with Y-980115, we will demonstrate that the combustion profiles appear quite different, possibly suggesting that the N isotope evolution mechanism could be different between these two kinds of CI-like samples.



Fig 3. Comparison of stepwise combustion profiles for Ryugu sample C0106-07 (bttm) obtained at Ibaraki Univ, and literature data [11] for Orgueil (top). The concentrations are plotted in arbitrary unit, although the areas of the bars between different temperature ranges, and also between the two samples for the same element correctly represent the relative concentrations.

References

[1] Hashizume K. 2015. In "Encyclopedia of Astrobiology" doi:10.1007/978-3-642-27833-4_1065-3. [2] Marty B. et al.
Science 332:1533. [3] Marty B. et al. 2016. Earth and Planetary Science Letters 441:91. [4] King AJ. et al. 2019. Geochemistry 79:125531. [5] Okazaki R. et al. 2022. Abstract #1348. 53rd LPSC. [6] Byrne DJ. et al. 2022. Abstract #2096. 53rd LPSC. [7] Naraoka H. et al. 2022. Abstract #1781. 53rd LPSC. [8] Kerridge JF. 1985. Geochimica et Cosmochimica Acta 49:1707. [9] Robert F. & Epstein S. 1982. Geochimica et Cosmochimica Acta 46:81. [10] Yang J. & Epstein S. 1983. Geochimica et Cosmochimica Acta 47:2199. [11] Grady MM. et al. 2002. Meteoritics & Planetary Science 37:713. [12] Pearson VK. et al. 2006. Meteoritics & Planetary Science 41:1899. [13] Chan QHS. et al. 2016. Earth, Planets and Space 68:7.

Visible to Near-Infrared Spectrophotometry of C0002 Powder Samples of Asteroid 162173 Ryugu in Comparison with ONC-T and NIRS3 Instruments Onboard Hayabusa2 Spacecraft

T. Hiroi¹, R. E. Milliken¹, K. M. Robertson¹, C. D. Schultz¹, K. Amano², T. Nakamura², H. Yurimoto³, T. Noguchi⁴, R.

Okazaki⁵, H. Yabuta⁶, H. Naraoka⁵, K. Sakamoto⁷, S. Tachibana⁸, T. Yada⁷, M. Nishimura⁷, A. Nakato⁷, A. Miyazaki⁷, K.

Yogata⁷, M. Abe⁷, T. Okada⁷, T. Usui⁷, M. Yoshikawa⁷, T. Saiki⁷, S. Tanaka⁷, T. Fuyuto⁹, S. Nakazawa⁷, S. Watanabe¹⁰, Y.

Tsuda⁷, S. Sasaki¹¹, H. Kaiden¹², K. Kitazato¹³, M. Matsuoka¹⁴, and E. Tatsumi¹⁵

¹Brown University, ²Tohoku University, ³Hokkaido University, ⁴Kyoto University ⁵Kyusyu University, Japan, ⁶Hiroshima University, ⁷JAXA Institute of Space and Astronautical Science, ⁸University of Tokyo, ⁹Kanagawa Institute of Technology, ¹⁰Nagoya University, ¹¹Osaka University, ¹²National Institute of Polar Research, ¹³University of Aizu, ¹⁴National Institute of Advanced Industrial Science and Technology, ¹⁵Instituto de Astrofisica de Canarias.

Samples and Spectrophotometric Measurements

Powder samples of the largest sampled stone C0002 of asteroid 162173 Ryugu returned by Hayabusa2 mission were loaned for visible and near-infrared (VNIR) spectrophotometric studies. The powder samples were produced by physical-strength measurements and were partially contaminated with a glue (glycol phthalate). Part of the powder was washed with acetone, which turned it into a fine powder (<125 μ m estimate). Large glue fragments were handpicked from the remaining coarse powder (125-500 μ m estimate) and a bulk powder sample was produced by combining the two powder samples.

Bidirectional VNIR reflectance spectra (0.3-2.6 μ m) of the samples were measured at NASA Reflectance Experiment Laboratory (RELAB) using its bidirectional reflectance spectrometer at the standard viewing geometry of 30° incidence and 0° emergence angles, and their photometric properties were measured at a limited number of viewing geometries. The photometric property of a Labsphere Spectralon standard was measured relative to the standard viewing geometry at 550 nm in wavelength.

Biconical Fourier-transform infrared (FTIR) reflectance spectra (1-100 μ m) of the samples were measured in a dry-air purged environment. The VNIR and FTIR spectra were combined at 2.5 μ m in wavelength by scaling the FTIR reflectance to the VNIR reflectance.

Spectrophotometric Analyses

Phase-angle dependency of the powder samples at 550 nm in wavelength is plotted in Fig. 1, and VNIR-FTIR spectra up to 4 μ m are plotted in Fig. 2 along with sample photos under a microscope. The phase curve in Fig. 1 shows much brighter albedo and lower inclination than those obtained by ONC-T measurements in proximity of asteroid Ryugu [1]. It may be due to the difference between the flatter surface of the powder sample compared with the rough asteroid surface that includes shadows. Further photometric modeling analysis is warranted.

The OH and H₂O absorption bands near 3 μ m in spectra shown in Fig. 2 were analyzed in the same manner as [2]. Natural log reflectance spectra of the powder samples were fit with a linear-in-wavelength continuum background and Gaussians (in wavenumber) over the wavelength range of ~2.6-3.6 μ m (variable depending on spectral shape). One of the results (fine powder) is shown in Fig. 3. Because the first two Gaussian bands (labeled as 1 and 2 in Fig. 3) are believed to be characteristic of carbonaceous chondrite classes [2], their



Fig. 1. Phase-angle dependency of reflectances of C0002 powder samples at 550 nm in wavelength.



Fig. 2. VNIR-FTIR spectra $(0.3-4 \mu m)$ and photos of C0002 powder samples. Cup diameter is 4 mm.



Fig. 3. Gaussian fitting of C0002 fine powder spectrum.

Band 1 centers and Band 1 / Band 2 strength ratios are plotted in Fig. 4. Ryugu C0002 powders all plot very close to unheated CI1 chondrites and Ivuna heated up to 400°C. This result is consistent with previous studies of Ryugu being mostly unheated CI1 chondrite [e.g., 3], and low-degree heating may not be detected by this method.

Comparison with ONC-T and NIRS3 Observations

Shown in Fig. 5 is a plot of linear combinations of the VNIR-FTIR spectra of the C0002 fine and coarse powder samples to match average spectra of representative (but different) areas of Ryugu acquired by ONC-T and NIRS3. Most of the ONC-T band reflectance values, overall spectral shape, and 2.7 µm absorption band strength could be matched.

However, when the 2.7 μ m band region is closely examined, there are significant mismatches between the NIRS3 and C0002 spectra. The NIRS3 spectrum shows absorption bands at 2.65 and 2.81 μ m which are absent in C0002 spectrum. If this is not due to NIRS3 data calibration errors, there may be some unstable phases lost during the sample recovery.

Another mismatch is the 2.7 μ m band center position. Fig. 6 shows the NIRS3 spectrum and the modeled C0002 spectrum with its wavelength resolution matched with that of NIRS3 spectrum (18 nm). While the NIRS3 spectrum (open black squares) shows the band center at around 2.72 μ m asymmetrically expanded toward the longer wavelength, the modeled C0002 powder spectrum (solid purple circles) shows the band center clearly at a shorter wavelength near 2.71 μ m. When the C0002 powder spectra are artificially shifted toward the longer wavelength by 6 nm before resampling for the NIRS3 resolution, the resulting modeled spectrum (open purple circles) matches with the NIRS3 spectrum much better. A difference in band position is consistent with spectra of ejecta from an artificial crater showing shorter 2.7 μ m band positions [4].

Summary and Discussion

If the C0002 powder samples represent the average surface material of asteroid Ryugu, this study indicates that the global space weathering may have occurred mainly by solar wind that caused the 2.7 μ m absorption band center to be shifted toward a longer wavelength [*e.g.*, 5]. If such space weathering occurred, the 2.7 μ m band strength and the visible spectra measured with ONC-T might have been altered as well. This would influence the physical interpretation of the model fits shown in Fig. 5.

References

Tatsumi E. et al. 2020. A&A 639:A83. [2] Hiroi T. et al. 2021. Polar Science 29:100723. [3] Yokoyama T. et al. 2022. Science 10.1126:7850. [4] Kitazato K. et al. 2021. Nature Astronomy 5:246. [5] Lantz C. et al. 2015. A&A 577:A41.



Fig. 4. Band 1 center vs. Band 1 / Band 2 strength ratio of C0002 powder samples plotted with hydrous carbonaceous chondrites (modified from [2]).



Fig. 5. Comparison of C0002 powder spectra with ONC-T and NIRS3 data.



Fig. 6. Matching of the $2.7 \,\mu m$ absorption band feature between the modeled C0002 powder spectra and NIRS3 spectrum in Fig. 5.

Reflectance spectrum of Ryugu grains and their acid-extracted residues in the UV-VIS range

K. Yumoto¹, H. Yabuta², S. Sugita¹, The Hayabusa2 initial analysis IOM team, and the Hayabusa2 Initial Analysis Core team ¹Univ. of Tokyo, Japan. ²Hiroshima Univ., Japan.

Introduction: Reflectance spectrum in the ultraviolet to visible (UV–VIS) range is among the most frequently used wavelength range for observations of main-belt C-complex asteroids. Furthermore, distinctive spectral differences (e.g., spectral slope, absorption at UV) have been reported among C-complex asteroids [1]. However, their interpretation is not necessarily straightforward. This is because the UV–VIS spectrum is controlled by various physical (e.g., grain size) and/or chemical (e.g., mineralogy) state of the reflector. Thus, it is difficult to translate the UV–VIS spectral properties into physically and mineralogically well-defined constraint(s) on asteroid materials.

Studies on the UV–VIS spectra of samples returned from asteroid Ryugu may help us resolve this problem. This is because the physical/chemical state of the returned samples have been studied in detail and pre-processing of the samples allows us to control the sample state (e.g., extraction of certain minerals by acid treatments). Remote sensing by the Optical Navigation Camera (ONC) onboard Hayabusa2 revealed a dark/flat and homogeneous UV–VIS spectrum on the surface of Ryugu [2]. The dark/flat nature of the spectrum was confirmed by initial description of the returned samples [3, 4]. However, grain-to-grain spectral variation was substantially higher than those observed by remote sensing [5]. The variation in reflectance has been attributed to specular reflections caused by micro-scale facets, which were not resolved by remote sensing [5]. Such a result suggests that the texture of grains and abundance of opaque minerals with high reflectivity in the UV–VIS range can highly affect the reflectance of C-complex asteroids. However, the specific (sets of) minerals and/or organic matter that affect the spectra of returned samples have not been identified yet.

In this study, we compared the UV-VIS spectra of intact Ryugu grains with those of acid-extracted residues to evaluate how insoluble organic matter (IOM) contribute to Ryugu's dark and flat spectrum.

Samples and methods: We measured the UV–VIS spectra of returned samples with and without acid treatments that dissolve specific minerals: intact (i.e., un-extracted) grains, HCl-extracted residues, and HCl/HF-extracted residues. All samples were allocated to and processed by the Hayabusa2 IOM team. We measured 50 intact grains from aggregate samples A0106, A0108, and C0109 and 35 grains in the HCl-extracted residues from A0108. Minerals, such as carbonates, sulfides, and magnetite are removed by HCl extraction, and the residue mainly comprises of phyllosilicates and IOM. We also measured 19 grains in the HCl/HF-extracted residues from C0002 and C0107. HCl/HF extraction only leaves IOM within the residue. The sizes of all grains ranged from \sim 10 μ m to 200 μ m except for one \sim 1 mm intact grain from A0108.

The UV–VIS spectra were measured by a high-resolution multi-band spectrometer developed at the University of Tokyo. The spatial resolution is $\sim 2 \, \mu m$ at 550 nm with a 300 $\,\mu m \times 300 \, \mu m$ field of view. The spectrometer is equipped with 25 narrow (10 nm width) band-pass filters from 230 to 1000 nm. Energy of the light power was

reduced (30 μ W at 550 nm) to avoid sample alteration. A standard diffuse reflector with 99% reflectance (Spectralon/Labsphere) was used for radiometric calibration.

Results and Discussion: The reflectance image of the largest grain measured in this study is shown in Fig. 1. Areas with high reflectance in Fig. 1 are specular reflections. Such specular reflections were also observed in acid-extracted residues. These photometric effects were not corrected in our analysis but reflectance from the entire grain (within the dashed curve in Fig. 1) were integrated to obtain the average reflectance for each grain. The spectrum of a typical grain for each of the three mineralogic composition type is shown in Fig. 2. These spectra show that mineralogy have a significant effect on the 1) reflectance, 2) UV absorption feature, and 3) VIS spectral slope as follows.

1. *Reflectance*: Though reflectance has large grain-to-grain variation, Fig. 2 shows that phyllosilicate + IOM residues (i.e., HCl-extracted residues) have a significantly darker reflectance. Such correlation of reflectance with mineralogy



Fig 1 Reflectance image of the largest grain (from A0108) measured in this study. The dashed curve shows the rim of the grain.

provides insights into the reason for the dark nature of carbonaceous materials. Our result implies that the mixing state of phyllosilicates with IOMs may be important in effectively darkening the carbonaceous material. However,

reflectance of acid-extracted residues can be affected by physical and/or chemical alteration caused by the extraction process. Characterization of such alteration is needed to verify the implication of our result.

- 2. UV absorption feature: Fig. 2 shows that though spectra of intact grains are flat throughout the UV–VIS range, spectra of acid-extracted residues show a broad UV absorption centered at ~300 nm. The absorption shape of IOM in Ryugu samples, which is characterized by steepening of the spectral slope from VIS to UV, is consistent with those in Murchison meteorites [6]. Meteoritic studies show that such UV absorption may be caused by abundance of C-H bonds in organics [7] or deficit of magnetite [8]. Since acid extraction removes magnetite and increases the concentration of IOM in the residues, our result is consistent with both hypotheses.
- 3. *VIS slope*: Fig. 2 shows that IOMs exhibit a redder slope in the VIS range. Such trend is consistent with measurements of IOMs in carbonaceous meteorites [6, 9].

These correlation of the spectra with demineralization can be clearly observed in Fig. 3; residues have deeper UV absorption and IOMs have redder VIS slope. This result suggests that variations in UV absorption and spectral slope observed among C-complex asteroids [1] may represent difference in relative abundance of organics to other acid-soluble minerals.

Conclusion: We measured the UV–VIS spectra of Ryugu returned samples and their acid-extracted residues to evaluate how IOM contributes to the dark and flat spectra of Ryugu. Our results show that a variation of constituting minerals/organics, especially demineralization of opaque minerals with higher reflectivity and increase in concentration of IOM, has a significant effect on the reflectance, UV absorption feature, and VIS slope of Ryugu returned samples. This result implies that spectral variation in the UV–VIS range observed among C-complex asteroids may represent chemical variation such as abundance of organics and other acid-soluble minerals.



Fig 2 (Left) Average reflectance spectrum for each of the mineralogic composition. (Right) Reflectance spectrum after normalization at 550 nm. The patch represents the standard error observed among grains.



Fig 3 Correlation plot between UV and VIS spectral slope. Each plot shows the spectrum for each grain measured in this study.

References: [1] Bus & Binzel (2002). *Icarus*, *158*(1), 146-177. [2] Sugita et al. (2019). *Science*, *364*(6437), eaaw0422. [3] Yada et al. (2021) *Nat. Astron.*, *6*(2), 214-220. [4] Cho et al. (2022). *PSS*, *221*, 105549. [5] Yumoto et al. (2022). JpGU, #C002365. [6] RELAB, PDS Geosciences Node Spectral Library. [7] Hendrix et al. (2016) *MAPS*, *51*(1), 105-115. [8] Hendrix et al. (2019). *GRL*, *46*(24), 14307-14317. [9] Kaplan et al. (2019). *MAPS*, *54*(5), 1051-1068.

Nano-infrared spectroscopy of Ryugu samples using AFM-IR measurement

Van T. H. Phan¹, Pierre Beck¹, Rolando Rebois¹ and Takaaki Noguchi², the Hayabusa2-initial-analysis Sand team.

¹Université Grenoble Alpes, CNRS, Institut de Planétologie et d'Astrophysique de Grenoble (IPAG), France ²Kyoto University, Division of Earth and Planetary Science, Kyoto, Japan

Introduction: In late 2020, samples of Ryugu (C-type) were collected from its asteroid and returned to Earth, led by the Japan Aerospace Exploration Agency (JAXA), thought to be similar in composition to CI chondrites ¹. Understanding how and under what conditions the organic matter interacted with inorganic phases, is a key step in hypothesizing the mechanism of accreted organic matter. This "fresh" carbonaceous material allows us to investigate the best preservation sample without terrestrial impact ². In addition, the "bulk" Ryugu samples also show some spectral reflectance bands corresponding to the NH-rich compounds ³. Altogether, our study aims to characterize the minerology, organic matter and the possible N-bearing molecule. To gain insight into fine meteorites matrices containing an interplay of ingredients at the sub-micro scale, it requires analytical techniques with the sub micrometer spatial resolution to separate their composition and understand their petrographic relations. Infrared spectroscopy (IR) is an effective method and a non-destructive technique for molecular-atomic scale vibrations of organic and inorganic compounds in the extra-terrestrial materials ^{4,5}. However, conventional IR spectrometers use mirror-based optics to focus the beam on the sample and thus the spatial resolution is limited by the diffraction limit. This IR diffraction limitation can be overcome by using AFM-IR (Atomic Force Microscopy-Infrared Spectroscopy), based on the combination of infrared spectroscopy and atomic force microscopy to efficiently distinguish spectral signatures of the different constituents ^{6,7}.

Our study aims to characterize two different grains of Ryugu that can be affected by the weathering space prepared by "Min-pet fine team" (Sand team)⁸ as crushed sample between two diamond windows, as well as two different Orgueil samples: one comes from the Paris Museum (Orgueil Museum) and the another one expected "fresher" kept in the sealed flask (Orgueil Flask) from collection of M. Bizzaro. Here, we report the comparison of AFM-IR results between Ryugu and Orgueil as a CI chondrite both in minerology and organic structure.

