# Overview of S-type asteroid Itokawa, based on the studies on samples returned by Hayabusa.

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**Introduction:** Hayabusa spacecraft, which was launched in May 2003, reached near-Earth S-type asteroid 25143 Itokawa in September 2005. It landed onto the surface of the smooth terrain called "MUSES-Sea" of Itokawa twice in November 2005, even though its touchdown sampling system had not fully functioned [1]. Hayabusa spacecraft had overcome a series of troubles happened after the 2nd sampling and during its returning cruise back to Earth, and return its reentry capsule including its sample container to the Woomera prohibited area in South Australia in June 2010. After a series of procedures in the curation facility in JAXA, sub-mm sized mineral grains were recovered from its sample canister [2, 3]. A series of preliminary examination analyses on those grains revealed that they originated from surface regolith of asteroid Itokawa and that were comparable to equilibrated LL chondrites [4-9].

**Initial descriptions and distributions of Itokawa samples:** The sample canister is separated into two rooms, room A and B, and those from the 1st touchdown should be recovered into the room A and those from the 2nd one should be in the room B, even though the gap of the division plate between the two rooms sizes around 0.5mm and those smaller than the size of gap might be mixed up between the two rooms. The sample container was introduced into the clean chamber and opened in static vacuum condition in order to recover gas sample in the container even though it did not contain detectable amount of sample gas. The sample canister was extracted from the container in purified nitrogen condition and samples grains inside the sample canister were recovered onto quartz glass or aluminum plates due to compulsive fall by tapping the canister in upside down orientation. Individual sample grains were handpicked and handled with an electrostatically controlled micro-manipulation system developed for Hayabusa returned samples and installed in the clean chamber of purified nitrogen condition [10]. They were transferred to the sample chamber of the field emission secondary electron microscope equipped with the energy dispersive X-ray spectrometer (FE-SEM/EDS) Hitachi S-4300SE/N or SU6600 without exposing to the air and examined for their backscattered electron images and qualitative chemical composition. After sent back to the clean chamber, they were placed onto gridded quartz glass slides, lately individual quartz glass containers, to be stored in its purified nitrogen condition and given individual identification numbers. So far, 1344 of individual Hayabusa grains have been described and given sample IDs. The sample IDs start from "RA" are from room A, which comprise 605 grains, "RB" from room B, 404 grains, "RC" from a rotation cylinder situated between the two rooms, 86 grains, and "RX" are from both rooms, 249 grains [11]. All the initial description information of Hayabusa sample grains are also published on the sample catalog website (https://curation.isas.jaxa.jp/curation/hayabusa/index.html). Among them, 20 of grains and one Teflon spatula containing fine Itokawa grains have been distributed to NASA, based on Memorandum of Understanding between JAXA and NASA for the Hayabusa mission. On the other hand, international announcement of opportunity of Hayabusa samples have been conducted since 2012, and 254 of individual Hayabusa grains have been distributed to 69 of research plans of AO so far, which result in various kind of scientific achievements mentioned below.

**Equilibrated chondritic body Itokawa:** Modal abundance, average fayalite content in olivine and ferrosilite content in low-Ca pyroxene, and oxygen isotopic compositions of Itokawa grains match those of LL chondrites [4, 5, 12, 13], and distribution of fayalite contents in olivine and petrologic observation indicated its petrologic type ranges from type 4 to type 6 [4]. Olivine-spinel geothermometer and plagioclase geothermometer have been applied for Itokawa mineral grains, indicating that peak temperature they experienced during thermal metamorphism in asteroid should have reached 800˚C and it slowly cooled down to 600˚C, which corresponds to petrologic type <5 [4, 14, 15]. The thermal metamorphism it experienced should have occurred in a body predate asteroid Itokawa. Assuming $^{26}Al$ as a heat source of such body, the size of the precursor body of asteroid Itokawa should have sized 20km in radius based on numerical simulation [16]. Concerning about its shock stage, detailed studies on olivine and plagioclase in Itokawa grains indicate they experienced shock stage 2, moderately shocked, which corresponds to 5-10 GPa in shock pressure. Thus, Itokawa is an LL chondritic breccia body of various petrologic type ranging from type 4 to 6. The U-Pb chronology obtained from phosphates found in Itokawa grains show a single isochron age of 4.64 ± 0.18 Ga, indicating the precursor body should have formed in the early solar system [17]. Also a lower intersection age of the U-Pb system is 1.51 ± 0.85 Ga, indicating catastrophic break-up event should have occurred for the precursor body of Itokawa at this age. This age is consistent with a result of complete degas age estimated from $^{40}Ar$-$^{39}Ar$ system as 1.3 ± 0.3 Ga [18], whereas it is inconsistent with the degas age by $^{40}Ar$-$^{39}Ar$ system as 2.3 ± 0.1 Ga [19]. It seems that further confirmation is needed for the chronological study.

**What happens on asteroid Itokawa:** Because Itokawa samples are the only surface regolith sample of the S-type asteroid among all kinds of planetary samples, a series of studies for space weathering have been conducted for these samples. Surface of Itokawa grains shows thin (30-60 nm) amorphous layer, containing ~2nm of nano phase Fe particles [7]. The very surface of the amorphous layers are enriched in not only Fe but also S, redeposition of nano phase FeS after micrometeoroids impact should occur and this must redden reflectance spectrum of the asteroid effectively. Solar flare tracks are recognized in olivine in Itokawa grains just below the amorphous phase and its track densities indicate their short surface exposure time on the order of $10^3$ to $10^4$ years [20]. The fact that the exposure ages of Itokawa grains much shorter than that of Lunar regolith (>several tens million years) are consistent with the result of exposure age estimated from cosmogenic $^{21}$Ne concentrations of Itokawa grains as 3 million years, which is much shorter than Lunar regolith as ~400 million years [9]. Short exposure time of Itokawa grains also pointed from little cosmogenic $^{10}$B contribution in B isotopic composition observed in Itokawa grains [21]. The short exposure time of Itokawa regolith also indicates that large surface mass loss rate such as several tens of cm per million years, further implied the lifetime of Itokawa as 100 to 1000 million years [9]. Different from silicate minerals, space weathering on the surface of sulfides cause ~1 μm to several hundreds nm of iron whiskers on their surfaces caused by loss of sulfur from sulfide surfaces and deposition onto them due to long exposure to the energetic ions of the solar wind [22]. As mentioned before, surfaces of