Samples preparation and methods: Two grains of Ryugu (P0032 and P0038), received from the Sand initial analysis team, were prepared by crushing $10 - 20 \mu m$ fragments between two diamond windows. As with Ryugu, the Orgueil Museum and Orgueil Flask samples were also pressed down to the appropriate thickness for AFM-IR measurement. Before AFM-IR analysis, all samples were performed the micro-FTIR analysis to select the region of interests (ROI).

IR spectroscopy and AFM-IR measurement: The micro-infrared spectra were first analyzed with a Bruker Hyperion 3000 infrared microscope. The nano-IR measurements were obtained with a Bruker nanoIR3s at IPAG (Grenoble, France), which includes an AFM probe capable of scanning the sample and generating topographic images at nm vertical resolution. The AFM-IR measurement can be performed in two acquisition modes: AFM and chemical imaging, and local, single point IR spectrum. First, the wavenumber is fixed and the tip moves along the surface to obtain the AFM topography and IR absorption at the given wavenumber. Second, the position of the tip is fixed and the IR laser is tuned to the possible spectral range (2000 – 700 cm⁻¹ with the APE laser at IPAG) which provides the local absorption spectrum at the point of interest ⁶.

Results and Discussion: We are able to characterize two bulk grains of Ryugu with the region of interest $5 \times 5 \ \mu m^2$ (grain P0032) in the in Figure 1 and the ROI of $3 \times 3 \ \mu m^2$ (grain P0038) in Figure 2.





Figure 1. AFM-IR of a 5×5 μ m2 region of interest (ROI) acquired with the NanoIR3s at IPAG (Grenoble, France) of grain P0032. Left images: AFM image, the AFM-IR images of 1720 (red), 1450 (blue), 1100 (yellow), 1000 cm⁻¹ (green) corresponding to C=O, carbonate, sulfate and Si-O; and RGB (red, green, blue) composition image from the combination of three AFM-IR absorption images: 1720, 1450 and 1000 cm⁻¹ respectively. Right panel: comparison of local AFM-IR spectra on the carbonate rich area (in blue), and the phyllosilicate area (in green) with phyllosilicate signature of Orgueil Flask, μ -FTIR spectra of Ryugu, calcite and dolomite minerals.

In the first grain, P0032, AFM-IR images at different wavenumber were obtained at 1720, 1450, 1100 and 1000 cm⁻¹ in the left panel corresponding to carbonyl (C=O), carbonate, sulfate and phyllosilicate (Si-O), respectively (Figure 1). The three maps of 1720, 1450 and 1000 cm⁻¹ wavenumber were overlaid in the RGB composite image, allowed us to identify the two different domain compositions in the mapped area: the green area can be distinguished by a strong absorption at 1000 cm⁻¹ attributed to the presence of phyllosilicate; the blue/purple area shows a strong absorption at 1450 cm⁻¹ related to carbonate. Numerous spectra were obtained across this ROI shown in the right panel and compared to AFM-IR spectra of Orgueil Flask, dolomite, calcite and μ -FTIR of the same P0032 grain. Spectrum A, the average of hundreds of spectra in the green region shows signature at 1020 cm⁻¹ corresponding to phyllosilicate (e.g., saponite, serpentine). Compared to the Orgueil phyllosilicate spectra, Ryugu is lack of a sulfate signature at 1100 cm⁻¹. However, we observed that some purple areas have stronger absorption at 1100 cm⁻¹ and AFM-IR spectra also confirm the two peaks at 1100 and 840 cm⁻¹ (B spectrum). This Ryugu sample was collected in the fine-grained fraction, affected by space weathering ⁸, the phyllosilicate-rich region can be modified. C spectrum in the blue region suggests the presence of carbonate with two strong signatures at 1440 and 860 cm⁻¹, all indicative of dolomite or calcite.

In the second Ryugu grain, P0038, we first collected the different images at 1720 (red), 1450 (blue) and 1000 cm⁻¹ (green) in ROI of $20 \times 20 \ \mu\text{m}^2$ and overlaid them in the RGB composite image in the upper left panel. We found a ~ 1µmdiameter globule with strong absorption at 1720 cm⁻¹ corresponding to C=O in the organic material (Figure 2). Therefore, the ROI of $3\times3 \ \mu\text{m}^2$ was selected to obtain the different images at 1720, 1600, 1450 and 1000 cm⁻¹. The RGB composite (combined between the images at 1720, 1450 and 1000 cm⁻¹) show an organic globule in red with strong absorption at 1720 cm⁻¹. Later, the contact AFM-IR spectra also confirm the presence of organic matter with two distinct features at 1720 and 1610 cm⁻¹ corresponding to C=O and C=C, respectively. Although the AFM-IR images only show the strong organic appearance, the AFM-IR spectra of organic globule still mixes with the minerals. Compared to the organic matter obtained at Orgueil described in ⁹, the Ryugu organic material is more aromatic. The more diffuse organic may present in this ROI but still finely mixed with phyllosilicate.



Figure 2. AFM-IR of a 3×3 µm² region of interest (ROI) acquired with the NanoIR3s at IPAG (Grenoble, France) of grain P0038 from the RGB image of 20×20 µm² region on the upper left panel. Right images: AFM image, the AFM-IR images of 1720 (red), 1600 (pink), 1450 (blue), 1000 cm⁻¹ (green) corresponding to C=O, C=C, CO₃/CH₂ bend, and Si-O; and RGB (red, green, blue) composition image from the combination of three AFM-IR absorption images: 1720, 1450 and 1000 cm⁻¹, respectively. Lower left panel: comparison of local AFM-IR spectra on the organic globule (red), and the phyllosilicate area (green) with organic matter of Orgueil and µ-FTIR spectra of Ryugu.

Conclusion: The complete results and discussion of this study will be presented at the conference. So far, we confirm that the AFM-IR technique allows us to disentangle the IR signatures of phyllosilicate, carbonate and organic matter in Ryugu at the sub-micron scale. In minerology, compared to Orgueil, the sulfate signatures almost absent from the phyllosilicate, but some modifications in Si-O-rich areas were observed. In the organic structure, the weak organic signature is diffuse and significantly intermixed with phyllosilicate, similar to the diffuse organic of Orgueil. A 1 μ m-organic globule was also observed with clear C=O and C=C features in its structure. This organic matter globule is more aromatic compared to the organic matter in Orgueil meteorites.

Reference: [1] Yokoyama T. et al. 2022 Science (80). [2] Yada T. et al. 2021 Nat Astron. [3] Pilorget C. et al. 2022. Nat Astron. [4] Orthous-Daunay FR. et al. 2013. Icarus. [5] Phan VTH. et al. 2021. Spectrochim Acta - Part A Mol Biomol Spectrosc. [6] Dazzi A, Prater CB. 2017. Chem Rev. [7] Mathurin J. et al. 2019. Astron Astrophys. [8] Noguchi T. et al. 2022. Abstract #1747. 53rd LPSC. [9] Phan VTH. et al. 2022. Meteorit Planet Sci.

Multi-scale variations of the ~2.7µm feature in Ryugu samples, observed by MicrOmega

¹Le Pivert-Jolivet, T.; ^{1,2}Pilorget, C.; ¹Brunetto, R.; ¹Bibring, J.-P.; ³Nakato, A.; ¹Hamm, V.; ^{3,4}Hatakeda, K.; ¹Lantz, C.; ¹Loizeau, D.; ^{1,5}Riu, L.; ³Yogata, K; ¹Baklouti, D.; ¹Poulet, F.; ¹Aléon-Toppani, A.; ¹Carter, J.; ¹Langevin, Y.; ^{3,6}Okada, T.; ³Yada, T.; ^{3,6}Usui, T. and the MicrOmega ISAS Curation Team

¹IAS, Université Paris-Saclay, CNRS, France, ²Institut Universitaire de France, ³Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, ⁴Marine Works Japan, Ltd, ⁵ESAC, ESA, Madrid, Spain, ⁶University of Tokyo, Bunkyo, Tokyo 113-0033, Japan

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. The second touchdown was performed near the artificial crater created by the small carry-on impactor [2] to collect both surface and subsurface materials. The samples were delivered to JAXA (Japan Aerospace eXploration Agency) Extraterrestrial Curation Center for preliminary analyses. They were extracted from chambers A and C, corresponding to TD1 and TD2 respectively, weighed and analyzed in a controlled N₂ environment by an optical microscope, a FTIR, and MicrOmega, a near-infrared (0.99-3.65 μ m) hyperspectral microscope. MicrOmega acquires images of 256x250 pixels with a spatial resolution of 22.5 μ m. The total field of view covers ~5.7x5.7mm² [3]. The first spectral characterization of the bulk samples within the Curation Facility [4,5] showed that the grains are extremely dark and exhibit absorption features at 2.72 μ m, 3.1 μ m and 3.4 μ m due to phyllosilicates, NH-rich compounds, and organics and/or carbonates respectively. The ~2.7 μ m feature was also observed on the asteroid's surface by the NIRS3 spectrometer [6]. In addition to the bulk samples, observations of individual grains, extracted from the bulks, were performed with MicrOmega. We investigate here the variations of the ~2.7 μ m feature at different scales, from the millimeter scale to the hundred microns scale, on 177 grains (typical size 1-7 mm) from chambers A and C.

In order to extract an average spectrum of each grain but also to delimit the region of interest to study the spectral heterogeneities inside the grains, we developed a procedure using thermal emission maps measured by MicrOmega. First, each grain was isolated from the rest of the field of view (the sample holder) thanks to their difference in terms of thermal emission. Then, we performed a study of the ~2.7 μ m band at two different scales. On one hand, all pixels within the mask where averaged to obtain the millimeter scale spectrum of each grain. On the other hand, to better understand the variations at millimeter scale, we looked at smaller scales (<200 μ m) to highlight possible heterogeneities within the grains. Two spectral parameters were calculated to characterize the ~2.7 μ m OH feature: the peak position was estimated using a gaussian fit, and the band depth was calculated between the minimum of reflectance and a linear continuum.

At millimeter scale, the position of the ~2.7 μ m OH feature is consistent with the position found in highly aqueously altered carbonaceous chondrites [7]. Contrary to the bulk spectra where the ~2.7 μ m OH feature was very similar between the two chambers [5], the position of the band varies within an interval of 10 nm at individual grain scale and the peak position distribution varies between the two chambers: there is an excess of grains from chamber A with a position at longer wavelength. Another difference is that the band depth of the grains varies within a larger range in chamber A than in chamber C. The analysis at smaller scales (<200 μ m) is still ongoing and will be presented at the time of the conference.

We will discuss the spectral differences between the collected grains, in particular between chambers A and C, and what information they carry about the composition of phyllosilicates and the space weathering processes affecting Ryugu's surface materials. Indeed, the OH feature position can change with the Mg/Fe ratio in phyllosilicates [8]. Moreover, space weathering experiments on carbonaceous chondrites [9] have shown that the band position was shifted towards longer wavelength after irradiation. The slight variation of band position we observe at the grain scale is consistent with the shift observed on Ryugu's surface spectra, between the artificial crater and the surrounding surface [10]. We expect that the smaller scale analysis will give hints on the involved processes.

References

[1] Tachibana et al. (2020) LPS XXXXI Abstract #2027. [2] Arakawa et al. (2017) Space Sci. Rev. 208, 187-212. [3] Bibring et al. (2017) Space Sci. Rev. 208, 401-412. [4] Yada et al. (2022) Nat Astron, 6, 214-220. [5] Pilorget et al. (2022) Nat Astron,

6, 221-225. [6] Kitazato et al. (2019) Science, 364, 272-275. [7] Takir et al. (2013) M & PS 48, 1618-1637. [8] Besson and Drits (1997), CCM, 45, 158. [9] Lantz et al. (2017) Icarus 285, 43-57. [10] Kitazato et al. (2021) Nat Astron, 5, 246-250.

Organics in Ryugu samples, from MicrOmega and FTIR analyses within the ISAS curation facility

¹Bibring, J.-P.; ^{2,3}Hatakeda, K.; ¹Brunetto, R.; ¹Baklouti, D.; ¹Carter, J.; ^{1,4}Pilorget, C.; ¹Loizeau, D.; ²Yogata, K; ^{2,5}Okada, T.; ^{2,5}Usui, T. and the IAS and ISAS MicrOmega Curation Team.

¹IAS, Université Paris-Saclay, CNRS, France; ²Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency; ³Marine Works Japan, Ltd; ⁴Institut Universitaire de France; ⁵University of Tokyo, Bunkyo, Tokyo 113-0033, Japan

Within the ISAS/JAXA facility, in which all samples collected by the Hayabusa 2 JAXA are maintained preserved from any terrestrial contamination [1], the MicrOmega instrument [2] has analyzed bulk samples from both collection sites, spread onto 6 main dishes, as well as hundreds of grains extracted from them. Two features show up in the NIR (0.99 μ m to 3.6 μ m) spectra of essentially all grains, as acquired by MicrOmega: one, peaked around the 2.7 μ m, is diagnostic of OH stretch, primarily within the matrix material [3] while a second one, at ~3.4 μ m, is due to either or both carbonates [4] and organics [5]. This paper focusses on the later one, with updated results and interpretation.

Most of the ~3.4 organics-related features within MicrOmega spectra are peaked at 3.42 μ m, diagnostic of CH₂ asymmetric stretch, with less significant CH₃ absorption, around 3.38 μ m (asymmetric) nor 3.45 (symmetric), pointing at aliphatic methylenic moieties, with high CH₂/CH₃. MicrOmega spectra of a number of grains exhibit several other features, in a variety of intensities, often coupled with the 3.42 μ m and/or among themselves, primarily peaked around 2.9 μ m, 3.05 μ m, 3.25 μ m, 3.55 μ m. The candidate functional groups they are diagnostic of, are: aldehyde, alcohol, organic acid, amine and amide, and aromatics. The recent spectral upgrade of the FTIR within the curation facility, ranging up to 8.5 μ m, has demonstrated, through preliminary analyses of the larger grain of the collection (C9000, > 1 cm wide), the potential of joined MicrOmega/FTIR measurements on the same grain.

Specifically, the FTIR provides means to discriminate between distinct potential compounds in two spectral domains: 5.2-6.2 μ m, and 6.8-7.8 μ m. Noticeably, C=O bonds (absorptions peaked at ~5.8 μ m) can be distinguished from C=C bonds (absorptions peaked at ~6.2 μ m). In addition, in a few spots, a critical feature shows up around 4.7 μ m, potentially tracing nitrile (-C=C-) or cyanate (O=C=N⁻). In addition to N-rich compounds, P-rich bonds [6] could be confirmed and characterized by FTIR.

We shall review all measurements performed up to now, by both MicrOmega and the upgraded FTIT within the curation facility, and discuss them in the frame of the evolution of the pristine organic constituents within Ryugu.

References

- [1] Yada et al. (2022) Nat Astron, 6, 214-220
- [2] Pilorget et al. (2022) Nat Astron, 6, 221-225
- [3] LePivert et al. 2022, this symposium
- [4] Loizeau et al. 2022, this symposium
- [5] Carter et al. (2022) 53rd LPSC contrib. N°1495
- [6] Pilorget et al. 2022, this symposium

MicrOmega detections of carbonates in Ryugu returned samples within the Hayabusa2 JAXA Extraterrestrial Curation Center

Loizeau, D.¹; Pilorget, C.¹; Riu, L.²; Brunetto, R.¹; Bibring, J.-P.¹; Nakato, A.³; Aléon-Toppani, A.¹; Hatakeda, K.³; Yogata, K.³; Carter, J.¹; Le Pivert-Jolivet, T.¹; Yada, T.³; Okada, T.³; Usui, T.³; Langevin, Y.¹; Lantz, C.¹; Baklouti, D.¹; Miyazaki, A.³; Nishimura, M.³; Nagashima, K.³; Kumagai, K.³; Hitomi, Y.³; Sugiyama, Y.³; Abe, M.³; Saiki, T.³; Tanaka, S.³; Nakazawa, S.³; Tsuda, Y.³; Watanabe, S.⁴;

¹Institut d'Astrophysique Spatiale, Université Paris-Saclay, CNRS, France, ²ESAC, ESA, Madrid, Spain, ³Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, Japan, ⁴Nagoya University, Nagoya 464-8601, 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 sub-bulks and 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 within the curation facility [2]. The MicrOmega instrument used in the JAXA Extraterrestrial Curation Center is a NIR hyperspectral microscope. This configuration allows a mineralogical characterization of pristine Ryugu samples, as they have never been exposed to terrestrial environment.

MicrOmega has a total field of view of 5 mm x 5 mm, with resolution of ~22.5 μ m/pixel in the focal plane. It covers the spectral domain from 0.99 μ m to ~3.6 μ m. 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 Hayabusa2 returned capsule, and then on extracted individual grains and sub-bulks, each stored in their sapphire dishes. For this study, we analyzed MicrOmega data of ~180 extracted individual grains (a few mm in size) and 14 sub-bulks (all observed with MicrOmega within the Curation Center in 2021). This is a unique opportunity for mapping mineral and organic species over a very large set of samples from Ryugu.

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

Detections of carbonates were made in grains included in the bulk samples from both chambers A and C. In the bulks, some small detached grains seem to be entirely carbonate-rich and are up to ~450 μ m, down to <50 μ m in size. In larger, extracted grains, carbonate inclusions are also detected, with sizes up to >500 μ m in a 3mm-sized grain, and down to <50 μ m.

Spectrally, two carbonate populations are detected: many detections, mostly $<100 \ \mu m$ in size, have spectral bands centered at 2.30, 2.50, and 3.30-3.43 μm , similar to CaMg(CO₃)₂ dolomite; and few detections, mostly $>100 \ \mu m$, have bands at 2.32, 2.51, 3.31-3.45 μm together with a strong absorption $<1.5 \ \mu m$, similar to (Mg,Fe)CO₃ breunnerite. We also report 3 small detections ($<50 \ \mu m$ in size) with spectra with bands at 3.35-3.48 μm , similar to CaCO3 calcite. Both dolomite and breunnerite-like areas are detected in samples from both chambers, but we record more detections from chamber C than from chamber A.

The largest detection was made on grain C0041, covering ~0.25 mm², or ~10% of the visible surface of the grain. This grain is one of the grains with "White regions" as described in [5]. The carbonate inclusion shows a complex morphology with three branches, 100s μ m long, around a main area. Spectra of this detection are breunnerite-like.

Another large and complex carbonate inclusion was detected in grain C0181. In this example, bright carbonate detections surround a darker, $300 \ \mu m$ long carbonate inclusion that seem to correspond to a single crystal where both bright and dark carbonates correspond to breunnerite-like spectra.

Carbonates detected by MicrOmega are distributed in two main populations both different in composition and size/morphology, questioning the formation process or processes that led to this two populations. We did not detect any spatial transition from dolomite to breunnerite, that would have indicated a possible gradient during a single formation event. We propose two distinct formation processes: dolomites may have formed within small pores in the precursor material, limiting their size, very early in the solar system [6], while breunnerite may have formed in fractures between grains, possibly after an impact on Ryugu's parent body, or even triggered by the impact. At what scale these processes were distinct in time is still questionable.

References

[1] Tachibana S. et al. (2021) LPS, XXXXXII, Abstract #1289. [2] Yada T. et al. (2021) *Nature Astronomy 6, p.214-220.* [3] Pilorget et al. (2021) *Nature Astronomy 6, p.221-225.* [4] Pilorget C. and Bibring J.-P. (2014) *PSS 99, 7-18.* [5] Nakato A. et al. (2021) *8th Hayabusa Symposium.* [6] McCain K. A. et al. (2022) *85th METSOC annual meeting.*

Oxygen and carbon isotope compositions of Ryugu's carbonates: Constraints on the conditions of aqueous alteration

Wataru Fujiya¹, Noriyuki Kawasaki², Kazuhide Nagashima³, Conel M. O'D. Alexander⁴, Hisayoshi Yurimoto², The

Hayabusa2-initial-analysis chemistry team, and The Hayabusa2-initial-analysis core.

¹Ibaraki University, ²Hokkaido University, ³University of Hawai'i at Mānoa, ⁴Carnegie Institution for Science

The Hayabusa2 spacecraft collected CI-chondrite-like materials from the near-Earth asteroid 162173 Ryugu [1]. Ryugu materials are mainly composed of secondary minerals that formed by aqueous alteration, e.g., phyllosilicates, carbonates, sulfides, and oxides. In this study, we performed *in-situ* O and C isotope measurements of calcite (CaCO₃) and dolomite (CaMg(CO₃)₂) in Ryugu samples A0058 and C0002 as well as the Ivuna meteorite to investigate the conditions of the aqueous alteration. We used secondary ion mass spectrometry (SIMS; CAMECA ims-1280HR) at Hokkaido University with a suite of dolomite-ankerite standards [2] and a calcite standard "UWC3" [3].

The δ^{18} O values of the calcites (24‰ to 46‰) in C0002 and Ivuna show a larger variation than those of the dolomites in C0002, A0058, and Ivuna (26‰ to 31‰) (Fig. 1). The average Δ^{17} O value of the C0002 and Ivuna calcites is $1.37 \pm 0.40\%$ (2SE). The Δ^{17} O values of the C0002, A0058, and Ivuna dolomites are systematically lower than those of the calcites, and the average Δ^{17} O value of the dolomites (0.26 ± 0.23‰, 2SE) is closer to the whole-rock values of two Ryugu samples [4] (0.30‰ and 0.58‰). Like the δ^{18} O values, the dolomites in A0058, C0002, and Ivuna have a relatively narrow range of δ^{13} C values from 67‰ to 75‰ (Fig. 2). On the other hand, the δ^{13} C values of the calcites in C0002 and Ivuna are highly heterogeneous, ranging from 65‰ to 108‰, and they are commonly higher than those of the Ryugu and Ivuna dolomites.

If, when the carbonates precipitated they were in O and C isotope equilibrium with the aqueous fluid, their O and C isotope compositions would have been determined by the mass dependent equilibrium isotopic fractionation, which depends on temperature, between carbonates and water for O, and that between carbonates and dissolved CO_3^{2-} (and other dissolved C-bearing chemical species) for C [5]. Thus, the O and C isotope compositions of carbonates would reflect those of water and CO_3^{2-} as well as their formation temperatures. The δ^{18} O variation of ~22‰ observed in the Ryugu calcites (Fig. 1) corresponds to formation temperatures that varied from 0 °C to 150 °C. However, the lack of a correlation between δ^{18} O and δ^{13} C values implies that variable formation temperatures alone cannot explain the observed δ^{18} O and δ^{13} C variations (Fig. 2). Rather it seems likely that both the δ^{18} O value of water and the δ^{13} C value of CO_3^{2-} varied temporally. Because the Δ^{17} O values of the fluids likely decreased as water-rock interaction progressed [6], the calcites with systematically higher Δ^{17} O values should have formed from less "evolved" fluids and likely crystallized earlier than the dolomites (Fig. 1).

It seems likely that the temporal variation in the δ^{13} C values of the C reservoirs and in their chemical speciation occurred due to a change of O fugacity (fO_2). Oxygen fugacity varied along with the production of H₂ via the oxidation of Fe in metal and silicates by H₂O and the subsequent escape of H₂ from the system. To see how the δ^{13} C values of carbonates will change with varying fO_2 , we consider a rather simple model, where gaseous CO₂ and CO and carbonates (and dissolved CO₂, HCO₃⁻, and CO₃²⁻) are in C isotopic equilibrium and the CO₂/CO ratio increases with increasing fO_2 . At first, the CO₂/CO ratio may have been characterized by that of the accreted ices, which may be around unity or higher as observed in cometary ices [7]. We assume that the δ^{13} C value of the bulk gas (CO₂+CO), δ^{13} C_{bulk}, is constant regardless of the CO₂/CO ratio. Because the C isotopic fractionation factor between CO₂ and CO is positive at any temperature, e.g., 93‰ at 0 °C [8], both the δ^{13} C values of CO₂ and CO will decrease monotonically with increasing fO_2 to keep δ^{13} C bulk constant, and the δ^{13} C values of carbonates will also decrease (Fig. 2). In this context, the dolomites with lower δ^{13} C values likely formed at higher fO_2 and/or temperature than the calcites. This, combined with the O isotope signatures of the carbonates, implies that the calcites formed during prograde alteration over wide ranges of fO_2 and temperature, whereas the dolomites formed later from peak temperature to retrograde cooling when the aqueous fluids and silicates approached O isotope equilibrium [9].

References:

[1] Yokoyama T. et al. Science, 10.1126/science.abn7850 (2022) [2] Śliwiński M. G. et al. Geostand. Geoanal. Res. 40, 173-184 (2016). [3] Kozdon R. et al. Chem. Geol. 258, 327-337 (2009). [4] Tang H. et al. Sci. Adv., submitted. [5] Alexander, C. M. O'D. et al. Meteorit. Planet. Sci. 50, 810-833 (2015). [6] Clayton R. N. & Mayeda T. K. Earth Planet. Sci. Lett. 67, 151-161 (1984). [7] Ootsubo T. et al. Astrophys. J. 752, 15 (2012). [8] Richet P. et al. Ann. Rev. Earth Planet. Sci. 5, 65-110 (1977). [9] Nagashima et al. this meeting.



Figure 1. Oxygen isotope compositions of the calcite and dolomite grains in Ryugu and Ivuna samples.

Figure 2. Comparison between C and O isotope compositions of the calcite and dolomite grains in Ryugu and Ivuna samples. A putative evolutionary trend of δ^{18} O and δ^{13} C values is shown by the green arrow.

The Hayabusa2-initial-analysis chemistry team: T. Yokoyama, K. Nagashima, Y. Abe, J. Aléon, C.M.O'D. Alexander, S. Amari, Y. Amelin, K. Bajo, M. Bizzarro, A. Bouvier, R. W. Carlson, M. Chaussidon, B.-G. Choi, N. Dauphas, A.M. Davis, T. Di Rocco, W. Fujiya, R. Fukai, I. Gautam, M.K. Haba, Y. Hibiya, H. Hidaka, H. Homma, P. Hoppe, G.R. Huss, K. Ichida, T. Iizuka, T.R. Ireland, A. Ishikawa, M. Ito, S. Itoh, N. Kawasaki, N.T. Kita, K. Kitajima, T. Kleine, S. Komatani, A.N. Krot, M.-C. Liu, Yuki Masuda, K.D. McKeegan, M. Morita, K. Motomura, F. Moynier, I. Nakai, A. Nguyen, L. Nittler, M. Onose, A. Pack, C. Park, L. Piani, L. Qin, S.S. Russell, N. Sakamoto, M. Schönbächler, L. Tafla, H. Tang, K. Terada, Y. Terada, T. Usui, S. Wada, M. Wadhwa, R.J. Walker, K. Yamashita, Q.-Z. Yin, S. Yoneda, E.D. Young, H. Yui, A.-C. Zhang, H. Yurimoto.

The Hayabusa2-initial-analysis core: S. Tachibana, T. Nakamura, H. Naraoka, T. Noguchi, R. Okazaki, K. Sakamoto, H. Yabuta, H. Yurimoto, Y. Tsuda, S. Watanabe.

Extraterrestrial Amino Acids and Amines Identified in Asteroid Ryugu Samples Returned by the Hayabusa2 Mission

Eric T. Parker¹, Hannah L. McLain^{1,2,3}, Daniel P. Glavin¹, Jason P. Dworkin¹, Jamie E. Elsila¹, José C. Aponte^{1,2,3}, Hiroshi Naraoka⁴, Yoshinori Takano⁵, Shogo Tachibana⁶,

The Hayabusa2-initial-analysis SOM team, The Hayabusa2- initial-analysis core

¹Astrobiology Analytical Laboratory, Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, MD 20771, U.S.A.

²Center for Research and Exploration in Space Science and Technology (CRESST), NASA Goddard Space Flight Center, Greenbelt, MD 20771, U.S.A.; ³Department of Physics, The Catholic University of America, Washington, D.C. 20064, U.S.A.;

⁴Department of Earth and Planetary Science, Kyushu University, Nishi-ku, Fukuoka, 819-0395, Japan; ⁵Biogeochemistry

Research Center (BGC), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Yokosuka, Kanagawa, 237-

0061, Japan; ⁶UTokyo Organization for Planetary and Space Science (UTOPS), The University of Tokyo, 7-3-1 Hongo, Tokyo

113-0033, Japan

Analyses of amino acids and aliphatic amines were performed on the hot water extracts of two asteroid Ryugu samples returned by the JAXA Hayabusa2 mission. The two samples were A0106, which was comprised of surface material, and C0107, which was comprised of both surface and possible subsurface material. Prior to amino acid analysis, portions of each sample extract underwent acid vapor hydrolysis, while other portions remained unhydrolyzed to allow for a respective comparison between bound and free amino acids. Subsequently, these extracts were derivatized with *o*-phthaldialdehyde/N-acetyl-L-cysteine, a chiral, fluorescent tag that enhances analytical specificity and sensitivity for primary amines, and then analyzed using ultrahigh performance liquid chromatography with fluorescence detection and high-resolution mass spectrometry. Prior to the analysis of aliphatic amines, separate portions of each sample extract were derivatized with AccQ•Tag, a florescent tag that is insensitive to salts and targets primary amines and select secondary amines, and then analyzed by ultraperformance liquid chromatography with fluorescence detection and time-of-flight mass spectrometry. The analyses performed here focused on the abundances and relative distributions of amino acids and aliphatic amines, as well as determining the enantiomeric compositions of detected chiral amino acids. For contamination control and background subtraction purposes, procedural and analytical blanks were processed and analyzed in parallel with the Ryugu samples.

In total, 13 amino acids were detected and quantitated here. Five additional amino acids were tentatively identified, but not quantitated. Abundances of individual amino acids of the $C_2 - C_6$ variety were measured to vary between 0.02 and 15.8 nmol g⁻¹. Among those amino acids identified, several were non-protein amino acids that are uncommon in biology. These included β -aminoisobuytric acid (β -AIB) and β -amino-*n*-butyric acid (β -ABA), which were measured to be racemic or very nearly racemic, suggesting that these species were likely to be indigenous to the sample and extraterrestrial in nature. While trace quantities of select protein amino acids were found to be enriched in the L-enantiomer, elevated abundances of racemic, free alanine were observed, indicating that the Ryugu sample studied here were exposed to minimal terrestrial contamination.

The analyses of aliphatic amines revealed four species of the $C_1 - C_3$ variety, which were identified and measured above background levels. These aliphatic amines were methylamine, ethylamine, isopropylamine, and propylamine, in order of descending abundances. These aliphatic amine species were individually measured at abundances ranging from 0.05 - 34.14 nmol g⁻¹ in the unhydrolyzed hot water extracts of Ryugu samples A0106 and C0107.

It has been reported that Ryugu samples are chemically similar to CI-type chondrites [1,2]. However, the abundances and relative distributions of amino acids and aliphatic amines in Ryugu are strikingly different from those of CI1.1/2.0 Orgueil. More specifically, CI1.1/2.0 Orgueil contains upwards of 5.6x the total abundance of amino acids as Ryugu, and more than 5x the total abundance of aliphatic amines as Ryugu. These observed abundance differences could be caused by discrepancies in alteration conditions experienced by the parent bodies of Orgueil and Ryugu, or variabilities in original parent body chemical conditions. Additionally, it is plausible the lower overall abundances of amino acids and amines in the near-surface samples collected by Ryugu may be due to the loss of these compounds, or their volatile precursors, via such factors as space weathering and solar heating in a hard vacuum environment. These possible loss mechanisms are worthy of further exploration. Regarding amino acid distributions observed in Ryugu, α -amino acids, which could have been generated by the Strecker cyanohydrin synthesis, were identified, along with β -, γ -, and δ -amino acids. Examples of the latter included C₃ – C₅ straightchain *n*- ω -amino acids. The observed amino acid distribution indicates that more than one formation mechanism occurred on the Ryugu parent body and was responsible for the amino acids reported here. Lastly, the analytical techniques used here were sufficiently sensitive to detect and quantify the target analytes under the limited sample mass conditions of the current work, which offers strong evidence that these methods will likely perform similarly well when applied to the analyses of amino acids and aliphatic amines in asteroid Bennu samples returned by the NASA OSIRIS-REx mission in September 2023.

References

[1] Yada, T. et al. (2022) Nature Astronomy, 6, 214-220. [2] Yokoyama, T. et al. (2022) Science, eabn7850.

The Hayabusa2-initial-analysis SOM team: Hiroshi Naraoka, Yoshinori Takano, Jason P. Dworkin, Kenji Hamase, Aogu Furusho, Minako Hashiguchi, Kazuhiko Fukushima, Dan Aoki, José C. Aponte, Eric T. Parker, Daniel P. Glavin, Hannah L. McLain, Jamie E. Elsila, Heather V. Graham, John M. Eiler, Philippe Schmitt-Kopplin, Norbert Hertkorn, Alexander Ruf, Francois-Regis Orthous-Daunay, Cédric Wolters, Junko Isa, Véronique Vuitton, Roland Thissen, Nanako O. Ogawa, Saburo Sakai, Toshihiro Yoshimura, Toshiki Koga, Haruna Sugahara, Naohiko Ohkouchi, Hajime Mita, Yoshihiro Furukawa, Yasuhiro Oba, Yoshito Chikaraishi.

The Hayabusa2-initial-analysis core: Shogo Tachibana, Tomoki Nakamura, Hiroshi Naraoka, Takaaki Noguchi, Ryuji Okazaki, Kanako Sakamoto, Hikaru Yabuta, Hisayoshi Yurimoto, Yuichi Tsuda, Sei-ichiro Watanabe.

Carbon dust, from the ISM to the Solar System

E. Dartois¹

¹Institut des Sciences Moléculaires d'Orsay (ISMO), UMR8214, CNRS, Université Paris-Saclay 91405 Orsay Cedex, France

The spectral signatures of interstellar medium dust grains reveal a great diversity of allotropes. Astronomical observations give access to the molecular functionalities of these solids, setting constraints on the composition of organic solids and molecules in the cycling of matter in the Galaxy. Some of these grains and molecules can be reproduced in the laboratory. Other signatures still await for more precise identification of their carriers phases. Laboratory analogues help in constraining their physico-chemical composition and evolution under the harsh galactical radiation environments. This talk will particularly focus on dust materials from the far space environments, from diffuse ISM to protoplanetary disks. We'll present some commonalities and differences between materials found in the Solar System, protoplanetary disks and Interstellar dust.



Figure 1. Interstellar carbon allotropes (from Dartois et al. 2019).

References

[1] Dartois, E., Charon, E., Engrand, C., Pino, T., Sandt, C. 2020. *Mechanochemical synthesis of aromatic infrared band carriers. The top-down chemistry of interstellar carbonaceous dust grain analogues*. Astronomy and Astrophysics 637. doi:10.1051/0004-6361/202037725

[2] Dartois, E. 2019. Interstellar carbon dust. C, 5(4), 80.

[3] Dartois, E. and 17 colleagues 2015. *Interstellar and interplanetary solids in the laboratory*. Bulletin de la Societe Royale des Sciences de Liege 84, 7–14.

Utilizing Chemical Optical Sensor Technology to Assess Oxygen Permeability of Candidate Asteroid Regolith Sample Containers

Christopher J. Snead¹, Kevin Righter¹ and Nicole Lunning¹ ¹NASA Johnson Space Center

The Astromaterials Acquisition and Curation Office at NASA Johnson Space Center currently curates 500 mg (10%) of carbonaceous asteroid Ryugu regolith collected by the Japan Aerospace and Exploration Agency's Hayabusa II spacecraft and returned to Earth in 2021 [1] In September 2023, NASA's OSIRIS-REx spacecraft is expected to return at least 60 grams of regolith collected from the surface of Carbonaceous Asteroid Bennu [2]. These new astromaterials collections will be stored and handled in gloveboxes and desiccators that are continuously purged with ultrapure nitrogen, in order to minimize contamination and alteration of extraterrestrial samples from terrestrial environments, e.g. reaction with terrestrial oxygen. Ito et al. have previously reported on the development of containers to transport samples between facilities in inert, sealed environments [3]; Hayabusa2 samples allocated to investigators by JAXA's Extraterrestrial Sample Curation Center (ESCuC) are shipped in these Facility-to-Facility Transfer Containers (FFTCs). NASA curation has also been investigating sealed containers for storage, transportation, and allocation of Bennu and Ryugu regolith in sealed anoxic environments. In order to assess the ability of potential sample containers to maintain an inert atmosphere, we have acquired a PreSens Fibox 4 fiber optic oxygen meter and PSt9 chemical optical sensor spots. Oxygen measurements are performed as follows: A calibrated PSt9 sensor spot is fixed either mechanically or with adhesive to an internal transparent container surface (the container must incorporate at least one transparent surface into its design, i.e. the container cannot be completely opaque). The end of the oxygen meter's fiber optic attachment is placed normal to the exterior transparent face (opposite the sensor spot), and a measurement is made. This configuration provides a passive, non-invasive method of measuring an unmodified sample container [4]. The sensor can perform multiple measurements in time intervals as short as one second; by measuring the oxygen concentration of the internal container volume periodically, we can determine a rate of oxygen ingress into candidate sample containers. The PSt9 sensor has a measurement range of 0-200 ppmv; we therefore seal our containers and measure the internal sensor within a nitrogen purged glovebox. We compare the reading for the sealed container with a control sensor spot that is loose in the glovebox. The sealed container is then removed from the glovebox (as well as the fiber optic O_2 meter), and measurements are made in periodic intervals of 10 minutes to one hour (depending on ingress rate) to assess changes in the internal oxygen environment. We conducted very preliminary tests on a commercial stainless steel container sealed with a Viton gasket; an internal oxygen concentration of 200 ppmv was measured four days after removal from the ~30ppm glovebox environment. More controlled experiments are required to determine whether the increase in oxygen was due to diffusion through the Viton gasket, or whether outgassing internal contaminants contributed to the increased oxygen concentration; these experiments will be conducted in October 2022.

References

[1] Watanabe S. et al. 2017. Space Sciences Reviews, 208, p. 3-16. [2] Lauretta D. S. et al. 2017. Space Sciences Reviews, 212, p. 925-984. [3] Ito M. et al. 2020. Earth, Planets and Space. 72:133. [4] Huber C. et al. 2006. Monatsschrift für Brauwissenschaft, 59, 5-15.

Space Resources – From the Moon to Near-Earth Asteroids and Back

Dennis Harries¹

¹European Space Resource Innovation Centre (ESRIC), Luxembourg Institute of Science and Technology/Luxembourg Space Agency. 41, rue du Brill, 4422 Belvaux, Luxembourg (dennis.harries@esric.lu)

Space exploration is a frontier that challenges creative and sustainable use of extraterrestrial materials. Whilst space missions during the past decades entirely relied upon supplies brought from Earth, future missions aiming at long-term human and robotic activity outside of Earth's atmosphere require technologies to produce propellants, life support, and construction materials from local extraterrestrial resources. This in-situ space resource utilization (ISRU) is key for the exploration of the Moon and Mars and to make space transportation more economical and environmentally sustainable. Examples are in-orbit fuelling and refuelling of spacecrafts, as well as the resource-efficient and circular processing of materials for building habitats and photovoltaic energy infrastructures.

The Moon's south polar region will a primary target for long term exploration starting with the international Artemis missions led by NASA. This area is particularly interesting due to its permanently shadowed regions (PSRs) inside polar craters, which are expected to hold water ice and other volatiles trapped by the very cold temperatures within. Remote sensing and the impact experiment of NASA's LCROSS mission places constraints on the amount and composition of volatiles, confirming the presence of water ice at several volume percent of the regolith [1]. Hydrogen gas produced from PSR ices or imported from Earth is the basis of oxygen generation from lunar ilmenite through redox reaction (FeTiO₃ + H₂ -> Fe + TiO₂ + H₂O) and electrolysis of the produced water. Alternative to this is the electrolysis of lunar regolith itself in the FFC Cambridge process employing a molten calcium chloride electrolyte. The FFC process reduced not only ferrous oxides but almost the entire oxide components of the regolith to produce a high yield of oxygen. Both processes require volatiles (hydrogen, chlorine) that need to be efficiently recycled due to their limited abundance on the lunar surface.

Carbon and nitrogen compounds such as CO_2 and NH_3 are present in PSRs, but their overall abundance is uncertain and in case of CO_2 suitable traps may be rare [2]. With typical carbon and nitrogen concentration of 10s to a few 100s of ppm in the average lunar regolith, mainly through solar wind implantation, both elements are geochemically highly limited but, besides hydrogen, essential for life support and most propellants. For propellants a sustainable circularisation of volatiles is obviously not possible.

Ryugu and its potential near-Earth asteroid (NEA) siblings are now confirmed to contain up to $\sim 6.8 \text{ wt}\% \text{ H}_2\text{O}$ [3] chemically bound in serpentines and smectites. Up to $\sim 4.6 \text{ wt}\%$ of carbon are present as carbonates and organic matter that also contains considerable amounts of nitrogen. As discussed above, hydrogen, carbon, and nitrogen are critical resources for extended lunar presence and chemical manufacturing of propellants in space. As carbon and nitrogen are especially limited on the lunar surface, the retrieval of such resources from NEAs might become a long-term option for a sustained space economy. These asteroids are comparably easy to reach with low Δv requirements from and into cis-lunar space [4]. Exploratory heating experiments of C-type chondritic meteorites using high-vacuum extraction and mass-spectrometric detection of released volatiles indicated complex release patterns of H₂O, CO₂, CO and nitrogen compounds (Fig. 1). Thermodynamically valuable CO appears to be a major species and likely the result of redox reactions involving the carbonates, organic matter and magnetite. Extraction yields, energy requirements, and catalytic chemical conversion of this potential feedstock into further products, such as fuels and oxidizers, are some of the tobe-studied process constraints for NEA-based ISRU. Operating on small, nearly cohesionless rubble-pile asteroids is another extreme challenge for both small body exploration and any future ISRU.

References

[1] Colaprete A. et al. 2010. Science 330:463–468. [2] Schorghofer N. et al. 2021.
Geophysical Research Letters 48:e2021GL095533. [3] Yokoyama T. et al. 2022. Science eabn7850. [4] Jedicke R. et al. 2018. Planetary and Space Science 159:28–42.



Figure 1: Volatile species detected by quadrupole mass spectrometry during controlled high-vacuum heating of the Murchison CM2 chondrite at 10 K/min. A. normalized ion currents. B. Species after fragment pattern deconvolution.

Formation processes of spherulitic magnetite in the Ryugu samples

E. Dobrică¹, H. A. Ishii¹, J. P. Bradley¹, K. Ohtaki¹, T. Noguchi^{2,3}, T. Matsumoto⁴, A. J. Brearley⁵, the Min-Pet Fine Sub-team and the Hayabusa2 initial analysis core

¹Hawai 'i Institute of Geophysics & Planetology, University of Hawai 'i at Mānoa, Honolulu, HI 96822, USA

(dobrica@hawaii.edu), ²Division of Earth & Planetary Science, Kyoto University, Kyoto, Japan, ³Department of Geology and

Mineralogy, Kyushu University, Kyoto, Japan, ⁴Hakubi Center for Advanced Research, Kyoto University, Kyoto, Japan,

⁵Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM.

Introduction: Samples returned from the carbonaceous asteroid 162173 Ryugu by the JAXA Hayabusa2 mission allow us to investigate primitive materials of our Solar System and their evolution [1-2]. Recent studies have shown that the Ryugu samples are composed of minerals similar to those of CI (Ivuna-like) carbonaceous chondrites indicating that the parent planetesimal from which Ryugu was derived experienced severe aqueous alteration [e.g., 1-2]. Our previous study described that magnetite in the Ryugu samples from chamber A occurs as framboids, plaquettes, spherulitic, and irregularly shaped grains [3-5]. They are products of alteration, and their formation is controlled by variation in the diffusion and growth rates during aqueous alteration on the parent body [4]. In this new study, we focus on spherulitic magnetite grains in the Ryugu from chamber C to understand the evolution of the aqueous alteration processes on the carbonaceous (C-type) asteroids [4].

Samples and Methods: Multiple spherulitic magnetite grains were identified embedded in the fine-grained materials returned by the Hayabusa2 spacecraft collected during both touchdowns (chambers A and C). Figure 1 shows the spherulitic magnetite (~13 µm in diameter) analyzed in this study and collected during the second landing operation (chamber C, C0105-039024). The grain is associated with fine-grained phyllosilicates, euhedral sulfides, and framboidal magnetites Fig. 1). We prepared one FIB section for electron microscopy studies using the Helios 660 dual-beam focused ion beam SEM (FIB-SEM) instrument at the University of Hawai'i at Mānoa and examined the section by transmission electron microscopy (TEM) using the JEOL NEOARM 200CF at the University of New Mexico.

Results: The spherulitic magnetite has an internal texture composed of individual radiating fibers varying in length from 5 μ m to 8 μ m. The fibers radiate from a spherical pore (Fig. 1, ~130 nm in diameter) located off-center. The widths of the fibers vary in size from 70 nm to 140 nm. The spherulitic magnetites are characterized by high porosity, with randomly distributed pores ranging from a few nanometers up to 2.2 μ m in size; however, the magnetites with other morphologies (e.g., framboidal magnetite) are free of pores. Most pores are euhedral to subhedral in shape, located inside the fibers or at their boundaries. Additionally, we identified an amorphous rim (80- 350 nm in thickness) composed of 5 wt % Si, 4 wt% S, 2 wt% P, and 13 wt% C around the magnetite grain.

Discussion: Ryugu samples have been shown to a CI chondrite that exhibit some notable differences from CI meteorites [6-7]. One of the major similarities in Ryugu asteroid to CI chondrites is the presence of magnetites with different morphologies. Magnetite with a variety of morphologies has been studied for almost sixty years in one of the rarest groups of meteorites, the CI chondrites (only 9 meteorites belong to this group), and more recently in the unique, ungrouped Tagish Lake meteorite [8-9]. Our TEM observations further expand on the implications of magnetite formation in the Ryugu samples that show some difference to known CI chondrites [6-7]. The observations presented in this study show the presence of magnetite with different morphologies coexisting in close proximity.

Spherulites are common in terrestrial and extraterrestrial materials [8, 10-11]. They have been identified in a wide range of materials such as metals, alloys, polymers, oxides, liquid crystals, and various biological molecules. However, so far there is no generally accepted theory of spherulite crystallization mechanisms. The most important prerequisite for spherulitic growth is high crystallization driving forces, typical from a supersaturated or supercooled solution [11]. Furthermore, spherulites are ubiquitous in solids formed under highly nonequilibrium conditions [10, 12]. Systems that are in equilibrium tend to grow crystals with simple morphologies unless they are forced out of equilibrium by imposing a change in the environmental conditions [12]. Therefore, crystals can form complex spatial patterns in response to a disturbance from equilibrium that might induced kinetically driven growth to lower the free energy of the system. Though there are other factors that can influence the morphologies of crystals. For example, the presence of organic compounds can play a major role influencing growth of crystals by inhibiting growth on some crystal surfaces and favoring one morphology over another [6]. Similarly, it is also possible that certain anions or cations in solution can change the growth mechanism and change the morphology (Wark et al. 2008).

Previous studies of spherulites in meteorites suggested that this particular structure requires crystallization from a colloidal Fe hydroxide gel-like material [8]. Studies of terrestrial spherulite show that a viscous medium (i.e., gel) is not

always necessary for spherulitic growth; however, impurities encourage spherulite formation [11]. The conditions necessary for the spherulite precipitation must maintain the growth rates (G) of the crystal itself higher than diffusion rates (D, G >> D)[8, 13]. Any changes related to variation in D/G ratio could generate crystals with different morphologies [13]. Therefore, the presence of magnetite with varying crystal morphologies in the returned samples suggests a variable range of crystal growth and diffusion rates in the Ryugu parent body. Petrographic observations suggested that magnetites with a spherulitic morphology are the one of the first minerals to crystallize from an aqueous fluid on the Ryugu parent body [14]. More precisely, the crystallization sequence of magnetite as a function of their morphologies is: spherulitic - plaquette/framboidal equant/elongated [14]. This previous study indicated that the conditions during magnetite precipitation changed from high to low supersaturations [14], which supports our observations that the first magnetites that formed, the spherulitic crystals, precipitated from a highly supersaturated fluid that evolved in the degree of saturation. Our TEM study further expands on these results suggesting that at the beginning of the crystallization sequence, when the spherulitic magnetite formed, the fluid could have been under nonequilibrium conditions. These processes lead to polycrystalline growth structures imposed by the reach of the solution of a supersaturated state where nucleation is able to occur, resulting in the adjustment to a lower free energy condition. Furthermore, as the previous petrographic observations suggested [14], and the presence of numerous fragile, euhedral laths at the surfaces of these spherulitic magnetites, suggest that these crystals precipitated first in an unrestricted, high porous material.

Two important implications arise from the study of spherulitic magnetite. First, these crystals could potentially offer a unique opportunity to study the early aqueous fluids that circulated through the Ryugu parent body. No materials were identified in the unique pores identified in the spherulitic magnetite due to the sample preparation technique applied in this study; however, it is possible that these pores contain fluid inclusions prior to the FIB sample preparation. A second important implication that arises from the occurrence of spherulitic magnetite under nonequilibrium conditions is that a careful selection of the magnetite crystals is necessary for the use of the oxygen isotope fractionation between carbonates and magnetite to extract the temperature at which these minerals coprecipitated [15]. Since multiple generations of magnetite were identified in the Ryugu samples, the question is what type of magnetite forms in equilibrium with the carbonates, especially since dolomite and breunnerite formed after the formation of pentlandite, pyrrhotite, and apatite according to the crystallization sequence [14]. We suggest avoiding spherulitic magnetite for these measurement since the necessary assumption of equilibrium between minerals is not supported by our observations indicating rapid magnetite growth.



Figure 1. Backscattered electron (a), dark-field STEM (HAADF, b-c), and bright-field TEM images of the spherulitic magnetite analyzed in this study. The TEM data show the texture of the radiating fibers and the random distribution of euhedral to subhedral pores.

References

[1] Noguchi T. et al. (2022) 53rd LPSC, Abstract #1747. [2] Tachibana S. (2021) Sample Return Missions the Last Frontier of Solar System Exploration, Chapter 7, Elsevier, Editor Longobardo A., 147-162. [3] Alfing J. et al. (2019) Geochemistry, 79, 125532. [4] Dobrica E. et al. (2022) 53rd LPSC, Abstract #2188. [5] Lee M. R. et al. (2022) 53rd LPSC, Abstract #2203. [6] Nakamura T. et al. (2022), Science, doi 10.1126/science.abn8671. [7] Yokoyama T. et al. (2022) Science 10.1126/science.abn7850. [8] Kerridge J. F. (1979) Science 205, 395-397. [9] Kimura Y. et al. (2013) Nat. Comm. 4, 1-8. [10] Gránásy L. et al. (2005) Phys. Rev. E 72, 011605. [11] Shtukenberg A. G. et al. (2012) Chem. Rev., 112, 1805-1838. [12] Magill J. H. (2001) J. of Mater. Sci. 36, 3143-3164. [13] Lofgren G. (1974) Americ. J. Sci. 274, 243-273. [14] Tsuchiyama A. et al. (2022) 85th Annual Meeting of the Meteoritical Society, abstr. #6221. [15] Jilly-Rehak C. E. et al. (2018) Geochim. Cosmochim. Acta 222, 230-252.

The Aguas Zarcas breccia - similarities to surface features of C-type asteroids Ryugu and Bennu

Imene Kerraouch^{1,2}, Michael E. Zolensky² Addi Bischoff¹

¹Institut für Planetologie, University of Münster, Wilhelm-Klemm Str. 10, D-48149 Münster, Germany.

²Astromaterials Research and Exploration Science, NASA Johnson Space Center, Houston TX 77058, USA

(ikerraou@uni-muenster.de)

Knowledge of the materials originally present in the protosolar nebula is one of the most significant constraints for models of the formation of our solar system. The physicochemical properties of these original materials can be determined through two different and complementary approaches: (a) astronomical observations of nascent stellar systems and the dense clouds from which they originated and (b) laboratory studies of available astromaterials such as meteorites, interplanetary dust particles, comet coma grains, including returned mission samples (e.g., from Hayabusa -1 -2; OSIRIS-Rex). Laboratory study of these extraterrestrial materials provides valuable information about the first solid materials of the early solar system and their evolution. Here, we present petrographic and mineralogical characteristics of work on the polymict carbonaceous breccia Aguas Zarcas [1].

On April 23, 2019, at 21:07 local time, a meteorite fall occurred in Aguas Zarcas, San Carlos County, Alajuela province, Costa Rica. The rapid recovery of this brecciated carbonaceous chondrite after its fall provides an opportunity to investigate a freshly fallen, relatively uncontaminated, and highly-brecciated meteorite to compare with samples returned by the Hayabusa2 and OSIRIS-REx spacecraft from C-complex asteroids.

This study includes the examination of several pre-rain fragments. X-ray computed tomography (XCT) results show numerous different lithologies [1]. In this study, we describe the petrography and mineralogy of five different lithologies of the Aguas Zarcas meteorite. We also present data on the bulk oxygen isotopes of some of these lithologies. We describe all fragments in detail and attempt a classification of each lithology in order to better understand the origin and formation history of the Aguas Zarcas parent body.

Our results show that some lithologies of Aguas Zarcas are similar to those in CM chondrites, but others are unique. The different lithologies [1] also represent different degrees of hydration and heating, which are good analogues for the types of material returned from asteroids Bennu and Ryugu.

Spectroscopic observations of Ryugu and Bennus compared to laboratory measurements of meteorites suggest that the asteroids have some similarities to heated CM, heated CI, or CI chondrites [2-5]. Both asteroids are thought to be composed of materials altered by aqueous alteration (e.g., [5]) and formed by reaccretion after destruction by impacts and brecciation (e.g., [6-7]). Considering the different lithologies in Aguas Zarcas [2] and other CM chondrites [8-9], these types of carbonaceous chondrites can be considered good analogues for samples from Ryugu and Bennu. The presence of unique and rare lithologies in Aguas Zarcas, different from typical CM chondrite lithologies, requires complex mixing of different materials in a highly dynamic environment.

Fig.1: Left image: sample catcher chamber A from Hayabusa2, captured by an optical microscope, shows many particles larger than 1 mm (Photo by JAXA Dec. 24, 2021). The right image: XCT image of a sample of Aguas Zarcas, showing a dark homogeneous C1-clast (marked by a circle) (Kerraouch et al., 2021; 2022). Both materials exhibit a mixture of different lithologies resulting from impact fragmentation, mixing, and reaccretion during the evolution of their parent bodies.



References [1] Kerraouch et al., 2021. Meteoritics & Planet. Sci. 56, 277-310; [2] Kitazato et al., 2019. Science 364, 272–275; [3] Matsuoka et al., 2015. Icarus 254. 135–143; [4] Hanna et al., 2019. LPI abstract #2029; [5] Hamilton et al., 2019. Nature Astronomy. 3.332–340; [6] McCoy et al., 2019. Metsoc54 abstract #6428; [7] Michel et al., 2020. Nature 11, 2655; [8] Kerraouch et al., 2019. Chemie der Erde 79, 125518; [9] Lentfort et al., 2020. Meteoritics & Planetary Sci. 56, 127-147.

An Astromaterial Curation Facility at MNHN-Paris, the National Center for Extraterrestrial Material

J. Duprat¹, M. Roskosz¹, B. Doisneau¹, S. Pont¹, M. Verdier-Paoletti¹, S. Bernard¹, M. Gounelle¹, J. Aléon¹, P.

Sans-Jofre¹, G. Avice², F. Moynier², R. Brunetto³, F. Poulet³, C. Engrand⁴, L. Delauche⁴, E. Dartois⁵

¹IMPMC, CNRS-MNHN-Sorbonne Université, UMR 7590, 57 rue Cuvier, 75005 Paris, France ; ²Université

Paris Cité, Institut de physique du globe de Paris (IPGP), CNRS, 75005 Paris, France ; ³IAS, Université Paris-

Saclay, CNRS, UMR 8617, Orsay, France ; ⁴IJCLab, Université Paris-Saclay, CNRS/IN2P3, Orsay, France ;

⁵ISMO, Université Paris-Saclay, CNRS, Orsay, France

The study of extraterrestrial samples requires developments in curation facilities to preserve, and allocate pristine samples to international scientific teams. During the last decades, the return to Earth of samples from the Stardust NASA mission [1], Hayabusa1 and Hayabusa2 JAXA missions (e.g. [2, 3]), allowed the first analysis of samples from an identified comet (81P/Wild2) and from two asteroids (Itokawa and Ryugu). Within the coming years, samples from asteroid Bennu will return to Earth thanks to the OSIRIS-REx NASA-led mission [4] and, on a longer term, samples from the Martian moon Phobos will be returned by the MMX JAXA-led mission [5]. After 2030, material currently sampled at the Martian surface is expected to be returned to Earth by the NASA/ESA Mars Sample Return (MSR) campaign [6]. Major curation facilities already exist at both NASA and JAXA [7-9] to receive, curate and handle samples directly returned from space missions. Advanced curation studies are ongoing [9, 10] while others facilities are currently into construction [11]. Beside space missions, extraterrestrial materials (meteorites and cosmic dust) have been collected for centuries in many environments, including hot and cold deserts, deep sea sediments, sediments, polar ice caps, and stratospheric collections [12-14]. As recently illustrated by the striking similarity between Ryugu samples and the C11 meteorites [15, 16], the comparison between returned samples (i.e. with known parent body) and meteorites or micrometeorites from terrestrial collections is an essential step in our understanding of these complex objects.

Together with the French spatial and scientific research agencies (CNES and CNRS), the Institut de physique du globe de Paris (IPGP) and Sorbonne University, the National Museum of Natural History (MNHN) launched a project to build a national curation facility, the CENAME (National Center for Extraterrestrial Materials) located at MNHN in the center of Paris. The CENAME will include instruments and advanced storage facilities developed by several French laboratories, including IAS and IJCLab at University Paris-Saclay. The CENAME will be designed to ensure long term curation of different major collections of extra-terrestrial samples including: the national meteorite collection from MNHN, large micrometeorites collections from Greenland and Antarctica, terrestrial analogues and samples from past and future space missions. The MNHN hosts an historical meteorite collection with more than 1500 different meteorites, including 521 falls, and a rich panel of Martian samples (Shergottites, Chassignites, Nakhlites) [17]. It contains the largest sample of the Orgueil CI-chondrite, a reference for cosmochemistry studies. The MNHN meteorite collection is actively used for cosmochemistry research projects and is constantly growing with new additions every year. Thanks to the pioneering work of M. Maurette in the 80s, large numbers of micrometeorites (interplanetary dust reaching Earth surface) with diameters ranging from a few tens up to a few hundred um have been recovered from both Greenland and Antarctica [18, 19]. Since 2000, this program was pursued, in the central regions of Antarctica, where collections have been performed with the support of the French polar institute (IPEV) [20, 21]. The Concordia micrometeorites collection contains thousands of particles. A part of this collection is now fully characterized and contains micrometeorites with minimal terrestrial weathering, including particles of cometary origin that are exceptionally rich in organic matter (Ultra-Carbonaceous micrometeorites [22, 23]). The Concordia Collection is currently stored in a dedicated cleanroom at IJCLab in Orsay and will be transferred to the CENAME when the facility will be completed. The CENAME will also host a suite of terrestrial natural and synthetic analogues that are essential for analysis of complex extraterrestrial matter, calibration and interpretation of remote sensing analyses (e.g. on Mars). The CENAME will benefit from the MNHN Geological collection of rocks and minerals located in the same building. It contains about a billion scientific samples accumulated over 2 centuries of worldwide scientific exploration. The collection has been recently enriched with samples recording early Earth surface environments and the earliest traces of life on Earth (more than 1200 specimens spanning 3.5 billion years of Earth History). Beside these natural

samples, several laboratories involved in the CENAME project have developed dedicated experimental protocols to synthetize analogues of asteroidal and cometary organic matter.

Beyond these historical and on-going collections, the objective of the CENAME will be to allow sample handling, pre-characterization and long-term preservation for the next generations of samples for current and future space missions. As a result of on-going agreements between JAXA and the French space agency CNES, a fraction of Phobos (MMX) samples are expected to be transferred to the CENAME at MNHN after the period of initial description at JAXA-ISAS sample receiving laboratory and after the first scientific analysis by the MMX Science Sub-Teams (i.e. after 2030). The design of the CENAME will be modular to allow flexible configuration of different environments for the curation of pristine samples from other space missions. The CENAME will consist in a clean-room infrastructure of about 180 m², divided in separated modules with ISO7 to ISO5 [24] environments, together with a laboratory for sample preparations and experiments that do not require a cleanroom environment. The cleanroom area will contain secured cabinets and glove boxes under controlled atmospheres (dry and purified N₂, Ar, vacuum, ...). In the long-term perspective of MSR, an ambitious program was recently launched, under the supervision of CNES, to study an apparatus for small sample (solid and gas) handling in clean and biocontained (BSL4-like) environment. The CENAME will include a dedicated space to allow rehearsal on such type of apparatus (before their operation in BSL4-like laboratories).

Instrumentation in the CENAME will focus on acquisition of the basic properties on samples with sizes going from µm to cm scales. It will include optical 2D and 3D microscopy and imaging, weighting, magnetic susceptibilities, scanning electron microscopy, Raman and infrared (IR) microspectroscopy with a dedicated suite of instruments, to achieve initial characterization and cataloging of samples before allocations. The magnetic environment of the samples and the magnetic properties of the handling tools will be monitored to ensure preservation of the genuine magnetic properties of the samples. A strict control of terrestrial contamination within CENAME cleanrooms will be achieved by real-time monitoring of inorganic, organic and biological contamination. The CENAME will develop research programs to improve existing curation techniques and new technological solutions for the mid to long-term curation of volatile elements (e.g., H₂O, N, noble gases) contained in samples collected by future space missions (e.g. ice and gas from cometary objects or planetary atmospheres). Specific tasks will include the characterization of materials outgassing properties. A specific setup will be developed at IAS in order to allow a multi-scale (from mm down to µm) IR reflectance micro-imaging characterization on the CENAME samples. The analysis will be fully non-destructive and non-invasive, and it will be performed within a dedicated bench in a controlled atmosphere (e.g., N₂), with no need for specific sample preparation. In the case of returned samples, the setup will allow measurements complementary to the IR characterization performed at other curation facilities hosting the main sample collection (e.g., JAXA [25]).

Acknowledgement: The CENAME is a joint project supported by MNHN, IPGP, Sorbonne University, University Paris Cité, CNES and CNRS. The curation-related instruments and apparatus currently under development benefit from funding by Région IIe de France (DIM-ACAV⁺ contract C³E), CNES, CNRS, MNHN and ANR contract (COMETOR 18-CE31-0011). The collection of micrometeorites benefited from the pluri-annual funding by IPEV and PNRA (Program #1020)

References : [1] Brownlee D. (2014) Ann. Rev. Earth Planet. Sci. 42, 179-205. [2] Yano H., et al. (2006)
Science 312, 1350-1353. [3] Watanabe S., et al. (2019) Science, eaav8032. [4] Lauretta D.S., et al. (2017) Space
Sci. Rev. 212, 925-984. [5] Kuramoto K., et al. (2022) Earth, Planets and Space 74, 12. [6] Beaty D.W., et al. (2019) Meteorit. Planet. Sci. 54, S3-S152. [7] Yada T. et al. Meteorit. Planet. Sci. 49, 135-153 [8] Evans C., et al. (2018) 42, B4.2-49-18. [9] McCubbin F.M., et al. (2019) Space Sci. Rev. 215, 48. [10] Hutzler A. et al. EURO-CARES D7.1 Final technical Report. [11] Helbert J., et al. (2020), EPSC2020-250. [12] Bland P.A., et al. (1996) Mon. Not. R. Astron. Soc. 283, 551-565. [13] Brownlee D.E. (2016) Elements 12, 165-170. [14] Taylor S., et al. (2016) Elements 12, 171-176. [15] Nakamura T., et al. (2022) Science 10.1126/science.abn8671. [16]
Yokoyama T., et al. (2022) Science, 10.1126/science.abn7850. [17] Caillet Komorowski C.L.V. (2006) Geol. Soc. London Spec. Pub. 256, 163-204. [18] Maurette M., et al. (1986) Science 323, 869-872. [19] Maurette M., et al. (2021) Earth Planet. Sci. Lett. 560, 116794. [22] Duprat J., et al. (2010) Science 328, 742-745. [23] Dartois E., et al. (2018) Astron. Astrophys. 609, A65. [24] ISO 14644-1 [25] Yada T., et al. (2022) Nature Astronomy 6, 214-220.

Distinct ages and temperatures of aqueous activities recorded in Ryugu samples

Kazuhide Nagashima¹, Noriyuki Kawasaki², Naoya Sakamoto², Wataru Fujiya³, Hisayoshi Yurimoto², The Hayabusa2-initial-

analysis chemistry team, and The Hayabusa2-initial-analysis core.

¹University of Hawai'i at Mānoa¹, ²Hokkaido University, ³Ibaraki University

The Ryugu asteroid is a rubble pile body likely composed of materials ejected by impact(s) from a larger parent asteroid [e.g., 1] that may have formed far from the Sun [e.g., 2,3]. The Ryugu samples collected by the Hayabusa2 spacecraft thus may have originated from different parts of the parent asteroid and experienced different thermal histories. We reported that Ryugu's secondary minerals such as dolomite and magnetite formed at $37\pm10^{\circ}$ C, ~5.2 Ma after the formation of the Solar System based on oxygen and Mn-Cr isotope systematics of the sample A0058 collected from the first touch-down site on Ryugu [4]. Here we report oxygen and Mn-Cr isotope systematics of secondary minerals found in a Ryugu sample, C0002, collected from the 2^{nd} touch-down site.

In contrast to A0058-C1001 section, C0002-C1001 section is composed of different lithological units recognizable by differences in BSE contrast and elemental distributions in X-ray maps, including less-altered lithologies [e.g., 3,5]. Most lithologies are dominated by phyllosilicate matrices with sub-micron magnetite and sulfide grains. Larger grains (>10 μ m) of magnetite, dolomite, and pyrrhotite are scattered throughout the major lithologies.

Figure 1 shows O-isotope compositions of dolomite, magnetite from the C0002 section, together with those from A0058-C1001. The O-isotope compositions of the dolomites are consistent with those in A0058, and are similar to the bulk Ryugu within uncertainty for their Δ^{17} O values [4,6,7]. In contrast to the majority of magnetites in A0058 having Δ^{17} O of ~ 0‰, all magnetites but one in C0002 have higher Δ^{17} O, ~ 2–3‰ (see also [8]). Some magnetites with high Δ^{17} O are included in overgrown dolomites with Δ^{17} O of ~ 0‰, suggesting earlier formation of these magnetites than the dolomite. These observations suggest that O-isotope composition of aqueous fluid was Δ^{17} O ~ +3‰ before crystallization of dolomite and was Δ^{17} O > +3‰ at the beginning stage of aqueous alteration because olivine and pyroxene in Ryugu have lower Δ^{17} O (–24 to –5 ‰) [3,9,10].

Using O-isotope thermometry [e.g., 11], the dolomite and magnetite pair in A0058 was used to estimate a temperature at which these minerals precipitated; their O-isotope compositions correspond to $37\pm10^{\circ}$ C [4]. In C0002, a pair of dolomite and magnetite in the same lithology has identical Δ^{17} O, ~+0.6‰. Assuming these grains were in O-isotope equilibrium with the same fluid, their difference in δ^{18} O, 25.2±2.0‰, corresponds to $104\pm22^{\circ}$ C.

Figure 2 shows Mn-Cr isotope systematics of dolomites in A0058-C1001, C0002-C1001, and Ivuna CI chondrite. Note we collected Mn-Cr isotope data from dolomites from which the O-isotope data were obtained. All ⁵³Cr excesses are well correlated with Mn-Cr ratios. The inferred initial ⁵³Mn/⁵⁵Mn ratios are $(2.55\pm0.35)\times10^{-6}$, $(3.78\pm0.34)\times10^{-6}$, and $(3.14\pm0.25)\times10^{-6}$ for A0058-C1001 [4], C0002-C1001 [this study], and Ivuna [4, this study], respectively. The initial ⁵³Mn/⁵⁵Mn ratio we obtained from C0002 is consistent with that in [10] and that from bulk Mn-Cr data [12] within uncertainty. If we use the initial ⁵³Mn/⁵⁵Mn ratio of the D'Orbigny angrite and the U-corrected Pb-Pb ages of D'Orbigny and CV CAIs [13–15], the initial ⁵³Mn/⁵⁵Mn ratios for A0058 and C0002 suggest that dolomite precipitation occurred at 5.2 (+0.8/-0.7) Ma and 3.1 (+0.5/-0.5) Ma after the CV CAI formation, at ~40°C and ~100°C, respectively. These ages could be systematically changed ±million years due to inconsistencies in CAI ages and proposed initial ⁵³Mn/⁵⁵Mn ratios of the Solar System [4 and references therein]. Other systematic changes may be introduced by inaccurate corrections of Mn/Cr sensitivity for dolomite by SIMS [4, 16–18]. Despite these systematic uncertainties, the relative age between the two isochrons is robust: 2.1±0.9 Ma. Therefore, during the aqueous alteration, one location in the Ryugu parent asteroid was at ~100°C. Then ~2 Ma later, possibly another location in the asteroid experienced ~40°C. These are new conditions to restrict thermal models of the Ryugu parent body. Thermal modeling to satisfy the conditions is in progress using methods in [19].

References: [1] Sugita S. et al. Science. 364. eaaw0422 (2019). [2] Hopp T. et al. Science Adv., accepted. [3] Kawasaki N. et al. Science Adv., in review. [4] Yokoyama T. et al. Science, 10.1126/science.abn7850 (2022) [5] Nakamura T. et al. Science, 10.1126/science.abn7850 (2022) [5] Nakamura T. et al. Science, 10.1126/science.abn8671 (2022). [6] Tang H. et al. Science Adv., in review. [7] Fujiya W. et al. this volume. [8] Kita N. T. et al. this volume. [9] Liu M.-C. et al. Nature Astron., 10.1038/s41550-022-01762-4 (2022). [10] Nakamura E. et al. Proc. Japan Acad. B., 98, 227–282. (2022). [11] Zheng Y.-F. Geochem. J., 45, 341–354 (2011). [12] Yokoyama T. et al. 53rd LPSC abstract #1272 (2022). [13] Glavin D. P. et al. MAPS, 39, 693–700 (2004). [14] Brennecka G. A. and Wadhwa M. PNAS, 109, 9299–9303 (2012). [15] Connelly J. N. et al. Science, 338, 651–655 (2012) [16] Steel R. C. et al. Geochim. Cosmochim. Acta, 201, 245–259 (2017). [17] McCain K. A. et al. J. Vac. Sci. Technol., 38, 044005 (2020). [18] Sugawara S. et al. this volume. [19] Fujiya W. et al. ApJL, 924:L16 (2022).

The Hayabusa2-initial-analysis chemistry team: T. Yokoyama, K. Nagashima, Y. Abe, J. Aléon, C.M.O'D. Alexander, S. Amari, Y. Amelin, K. Bajo, M. Bizzarro, A. Bouvier, R. W. Carlson, M. Chaussidon, B.-G. Choi, N. Dauphas, A.M. Davis, T. Di Rocco, W. Fujiya, R. Fukai, I. Gautam, M.K. Haba, Y. Hibiya, H. Hidaka, H. Homma, P. Hoppe, G.R. Huss, K. Ichida, T. Iizuka, T.R. Ireland, A. Ishikawa, M. Ito, S. Itoh, N. Kawasaki, N.T. Kita, K. Kitajima, T. Kleine, S. Komatani, A.N. Krot, M.-C. Liu, Yuki Masuda, K.D. McKeegan, M. Morita, K. Motomura, F. Moynier, I. Nakai, A. Nguyen, L. Nittler, M. Onose, A. Pack, C. Park, L. Piani, L. Qin, S.S. Russell, N. Sakamoto, M. Schönbächler, L. Tafla, H. Tang, K. Terada, Y. Terada, T. Usui, S. Wada, M. Wadhwa, R.J. Walker, K. Yamashita, Q.-Z. Yin, S. Yoneda, E.D. Young, H. Yui, A.-C. Zhang, H. Yurimoto. The Hayabusa2-initial-analysis core: S. Tachibana, T. Nakamura, H. Naraoka, T. Noguchi, R. Okazaki, K. Sakamoto, H. Yabuta, H. Yurimoto, Y. Tsuda, S. Watanabe.



Fig. 1. Oxygen isotope compositions of dolomite and magnetite from Ryugu samples, A0058-C1001 [4] and C0002-C1001 [7, this study]. Also shown are bulk O-isotope data of A and C samples [4,6].



Fig. 2. Mn-Cr isotope systematics of dolomites from (a) Ryugu samples, A0058-C1001 [4] and C0002-C1001 [this study], and (b) Ivuna [4, this study]. Several dolomite grains were analyzed from each sample and they are shown as different symbols. Note data from dolomite grain HK2-#7 in Ivuna, shown as green circles were obtained in the two measurement sessions when we analyzed A0058-C1001 and C0002-C1001 samples and showed no differences in their initial ⁵³Mn/⁵⁵Mn ratios.

Elastic property of Ryugu samples collected at the second touch-down site

Keisuke Onodera¹, Yuta Ino^{2,3}, Satoshi Tanaka³, Taichi Kawamura⁴, Takuya Ishizaki³, Ryota Fukai³, Rei Kanemaru³,

Takahiro Iwata³, Tomoki Nakamura⁵, HAYABUSA2 initial sample analysis team

¹Earthquake Research Institute, The University of Tokyo ²Kwansei Gakuin University ³Institute of Space Astronautical Science, Japan Aerospace Exploration Agency ⁴Institut de Physique du Globe de Paris, Université Paris Cité ⁵Department of Earth Sciences, Tohoku University

Introduction

Since the HAYABUSA2's successful return from the 6 years of space journey on December 5th 2020, many analyses of the collected samples have been conducted (e.g., [1]-[4]). Those studies help us better understand the ancient history of the solar system as well as the Ryugu's characteristics and its origin.

According to the initial analysis [1]-[3], it turned out that Ryugu showed high similarity to CI chondrites (e.g., Ivuna, Orgueil) from the petrological or mineralogical aspect. For example, Visible-Near infrared reflectance spectra of Ryugu samples show a sharp absorption at 2.72 μ m – consistent with the remote sensing observation [5] – and weak absorptions at 3.4 and 3.95 μ m as seen in CI chondrites. These observations provide us with chemical features, allowing us to interpret how these particles were formed under what kind of environment.

In addition to chemical aspects, physical properties such as density, porosity, and rigidity are also of great importance. Especially, rigidity is one of the paramount parameters to constrain the formation process from the catastrophic impact to re-accumulation to make a rubble pile body [4]. Also, the elastic behavior like seismic wave propagation is closely related to the asteroid's surface evolution (e.g., seismic shaking).

In this study, through the measurement of seismic wave velocity, we are trying to provide a detailed description on elastic properties such as seismic wave velocity, Young's modulus, and attenuation quality factor. Moreover, by comparing the derived parameters with those for other carbonaceous chondrites, we discuss which type is the most similar to Ryugu from the viewpoint of elastic property.

Samples used for measurements

For the measurements, C0002-No3 and No4 were allocated to us. Both particles are mm scale with a thickness of 0.5 - 1.0 mm, cut out of one of the largest samples collected at the second touch-down site. Figure 1 shows the micrographs of the respective particles. Note that the C0002-No4 was broken into two pieces over the course of the physical property measurements [4], and we measured their seismic waves individually.

Seismic wave velocity measurement and estimation of Young's modulus

We adopted the pulse transmission method [6] to measure P and S wave velocities. The experimental setting is shown in Figure 2, where a sample is sandwiched with two transducers placed on an electronic scale. This kind of setting allows us to measure the wave velocity monitoring the loading simultaneously. The principle is to transmit a pulse from one side transducer to another side for two settings: (i) transducers without sample, (ii) transducers with a sample interposed. Then, we can obtain the time delay by comparing two signals (Figure 3). Since the thickness and density of each sample are known, the seismic wave velocity and Young's modulus can be obtained in the end. As a result, we obtained $V_p=1.9 - 2.3$ km/s, $V_s=1.2 - 1.4$ km/s, and 6.2 - 8.6 GPa for Young's

(a) C0002-No3



(b) C0002-No4



Figure 1. Micrographs of Ryugu sample (a: C0002-No3, b: C0002-No4). For the measurements, we used the divided pieces of C0004-No4 (1&2).



Figure 2. Schematic illustration of the experimental setting.



Figure 3. Transmitted signal without sample (top) and with sample (bottom). Time delay between them gives seismic wave velocity.

modulus under 1 MPa loading (Table 1). While Nakamura et al. [4] reported the average values of these samples, this presentation will show the individual results. Moreover, we discuss whether Ryugu is similar to CI chondrites also from elastic property through the comparison of our results with those for various carbonaceous chondrites.

| Table 1.1 - and 9-wave velocities and 1 oung 5 modulus for each sample | | | |
|--|-----------------------|-----------------------|-----------------------|
| Sample name | V _p (km/s) | V _s (km/s) | Young's modulus (GPa) |
| C0002-No3 | 2.25 ± 0.01 | 1.42 ± 0.15 | 8.58 ± 3.17 |
| C0002-No4-1 | 1.94 ± 0.01 | 1.20 ± 0.01 | 6.24 ± 2.80 |
| C0002-No4-2 | 1.96 ± 0.01 | 1.32 ± 0.07 | 6.88 ± 2.34 |

Table 1. P- and S-wave velocities and Young's modulus for each sample

References

[1] Yada et al. (2022), Preliminary analysis of the Hayabusa2 samples returned from C-type asteroid Ryugu, *Nat Astron*, 6, 214–220, https://doi.org/10.1038/s41550-021-01550-6.

[2] Yokoyama et al. (2022), Samples returned from the asteroid Ryugu are similar to Ivuna-type carbonaceous meteorites, *Science*, 10.1126/science.abn7850.

[3] Ito et al. (2022), A pristine record of outer Solar System materials from asteroid Ryugu's returned sample, *Nat Astron*, https://doi.org/10.1038/s41550-022-01745-5.

[4] Nakamura et al. (2022), Formation and evolution of carbonaceous asteroid Ryugu: Direct evidence from returned samples, *Science*, 10.1126/science.abn8671.

[5] Kitazato et al. (2019), Surface composition of asteroid 162173 Ryugu as observed by the Hayabusa2 NIRS3 instrument. *Science*, 364, 272–275.

[6] Blair (1996), Estimates of seismic attenuation using vibrational resonance and pulse transmission in four large blocks of rock, *GJI*, 126, 135-146.

Slickenside as a record of shock metamorphism on asteroid Ryugu

M. Miyahara¹, T. Noguchi², T. Matsumoto², N. Tomioka³, A. Miyake², Y. Igami², Y. Seto⁴, T. Nakamura⁵, H. Yurimoto⁶, R. Okazaki⁷, H. Yabuta¹, H. Naraoka⁷, S. Tachibana⁸, S. Watanabe⁹, Y. Tsuda¹⁰, and the Hayabusa2 Initial Analysis "Sand" Team
 ¹Hiroshima Univ., Japan; ²Kyoto Univ., Japan; ³JAMSTEC, Japan; ⁴Osaka Metropolitan Univ., Japan; ⁵Tohoku Univ., Japan; ⁶Hokkaido Univ., Japan; ⁷Kyushu Univ., Japan; ⁸Univ. of Tokyo, Japan; ⁹Nagoya Univ., Japan; ¹⁰JAXA/ISAS, Japan.

Introduction: An asteroid is formed and evolved by repeated collisions. The Hayabusa2 spacecraft shows that boulders with layered structures occur on the asteroid Ryugu (1). The layered structure can be regarded as parallel cracks, which is one of the representative features related to shock metamorphism. Evidence of shock metamorphism is found in some polished Ryugu grains (C0055) (2). However, evidence of shock metamorphism has not been found on the surface of Ryugu grains. In the present study, we scrutinize the surface morphology of several Ryugu grains to find features of shock metamorphism.

Samples and experimental methods: Numerous small Ryugu grains, ~100 μ m across on average, were allocated to the M-P F sub-team. Several grains from the chamber A (surface particles collected by the first touchdown) were attached on a gold (Au) plate (sample plate number: AP 042) with small amounts of epoxy glue in an N₂ filled glove box for surface morphology observation. The surface morphology of grains without any coating was observed by JEOL JSM-7100F and Hitachi S-5200 field emission gun scanning electron microscopes (FEG-SEM) at Tohoku Univ. and Hiroshima Univ., respectively. Some portions in the grains were excavated and processed to be ultrathin foils by a Hitachi SMI4050 focused ion beam (FIB) system at Kochi Institute for Core Sample Research, JAMSTEC after coating with osmium and carbon. The ultrathin foils were examined by a JEOL JEM-2100F transmission electron microscope (TEM) equipped with an energy dispersive spectrometer (EDS) at Tohoku Univ. Chemical compositions were measured by EDS under scanning TEM (STEM) mode.

Results and discussion: More than 24 grains adhered on the sample plate AP 042 were observed by secondary electron (SE) imaging (at a low accelerating voltage of 3.0-5.0 kV) to scrutinize the surface morphology. Some grains were broken into finer grains when grains were put on an Au plate, follows that fresh surface appeared newly. Most grains had a bumped or rough surface, and some grains had evidence of space weathering (3). On the other hand, two grains had a smooth surface on one side of the grain (Fig. 1). The smooth surface is not a single crystal surface. An obscure liner texture was observed on the smooth surface of one grain. An ultrathin foil was prepared from the smooth surface with a liner structure to observe its cross-section. The smooth surface looks like a weathering vein consisting of carbonate or iron-hydro/oxide minerals which are found in some carbonaceous chondrites. However, X-ray elemental maps indicated that there is no distinct difference in chemical compositions near the smooth surface. Bright-field (BF)-TEM images showed that the ultrathin foil consists mainly of fibrous phyllosilicates (saponite and serpentine) assemblage embedding small amounts of iron-sulfide and iron-oxide grains. The fibrous phyllosilicate assemblage is porous, and pores are filled with organic matter. These mineralogical features are like the Ryugu grains investigated in other works (3, 4). However, there is a distinct difference: the fibrous phyllosilicates assemblage near the smooth surface is compacted and the compaction degree increases toward the smooth surface. Lattice fringes corresponding to phyllosilicates become obscure with approaching the smooth surface, indicative of vitrification or dehydration. A ~200 nm layer from the smooth surface is heavily compacted, where the (001) basal planes of fibrous phyllosilicates are sub-parallel to the smooth surface. The smooth surface with a liner texture is a characteristic feature of a slickenside, which is found in terrestrial fault rocks and shatter cones around impact craters (5). The slickenside is formed by friction



Figure 1. SE images. a) A grain with a smooth surface (dashed line) and b) a high-magnification image of the smooth surface with a liner structure (dotted line). Horizontal parallel stripes are artifact because of electron charge-up.

between rocks along the two sides of a fault. Hence, we propose that the smooth surfaces appearing on some Ryugu grains are the record of shock-induced shear deformation that occurred on the asteroid Ryugu. No evidence of decomposition is found in fibrous phyllosilicates near the smooth surface of Ryugu grains. This suggests that friction heating temperature is below the decomposition temperature of phyllosilicates (< \sim 700 °C) (6). A shock-melt vein is also formed by friction heating along a faulting zone in shocked meteorites (7). Such a melting texture is not observed in Ryugu grains. Ryugu's grains with slickensides do not adhere well to each other because shock-induced melting and subsequent quenching did not occur. Therefore, grains with slickensides can be easily detached from each other during fall into the earth. In addition, a slickenside is too thin to survive from atmospheric entry heating or terrestrial weathering. So, a slickenside could not be found in a meteorite.

References

- (1) S. Tachibana *et al.*, Pebbles and sand on asteroid (162173) Ryugu: In situ observation and particles returned to Earth. *Science* **375**, 1011–1016 (2022).
- (2) T. Nakamura *et al.*, Formation and evolution of carbonaceous asteroid Ryugu: Direct evidence from returned samples. Scince <u>https://doi.org/10.1126/science.abn8671</u> (2022)
- (3) T. Noguchi *et al.*, Mineralogy and space weathering of fine fraction recovered from asteroid (162173) Ryugu. the 53rd Lunar and Planetary Science Conference, Houston, 1747.pdf, 2022.
- (4) T. Matsumoto *et al.*, Mineralogical analysis of various lithologies in coarse Ryugu samples using transmission electron microscopy the 53rd Lunar and Planetary Science Conference, Houston, 1344.pdf, 2022.
- (5) D. Baratoux, W. U. Reimold, The current state of knowledge about shatter cones: Introduction to the special issue. *Meteorit. Planet. Sci.* **51**, 1389–1434 (2016).
- (6) J. N. Weber, R. T. Greer, Dehydration of serpentine: Heat of reaction and reaction kinetics at PH₂O=1 atm. *Am. Min.* **50**, 450–464 (1965).
- (7) P. Gillet, A. E. Goresy, Shock events in the Solar System: The message from minerals in yerrestrial planets and asteroids. *AREPS* **41**, 257–285 (2013).
Spectral variations in serpentine and saponite 2.7 µm band due to heating under vacuum.

S. Sidhu¹, D. Applin¹, E. A. Cloutis¹, and A. Maturilli²

¹Centre for Terrestrial and Planetary Exploration, University of Winnipeg, Winnipeg, Manitoba, R3B 2E9, Canada. ²Institute for Planetary Research, German Aerospace Center DLR, Rutherfordstr. 2, 12489 Berlin, Germany

Introduction: Carbonaceous chondrites (CCs) are scientifically significant as they present a window into the early Solar System. Many classes of meteorites are considered primitive and provide an opportunity to study early solar system chemistry [1]. Carbonaceous chondrites in the sub-group CM2 likely underwent aqueous alteration to various degrees, resulting in formation of alteration minerals such as phyllosilicates [2]. Here we present a heating experiment conducted on two phyllosilicates and a simple two-component phyllosilicate + carbonaceous phase spectral analogue powder created at the Centre for Terrestrial and Planetary Exploration (C-TAPE) at the University of Winnipeg, Canada.

Methods: Samples of saponite (C-TAPE ID: SAP104), serpentine (C-TAPE ID: ASB267), and CC spectral analogue, created in-house, MUD008 (C-TAPE ID) were heated up to 900°C under vacuum (~0.07 mbar) in 100°C increments for 1 hour at each temperature increment. Heating was conducted using an induction heating system in the external emissivity chamber at the Planetary Spectroscopy Lab (PSL) at DLR, Berlin. Samples were allowed to cool in the vacuum chamber and then removed from vacuum and transferred to the spectrometer. The sample was then evacuated down to ~0.1 mbar prior to the spectral measurements. Data were collected using a Bruker Vertex 80v FTIR spectrometer using the Bruker A513 bi-directional reflectance accessory. Reflectance data were collected over the VISNIR ($0.4 - 1.1 \mu m$) and MIR ($1.1 - 20 \mu m$), however for the purposes of this report, only results up to 5 μm are discussed and displayed in the figures below. A new sample was used for each temperature increment.

Results: Progressive heating of SAP104 generally displays a decrease in reflectance values as temperatures increase in the VISNIR ($0.4 - 1.1 \mu m$). In the MIR ($1.1 - 20 \mu m$), the spectra brighten slightly up to 300°C, after which the reflectance starts to decrease. The H₂O absorption feature ~2.7 μm decreases in depth with increasing temperature, displaying qualitatively the deepest band at the room temperature observation and the shallowest band at 900°C (see Figure 1).



Figure 1: MIR (1-5 µm) reflectance spectra of SAP104 (top), MUD008 (middle), and ASB267 (bottom) heated up to 900°C for 1 hour at each 100°C increment under vacuum.

ASB267 displays a similar trend upon heating as SAP104's spectra regarding reflectance values: generally, decreases in the VISNIR and slightly increases then decreases in the MIR with increasing temperature. Also, similar to SAP104, the \sim 2.7 µm absorption feature systematically decreases in depth as a function of increasing temperature.

MUD008 (90 wt.% SAP105 saponite, <45 μ m grain size + 10 wt.% LCA101 carbon lampblack, <0.021 nm grain size) gets spectrally brighter as a result of heating in both the VISNIR and the MIR, which may be due to the volatilization of carbon. MUD008 displays a slight ~2.7 μ m feature which gets shallower with increasing temperature, consistent with the spectra of SAP104 and ASB267 (serpentine).

Other OH/H₂O related features ~1.4 and 1.9 μ m are observable in both SAP104 and ASB267 spectra. After exposure to high temperatures, these absorption features also decrease in depth, consistent with the ~2.7 μ m feature. Metal-OH features near ~2.3 μ m are also visible in both phyllosilicate samples. By 900°C, the absorption features are drastically reduced in depth.



Figure 2: VISNIR ($0.4 - 1.1 \mu m$) reflectance spectra of SAP104 <45 μm (top), MUD008 <45 μm (middle), and ASB267 <45 μm (bottom) heated under vacuum up to 900°C in 100°C increments. Spectral artifact at ~0.64 μm .

Discussion: Our spectra show that several OH/H₂O absorption features at ~1.4, ~1.9, and ~2.7 μ m become shallower with increasing temperature in SAP104 and ASB267. In addition, the Mg-OH features near ~2.3 μ m also decrease in strength with increasing temperature in both saponite and serpentine samples. These results are part of an on-going study investigating the spectral and mineralogical variations in saponite, serpentine and MUD008 due to thermal exposure under vacuum conditions. Future work includes collecting X-ray diffraction data on the heated samples presented in this study and relate any mineralogical changes to the spectral variations observed.

Acknowledgements: This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 871149. Thanks are due to the Canadian Space Agency (CSA), the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canadian Foundation for Innovation (CFI), the Manitoba Research Innovation Fund (MRIF) and the University of Winnipeg for supporting this study.

References

[1] McSween. H. 1979. Reviews of Geophysics & Space Physics 17:5. [2] Rubin. A. E. et al. 2007. Geochimica et Cosmochimica Acta 71:9.

Mn/Cr relative sensitivity factors of SIMS determined for synthetic Mn-, Cr-, and Fe-bearing dolomites

Shingo Sugawara¹, Wataru Fujiya¹, Akira Yamaguchi², Ko Hashizume¹ ¹Ibaraki University ² National Institute of Polar Reserach

Dolomite [CaMg(CO₃)₂] is a carbonate mineral commonly found in aqueously altered carbonaceous chondrites and contains some amounts of Mn and Fe. Dolomite in meteorites formed in the early solar system and incorporated a short-lived radionuclide ⁵³Mn that decays to ⁵³Cr with a half-life of 3.7 million years [1]. Thus, the timescale of aqueous alteration and the formation age of parent bodies can be constrained by ⁵³Mn-⁵³Cr dating of meteoritic dolomite.

The Mn-Cr dating of dolomite has commonly been performed using secondary ion mass spectrometry (SIMS). For SIMS analyses, the relative sensitivity factor (RSF) defined as a Mn^+/Cr^+ ion intensity ratio divided by a Mn/Cr elemental ratio must be evaluated using a standard material with the same composition as the meteoritic carbonate to be analyzed to correct the matrix effect. However, because carbonates in the natural environment contain little Cr, it is challenging to utilize a proper Cr-bearing dolomite standard, and therefore, the previously reported Mn-Cr ages of meteoritic dolomite may have systematic uncertainties. To overcome this problem, the synthesis of Mn- and Cr-bearing dolomite has been attempted [8,9], although dolomite crystallization proceeds only under hydrothermal conditions, making it difficult to incorporate Cr. Alternatively, Mn-and Cr-bearing calcite [CaCO₃] [10], which can be synthesized in aqueous solution at room temperature, has been used [2-5], but the RSFs of calcite and dolomite may be different. Recently, natural dolomite to which Cr ions were implanted was produced as a Cr-bearing dolomite standard [11,12]. However, the depth of the implantation was within 1 μ m from the sample surface, and thus, the analytical conditions of this standard and meteoritic dolomite were much different, which may lead a systematic error on the obtained Mn-Cr ages.

In this work, we synthesized Mn-, Cr-, and Fe-bearing dolomites via amorphous carbonates. Amorphous calcium carbonate (ACC), which can incorporate large amounts of incompatible elements for crystal phases, crystalizes into calcite by heating [e.g., 13]. Applying this method, we synthesized Mn-, Cr-, and Fe-bearing dolomites via amorphous calcium magnesium carbonate (ACMC) with FeO contents of (i) 0 wt%, (ii) 0.95 wt%, and (iii) 3.17 wt%. Also, we synthesized Mn- and Cr-bearing calcite from ACC for comparison with previous studies [10].

We produced ACMCs by mixing a 0.2 M Na₂CO₃ solution and a 0.2 M (Mg, Ca, Cr, Mn, Fe) Cl₂ solution. The ACMCs were dehydrated at 270-300 °C and crystallized to dolomite by heating at 310-420 °C under a 1-22 bar CO₂ atmosphere. The heated samples were washed with ultrapure water and dried in a vacuum desiccator. The run products were identified as single-phase dolomite by powder X-ray diffraction (XRD). We observed the dolomites with a field emission scanning electron microscope (FE-SEM) and found that they were from several 10s nanometer- to submicron-sized particles. Also, a Mn-, and Cr-bearing calcite was synthesized via ACC [13]. The Mn-, Cr-, and Fe-bearing dolomite and Mn- and Cr-bearing calcite particles were separately put in a tungsten carbide piston cylinder and pressed using a hydraulic press to produce pellets. These pellets were embedded in resin, and their surfaces were polished and then coated with carbon. Electron probe micro analysis confirmed that the ⁵⁵Mn/⁵²Cr ratios of the dolomites were (i) 1.32 ± 0.02 (2SE, n = 185), (ii) 5.46 ± 0.14 (2SE, n = 391), and (iii) 2.70 ± 0.06 (2SE, n = 220), and that of the calcite was 0.86 ± 0.01 (2SE, n = 200).

Then, we analyzed the synthesized carbonates and a natural olivine from San Carlos using SIMS. Secondary ions of 43,44 Ca⁺, 52,53 Cr⁺, 55 Mn⁺, and 57 Fe⁺ were produced with a ~1 nA O⁻ primary ion beam focused to ~10 µm in diameter. The RSFs of olivine and calcite were 0.93 and ~0.75, respectively, consistent with previous studies [2-5, 10] (Fig. 1). We found that the RSFs of Fe-bearing dolomites increase with their FeO contents from ~0.81 to ~1.00, which is also consistent with the previous study [12] (Fig. 2). The observed variation in the RSFs between Fe-bearing dolomites and calcite could result in a systematic error on the ages of meteoritic dolomites by 1.6 Myr. We noted, however, that the reproducibility was worse when we used a primary ion beam with a lower intensity of 150 pA, probably due to the influence of the surface topography. This indicates that it is important to keep analytical conditions the same between the standard and meteoritic dolomites.



Fig.1. The relative sensitivity factors $[RSF = ({}^{55}Mn/{}^{52}Cr)_{SIMS}/({}^{55}Mn/{}^{52}Cr)_{EPMA}]$ of synthetic dolomites, synthetic calcite, and San Carlos Olivine. RSFs obtained by Jilly et al. [4] are shown by open symbols for comparison.



Fig. 2. The RSFs of synthetic dolomites as a function of Fe contents. RSFs obtained by McCain et al. [12] are shown by open symbols for comparison.

References

[1] Honda M. and Imamura M. 1971. Phys. Rev. C 4, 1182–1188. [2] Fujiya W. et al. 2012. Nat. Commun. 3, 627. [3] Fujiya W. et al. 2013. Earth Planet. Sci. Lett. 362, 130–142. [4] Jilly C. et al. 2014. Meteorit. Planet. Sci. 49, 2104–2117. [5] Jilly C. et al. 2017. Geochim. Cosmochim. Acta 201, 224–244. [5] Yokoyama T. et al. 2022. Science eabn7850. [7] Nakamura E. et al. 2022. Proc. Jpn. Acad., Ser. B 98, 227-282. [8] Ichimura K. and Sugiura N. 2015. Abstract #1795 LPSC. [9] Donohue P. et al. 2019. Abstract #1949 LPSC. [10] Sugiura N. et al. 2010. Geochem. J. 44, 11–16. [11] Steele R. et al. 2017. Geochim. Cosmochim. Acta 201, 245–259. [12] McCain K. et al. 2020. J. Vac. Sci. Technol. B38, 044005 [13] Miyajima Y. et al. 2020. Geostand. Geoanal. Res. 45, 189–205.

Winchcombe CM2 meteorite fall 2021 – first results of systematic LASER Raman Spectroscopy

V.H.Hoffmann¹, M. Kaliwoda^{1,2}, M. Junge^{1,2}, W.W. Schmahl^{1,2}

¹Faculty of Geosciences, Department of Geo- and Environmental Sciences, University of Munich;

²Mineralogical State Collection Munich (MSM-SNSB), Munich, Germany

In our (online) poster we will report the first results of detailed studies by 2/3 D digital microscopy and high resolution LASER Raman Spectroscopy on the Winchcombe CM2 meteorite. This project is part of our ongoing investigations on the mineralogy and phase composition on selected and recent falls of carbonaceous chondrites [1,2 and refs. herein]. Scientific background of these studies are preinvestigations and necessary technical/methodological developments in the fore-field of the planed projects on Hayabusa 2 (asteroid Ryugu) and Osiris Rex (asteroid Bennu) returned materials [3,4].

Introduction

The Winchcombe meteorite fireball and fall from 28th february 2021 was the first reported meteorite fall of a carbonaceous chondrite in the UK [5-10]. The next day after the fireball the first finds were made in the private yard of local people (Wilcock family) followed by a number of further finds in the Winchcombe area (total reported mass about 602gr). Most of the finds were not influenced by any rains. We obtained fragment(s) of the first find made by the Wilcock family for our investigations.

Samples

Figure 1a: Our sample(s), 3D digital microscopy: fragment(s) of the Wilcock find, heavily brecciated, relicts of chondrules and CAI; (b) Large Olivine particle - near forsterite in composition - in the very fine grained phyllosilicate (serpentine) matrix. (c) Calcite bearing well structured CAI.







Fig 1a.

Fig. 1b.

Fig. 1c.

Methods, techniques

The (surface) morphology and mineralogy of the samples was pre-investigated by digital microscopy followed by detailed and systematic investigations with LASER Raman Spectroscopy [see 11,12 for details]. All Raman experiments have been performed without further preparation (only cutting) in order to avoid any unwanted effects (e.g. alterations). The obtained results should be representative because we did a large number of mappings in different scales on matrix and further components/clasts. We used the 532 nm LASER, Raman shifts were detected between 50-2500 (4500 for water content) cm⁻¹ with a precision of +/- 1-2 cm⁻¹, and magnifications of 100-1000x (long distance lenses only), and a lateral resolution of 0.1 μ m. Large maps up to 15x15 points in 2D/3D at high resolution allowed to also detect accessory phases / submicron particles and inclusions. Acquisition times of 1-3 sec and accumulation numbers of up to 5 have been used which allowed to obtain large numbers of Raman spectra in short times within the high resolution mappings, and therefore the results should be representative. Si and graphite standards were used for calibration measures, in most cases we applied a 6th degree polynomial for background subtraction.

Results

The matrix of Winchcombe is dominated by phases of the serpentine mineral group which is a common feature of the CM chondrites and also of C1-C2 ungrouped CC such as Flensburg, Tarda or Tagish Lake [5]. On many matrix spots and different clasts the serpentine group member cronstedtite could be detected, generally intimately intergrown with the iron sulfide tochilinite (TCI).

Summarizing, the following phases and components could be found in our preliminary studies:

- Serpentine group members (main matrix component)
- Cronstedtite / tochilinite aggregates (CTI)
- Troilite, pyrrhotite?
- Orthopyroxene (OPX)
- Olivine (near forsterite)

- Tephroite like phase (as in Aguas Zarcas)
- Carbon phases (no or poor crystallinity)
- CAI, calcite bearing
- A significant H₂O content, more details elsewhere

We could not find any effects or influence of terrestrial alteration which confirms the high quality of the material. Further Raman experiments will focus on the minor / accessory phases, the chondrule components and on CAI. Summarizing, the found phase composition of our Winchcombe sample reflects the typical composition of a CM2 carbonaceous chondrite, with one exception – the tephroite like phase.

To perform successful LASER Raman spectroscopy experiments on carbonaceous chondrites, (in our recent projects on the Mukundpura, Flensburg, Tarda, Kolang, Aguas Zarcas and here Winchcombe meteorite falls) requires the design of a highly sophisticated experimental setup in order to avoid or at least minimize alteration effects already during the measurements on the one hand and to guarantee a reasonable signal/noise relationship on the other. Therefore we decided to investigate only naturally broken unprepared sample materials whenever possible. The representativity of the data obtained on the available sample material was also topic of our studies: large sets of high resolution mappings in 2D/3D can help to overcome the problem of tiny samples / fragments. Our main interests were on optimizing and fine tuning our experimental setup. So the series of recent meteorite falls which produced a new set of primitive carbonaceous chondrites provided us directly with unique fresh analogue materials for Hayabusa 2 (Ryugu) and Osiris Rex (Bennu) asteroidal samples in our laboratories.

Figure 2: Representative Raman spectra as obtained on our Winchcombe sample: (a) Olivine particle – near forsterite in composition and a significant concentration of non-crystalline carbon phases; (b) OPX (chondrule?) and indications for water in the matrix (Raman shift > 3000 cm^{-1}); (c) Raman spectrum of a tephroite – like olivine group phase which we also could find for example in Aguas Zarcas (CM2). A tephroite like phase was not reported to our best knowledge from CM meteorites.



Fig. 2a.

Fig. 2b.

Fig. 2c.

References

- [1] Hoffmann V.H. et al., 2021. 8th ISAS Symp. Solar System Mater. (Hayabusa 2021).
- [2] Hoffmann V.H., Kaliwoda M., Junge M., Schmahl W.W., 2022. LPSC conference, iposter, # 2231.
- [3] <u>https://www.hayabusa2.jaxa.jp</u>
- [4] https://www.nasa.gov/osiris-rex.
- [5] Meteoritical Bulletin: www.lpi.usra.edu/meteor/metbull Winchcombe, Tarda, Flensburg, Tagish Lake, last visit 10 / 2022.
- [6] Daly L., King A.J., Joy K.H., Rowe J., UK Fireball Alliance, 2021. Elements, DOI: 10.2138/gselements.17.5.363.
- [7] Simms M.J., 2021. Geology Today, 37, 237-240.
- [8] https://karmaka.de/?p=26757: Winchcombe meteorite fall (2022).

[9] Russell S.S., Salge T., King A., Daly L., Joy K., Bates H., Almeida N.V., Suttle M., Schofield P., UK Fireball Alliance Team, 2022. Microsc. Microanal. 28 (Suppl 1), 2732-2733.

[10] Winchcombe meteorite fall 2021 in: 85th Annual Meeting of the Meteoritical Society 2022, contributions no: 6443, 6408, 6356, 6431, 6379, 6345, 6285, 6123, 6076, 6262, 6219.

- [11] Hoffmann V.H., et al. 2022a. Inter. Mineral. Congress, iposter # 1477.
- [12] Hoffmann V.H., et al. 2022b. Inter. Mineral. Congress, iposter # 1498.

Asteroids as Localized Rocks with Mixed and Less Activity

Yasunori MIURA

Department of Earth System Sciences, Faculty of Science, Yamaguchi University

Introduction: Rocks beyond water-planet Earth have not discussed from those collection and laboratory classification comparatively because of less sampling projects through different celestial bodies widely in the Solar System. In order to make clear the differences with them including the Itokawa and the Rhygu Asteroids, the main points are described in this paper with short summary [1,2] (Table 1).

Rocks as all different bodies and planets: Planetary Earth System [3] is supported by fact that all different celestial bodies have different global data and collected meteorites, where activity factors of all rocks are different from aging data and variety of rock-type widely based on the youngest rocks of Earth (cf. Table 1).

Localized and globally melted rocks: All extreme condition are created by planet-type (volcano and quake) and by cosmic originated-types (impact and plasma), where the localized melted rocks are formed on all primordial bodies and planets including younger planet Earth. However, water-planet Earth shows the most active planet because of progressive global ocean-water system with dynamic separation of air-water-solid rock (VLS) phasewidely to be possible for mixing and separation processes including purification to generate pure crystallized minerals and life with giant carbon-bearing molecules exclusively. In other words, planetary scientists should take care for any experiments on active space, reaction and description definitely (on volatile elements and molecule) including plasma-state reaction in any laboratory observation [1-8].

Significant roles of global VLS system: Although all localized impact event on all celestial bodies are produced a few melted and evaporated remains on the rock, the ranges are impacted areas with limited VLS growth during the melting. On the other hand, global VLS systems of Earth are produced solid system (continents and islands) changed as moved and changed with earthquake and volcano [5], and well-known geological impact layers [7,8] formed various kinds of rocks and many regional products. Therefore, local geological evidences produced regional products, however global system of Earth can form active factor of mixing and selection for rocks and life products exclusively [7,8]. Asteroids show limited mixing and selection of primordial products mainly.

Complicated formation VLS products locally in Asteroids: As there are evaporating elements and molecules beyond planet Earth, global VLS system of Earth are started as mixed grains of the VLS mixed micro-grains (as colloid solution and gel solid), which might be observed in the Asteroids separately as localized products (including plasma injection to the Asteroids' rocks). In Asteroids the localized products are the similar on the whole body with various impacts and injections [6,7,9,10].

Carbon-bearing grains in Asteroids: Carbon element is existed all meteorites and Asteroids micro- and macroscopically because it is stable molecules and solids after melting and pressing. Any Asteroids include texture of vacancy voids with carbon-bearing rims or grains formed by the plasma-injection (used by artificial technology). When it is formed mixed grains of colloids or quasi-solid, it might be remained in the rock's interior without separation (even at no global VLS system of any Asteroids), though mixed fluids are not pure water or CO_2 gas obtained in close system of Earth [2,5].

Less active life formation beyond Earth in the Solar System: Any mixed state grains with fluids are possible to bring to water planet or impacted planets under the room-temperature orbit zone even lower temperature as its unstable phase diagram. It might be exceptional case for mixed states of micro-gel states on the VLS planet Earth, where carbon-bearing VLS grains might kept in the void interiors of rock to produce pure water and CO₂ gas by slow and longer reaction process on dry Earth to water planet finally [11]. We can find carbon-bearing Egg shows mixed aggregates of colloidal solution and gel solids of organic compounds in life-type event now (Table 1).

Problem of observation and analyses: The carbon and/or hydrogen-bearing grains under electron-beam or ion sputtering for longer experimental run which might be evaporated to reacted molecules (obtained at wide temperature). Impact-run collection to the Asteroids surface might be reacted between gun-metal with industry contamination (cf. metal with carbon buffer control to be broken at collected procedure) [7-9].

Naming of minerals on Asteroids and any planets: Mineral name is exclusively defined as well-crystallized end-products on globally VLS system of planet Earth. Therefore, mixed grains or reacted (at the Earth's experiments) are not used as its crystal name, but it is recommended to be used as fixed word before mineral names (cf. "celestial body name" + mineral) because of its mixture (especially volatile elements) [1,2].

Summary: The present results are summarized as follows:

Any rocks beyond Earth are not the same of water-planet Earth as mineral name used as paper, it should be used as adjective word before mineral names (cf. "celestial body name" + mineral) because of its mixture with volatile elements) for written paper.
 All investigated rock data of planets and Asteroids previously are different in recorded database.

3) Melted rocks should take care for the effects from beam- and ion-sputtering naturally in the Solar System.

4) Local geology describes regional products, though global system of Earth can form active factor of mixing and selection processes for rocks and life products. Asteroids are the similar on the whole body by impacts and injections, where there is no global active factor triggered by the macro-ocean water system.

5) Carbon element is existed all meteorites and Asteroid, where they include texture of voids with carbon-bearing rims/grains formed by the plasma-injection as mixed grains of colloids, though mixed fluids are not pure water or CO_2 gas of Earth case. 6) Any mixed gel grain with fluids of Asteroids might be saved in the rocks globally. Carbon-bearing VLS grains might kept in the void interiors of rock to produce pure water and CO_2 gas by slow and longer reaction process on dry Earth to water planet. 7) The carbon and/or hydrogen-bearing grains under electron-beam or ion sputtering experimen might be evaporated to reacted molecules from previous impact-run collection.

| Celestial bodies | Mineral | Life |
|----------------------|-------------------------|-----------------------------|
| Earth (water planet) | Earth Solid(3macro-VLS) | Water Earth (3micro-VLS) |
| Bodies (dry sites) | Returned &collected | No real samples (No fossil) |

Table.1 Characterization of mineral & life systems of Earth & extraterrestrial bodies.

References:

[1] Miura Y. (2018) In Mineralogy past, present and future: preparing for the next 100 Years of the Mineral. Soc. America (IMA-22),1189.
[2] Miura Y. (2022) Jour. Mineral. Petrol. Sci. (Japan) (submitted).
[3] Wilson J.T. (1965) Nature, 207 (4995), 343-347.
[4] Miura Y. (1996) In Shock-Wave Handbook (Springer-Verlag Tokyo),1073-1209.
[5] Grove T.L. (2012) Ann. Review. Earth Planet. Sci. An. Rev. Earth and Planetary Sci. 40 (1), 413-439.
[6] Miura Y. (1993) Amer. Inst. Physics (AIP) Conf. Proc., 283 (Earth & Space Sci. Inf. Systems), 488-492.
[7] Miura Y. (1991) The Future of AMS (NSERC Grand. Carlisle Ed.), Vol.1, 45.
[8] Miura Y. (1992) Celestial Mechanic. & Dynamical Astro. (Kluwer Academic), 54, 249-253.
[9] Miura Y. (2008) Acta Crystal., 64, 55-55.
[10] Miura Y. and Tomisaka T. (1984) Mem. Natl Inst. Polar Res., Spec. Issue (NIPR), 35, 210-225; 226-242.

Grains to Press: Outreach ideas for sharing analysis results from the Ryugu sample

Elizabeth Tasker, Makoto Yoshikawa, Ayumu Tokaji, Masaki Fujimoto ISAS/JAXA

Planetary science missions are sometimes described as "science theatre" due to often having a series of big events such as launch, arrival and touchdown that can be leveraged to share scientific and engineering mission news with a broad audience. While publishing accurate and timely information remains challenging during a mission, images from the spacecraft can often be quickly appreciated, and act as a gateway to sharing more in-depth content. It is more difficult to keep up this dissemination of information during the sample analysis stage, where the careful work required (and the publication process itself) means that timing of the results cannot be controlled, the images not so quickly understood, and the conclusions one part of a large jigsaw puzzle being performed that may initially offer contradictions.

The information we discover from the analysis of the sample from asteroid Ryugu is the reason that Hayabusa2 flew. The questions being tackled concerning the origins of life are relevant to everyone on Earth, and the mission has generated strong interest in what might be discovered in the grains. Therefore, it is important that we meet this additional mission challenge to develop outreach material that can explain the process of the analysis, and share results in a way that is interesting and accurate.

This talk takes a look at some of the material used at ISAS to share information about the analysis, including videos, articles and Q&A events on social media. Suggestions will be asked for (be ready!) and ideas about the content that could be shared as we unpick the secrets held in this sample, and prepare for the sample from asteroid Bennu.



(Snapshot from the video on the Ryugu/Bennu social media Q&A)

TOF-SIMS analysis of macromolecular organic matter in Ryugu samples

M. Hashiguchi¹, D. Aoki¹, K. Fukushima¹, H. Yabuta², H. Yurimoto³, T. Nakamura⁴, T. Noguchi⁵, R. Okazaki⁶, H. Naraoka⁶, K. Sakamoto⁷, S. Tachibana^{7,8}, S. Watanabe¹, Y. Tsuda⁷ and the Hayabusa2-initial-analysis IOM team

¹Nagoya University, Nagoya, 464-8601, Japan, ²Hiroshima University, Higashi-Hiroshima,739-8526, Japan, ³Hokkaido University, Sapporo,001-0021, Japan, ⁴Tohoku University, Sendai, 980-8577 Japan, ⁵Kyoto University, Kyoto,606-8501 ⁶Kyushu University, 819-0395, Japan, ⁷ISAS/JAXA, Sagamihara, 252-5210, Japan, ⁸The University of Tokyo, Bunkyo-ku, 113-8654, Japan.

Introduction: The Hayabusa2 spacecraft returned samples with total mass of \sim 5 g from surface of asteroid Ryugu in December 2020 [1]. Chamber A aggregates collected upon the first touchdown and chamber C aggregates collected upon the second touchdown were investigated by the Hayabusa2 initial analysis team from June 2021 to May 2022.

The initial analysis organic macromolecule team has performed chemical, molecular, and isotopic analysis on the intact Ryugu grains and insoluble organic matter (IOM) isolated from Ryugu samples by μ -FTIR, micro-Raman spectroscopy, STXM-XANES, STEM-EELS, AFM-IR, and NanoSIMS [e.g., 4–8]. The result showed that chemical and isotopic compositions are broadly similar between Ryugu IOM and CI chondritic IOM, although some differences between the two IOM were reported by FTIR.

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is useful to analyze the molecular species present on the sample surface. This technique has been applied for a variety of organic matter from macromolecular materials [e.g., 9] and extraterrestrial samples [e.g., 10–11]. In this study, we conducted in-situ analysis on bulk Ryugu samples and the isolated IOM using TOF-SIMS to investigate the chemical structure of macromolecular organic matter in asteroid Ryugu.

Experimental: IOM were extracted from two Ryugu aggregate samples (A0106 and C0107) with 6M HCl and 1M HCl/9M HF at Hiroshima University [4]. Those Ryugu IOM samples and intact Ryugu grains A0106 and C0057 were used in this study. For comparison, Tagish Lake IOM and bulk samples of Tagish Lake (C-ungrouped) and Orgueil (CI) were used. All those samples were pressed onto clean copper disks (~ 2.1 mm φ) and mounted in in-house stainless steel holder for TOF-SIMS analysis. Roughness of the sample surface and copper disks were < 10 μ m for fragment samples, < 5 μ m for IOM samples, respectively. The TOF-SIMS measurement was performed using a TRIFT III spectrometer (ULVAC-PHI, Inc., Chigasaki, Kanagawa, Japan) at Nagoya University. Positive and negative ion spectra were obtained using Au⁺ gold primary ion (22 keV, 1.2 nA). The measured surface areas were 200 × 200 μ m and acquisition time of about 5 min for each sample. The ion intensity of each species was obtained from region of interest (ROI) of the sample of all samples, and were normalized by using total ion intensity of signals at *m/z* 0 to 150. After the TOF-SIMS analysis, mineralogical observation was performed on the sample using SEM/EDS.

Results and Discussions: Various ions derived from hydrocarbon moieties ($C_nH_x^+$), which containing 1-10 carbons, were detected from both of extracted IOM and bulk samples from asteroid Ryugu samples and Tagish Lake and Orgueil meteorites at m/z 10–150 of TOF-SIMS spectra.

Normalized intensities of these fragment ions and the fragment patterns were almost similar between A0106 and C0107 IOM. Most abundant fragment ion was $C_2H_3^+$ or $C_2H_5^+$ for both extracted IOM and bulk samples from Ryugu and Tagish Lake. Lower mass fragment ions (C_1 ~ C_4) were more abundant than higher mass fragment ions for both Ryugu and the carbonaceous chondrite samples. Furthermore, intensity of $C_nH_{2n+1}^+$ (n = 1~4) and $C_nH_{2n-1}^+$ (n = 3~5) ions from Ryugu IOM were higher than from Tagish Lake IOM. This trend implies that Ryugu IOM contains more abundant hydrogen than Tagish Lake IOM. On the other hand, Tagish Lake IOM showed higher intensity of $C_nH_{2n+1}^+$ (n > 5) and/or $C_nH_{2n-1}^+$ (n > 6) ions than Ryugu IOM. Although it is not clear whether these ions are derived from aromatic carbon or aliphatic carbon, the high mass fragment ions would indicate the presence of aromatic rings [12]. A previous TOF-SIMS study suggests that $C_nH_2^+$ radical cations and C_n^- radical anions are the fragmentation ions derived from aromatic moieties [12]. In this study, these radical cations or anions were detected from both Ryugu and Tagish Lake IOM, while their abundances from Tagish Lake IOM were higher than those from Ryugu IOM, except $C_3H_2^+$. The result suggests that Ryugu IOM is less molecularly evolved relative to Tagish Lake IOM, which is consistent with the solid-state ¹H-NMR results for organic matter in Ryugu samples [13]. Also, the abundances of intensity of C_n^- radical anions from the bulk Ryugu samples were lower than those from Tagish Lake, which also supports our observation for the extracted IOM.

Compared to bulk samples of Tagish Lake and Orgueil, it was hard to see clear difference on hydrocarbon fragment ions such as their intensity and H/C ratio between Ryugu samples like result of IOM samples, except $C_5H_x^+$. This may probably be due to sample heterogeneity. However, Tagish Lake and Orgueil bulk samples showed clearly developed $C_5H_x^+$ peaks relative to the bulk Ryugu samples. On the other hand, the extracted IOM showed the opposite trend: the peak intensities of $C_5H_x^+$ ions from Ryugu IOM, especially $C_5H_7^+$, were very high relative to those from Tagish Lake IOM. Such a large difference between bulk sample and IOM from the same sample has not been observed from meteorites, and therefore the observation implies the different chemical structures of Ryugu IOM and organic matter from bulk samples, which could be result from the acid-susceptible nature of the Ryugu samples. Different chemical structure of organic matter between Ryugu and Tagish Lake may result from freshness of Ryugu organic matter with no or little terrestrial alteration and/or different aqueous alteration process. Further TOF-SIMS analysis on CI chondrite IOM will provide more detailed firm interpretation for chemical evolution of Ryugu OM.

Acknowledgements

We thank to Mr. R. Nishimura at Nagoya University for making in-house holder for TOF-SIMS analysis in this study.

References

[1] Yada T. et al. (2021) Nat. Astron. 6, 214–220. [2] Arakawa M. et al. (2020) Science, 368, 67–71. [3] Tsuda, Y. et al. (2020), Acta Astronautica 171, 42–54, 2020. [4] Yabuta H. et al. (2022) Science, in revision. [5] Kebukawa Y. et al. (2022) 53rd LPSC.
#1271. [6] Stroud R. M. et al. (2022) 53rd LPSC. #2052. [7] Remusat L. et al. (2022) in 53rd LPSC. #1448. [8] Quirico E. et al. (2022) this meeting. [9] Stephan T. et al. (2003), Meteorit. & Planet.Sci. 38, 109–116. [10] Noun M.et al. (2020) Life, 9, p.44. [11] Hashiguchi M. et al. (2022) 53rd LPSC. #1867. [12] Sjövall P et al. (2021) Fuel, 286, 119373. [13] Cody G. D. et al. (2022) this meeting.

Continuing preparations for NASA curation of the OSIRIS-REx asteroid sample

N.G. Lunning¹, K. Righter¹, R. C. Funk², C.S. Snead¹, W. D. Connelly², S. Martinez², M. Montoya², J. L. Plummer², K. K. Alums², M. Rodriguez²,

¹Astromaterials Curation, NASA Johnson Space Center, 2101 NASA Pkwy, Houston, TX 77058 USA

²Jacobs/JETS, Astromaterials Curation, NASA Johnson Space Center, 2101 NASA Pkwy, Houston, TX 77058 USA

The OSIRIS-REx spacecraft collected an estimated 250-gram asteroid sample, completed its Bennu asteroid operations phase, and is on its way to return the asteroid sample to Earth on September 24, 2023 [1]. Construction of the OSIRIS-REx curation cleanroom (ISO 5) at NASA Johnson Space Center was completed in late 2021 and has been subject to ongoing monitoring for contamination knowledge [2,3]. The OSIRIS-REx curation cleanroom is inside of a lab suite with pass-throughs to an adjacent staging area and to an adjacent microtomy lab (ISO 7), which also separate it from the NASA Hayabusa2 cleanroom (ISO 5). In addition, a non-cleanroom space (OSIRIS-REx section lab) was built outside of the cleanroom suite for anticipated sample preparation activities that cannot be conducted in the curation cleanroom. Preparations for sample recovery and curation build on work that spans most of the last decade [e.g., 4] This presentation will cover curation preparation for the OSIRIS-REx sample over the last few years and plans for curation immediately following Earth return.

Recovery

The OSIRIS-REx curation team is involved in detailed planning for recovery of the sample return capsule (SRC) at the Utah Testing and Training Range (UTTR). This planning and preparation builds on lessons learned from the Genesis and Stardust recovery operations that also took place at UTTR. Our preparations involve plans for both nominal and off-nominal landing scenarios. For off-nominal landing scenarios, as a lesson learned from the environmental sensitivity of the returned Ryugu samples, a substantial factor is the potential sensitivity of the returned Bennu asteroid sample to environmental contamination and degradation, which may be much greater than that of the Genesis and Stardust samples. This includes the importance of, as rapidly as safe and feasible, getting the returned sample onto a nitrogen gas (GN2) purge to protect it from oxygen and humidity. In nominal landing scenarios, the sample canister that includes the Touch-And-Go Sample Acquisition Mechanism (TAGSAM) head will be flown from Utah to Houston for further disassembly at NASA JSC.

Spacecraft disassembly at NASA JSC

In Houston, the sample canister will remain under GN2 purge until it is transferred to a GN2 glovebox in the OSIRIS-REx curation cleanroom. The sample canister will be opened inside of a glovebox that was specifically designed to accommodate removing its lid. The curation team has been rehearsing this process and other hardware disassembly and sample handling processes in glovebox mockups to refine disassembly techniques. In addition, rehearsals are helping to prepare the team for the intense hardware and sample handling that will occur during preliminary examination (PE). After the sample canister lid is removed, the TAGSAM head will be revealed and its condition documented. It is unknown to what extent Bennu dust will have migrated from inside the TAGSAM head outward to cover the interior of the canister lid. Shortly after documentation of the interior of the canister lid and the exterior of the TAGSAM head, the TAGSAM head will be removed and weighed on a stand. The nominal weight of the empty TAGSAM (and the stand) will be subtracted from the weight of the returned TAGSAM head holding sample to get the first estimate of the mass of the returned bulk sample. Next, the TAGSAM head will be sealed inside of a transfer container and moved to a second specially designed glovebox for further documentation and disassembly.

The first operations in the glovebox designed for TAGSAM head disassembly will focus on the contact pads, which have been previously described [5]. The contact pads and associated particles will be visually examined, carefully documented in place, relevant hardware will be further disassembled, then the contact pads will be removed and containerized. Following containerization of the contact pads, disassembly of the TAGSAM head will continue until only several components remain holding the returned asteroid sample. At this point the sample will be gently poured off the remaining hardware, which will be followed by documentation of the bulk sample poured from inside the TAGSAM head into a set of trays for more detailed imagery and storage. The containers that returned samples, contact pads, and flight witness plates are stored inside of will be tested to quantify the time internal they are able to maintain an anoxic environment outside of a curation glovebox [6].

Laboratory monitoring described by [3] will continue throughout PE (the six months of after Earth return) and beyond. In addition, witness plates will be deployed to monitor the interiors of gloveboxes in which the spacecraft hardware will be disassembled and asteroid samples will be processed.

Catalog Release

PE will culminate in the initial public release of the OSIRIS-REx returned sample catalog around the end of March 2024. We anticipate the OSIRIS-REx return sample catalog will grow over time as more individual particles undergo basic characterization. After the release of the catalog in March 2024, the collection will be open for sample requests from the entire community. As is the case for all NASA's astromaterials collections, a collection-specific allocation board will be convened to review OSIRIS-REx sample requests.

References

[1] Lauretta, D. S., Adam, C. D., Allen, A. J., Ballouz, R. L., Barnouin, O. S., Becker, K. J., Becker, T., Bennett, C. A., Bierhaus, E. B., Bos, B. J. and Burns, R. D., 2022. Spacecraft sample collection and subsurface excavation of asteroid (101955) Bennu. Science, 377(6603), pp.285-291 [2] Dworkin J. P., Adelman L. A., Ajluni T., Andronikov A. V., Aponte J. C., Bartels A. E., Beshore E., Bierhaus E. B., Brucato J. R., Bryan B. H., Burton A. S., Callahan M. P., Castro-Wallace S. L., Clark B. C., Clemett S. J., Connolly H. C., Cutlip W. E., Daly S. M., Elliott V. E., Elsila J. E., Enos H. L., Everett D. F., Franchi I. A., Glavin D. P., Graham H. V., Hendershot J. E., Harris J. W., Hill S. L., Hildebrand A. R., Jayne G. O., Jenkens R. W., Johnson K. S., Kirsch J. S., Lauretta D. S., Lewis A. S., Loiacono J. J., Lorentson C. C., Marshall J. R., Martin M. G., Matthias L. L., McLain H. L., Messenger S. R., Mink R. G., Moore J. L., Nakamura-Messenger K., Nuth J. A., Owens C. V., Parish C. L., Perkins B. D., Pryzby M. S., Reigle C. A., Righter K., Rizk B., Russell J. F., Sandford S. A., Schepis J. P., Songer J., Sovinski M. F., Stahl S. E., Thomas-Keprta K., Vellinga J. M., and Walker M. S. 2018. OSIRIS-REx Contamination Control Strategy and Implementation. Space Science Review 214, 1-19. [3] Righter, K., Lunning, N.G., Snead, C.S., 2022. Contamination monitoring of the OSIRIS-REx ISO5 asteroid sample cleanroom. this symposium. [4] Righter, K. and Nakamura-Messenger, K., 2017. Sample curation in support of the OSIRIS-REx asteroid sample return mission. Hayabusa Symposium. [5] Bierhaus E. B., Clark B. C. Harris J. W., Payne K. D., Dubisher R. D., Wurts D. W., Hund R. A., Kuhns, Linn T. M., Wood J. L., May A. J., Dworkin J. P., Beshore E., Lauretta D. S., and the OSIRIS-REx Team. 2018. The OSIRIS-REx spacecraft and the Touch-and-Go sample acquisition mechanism (TAGSAM). Space Science Reviews 214, 1-46. [6] Snead, S. C., Righter, K., Lunning, N. G., 2022., this symposium.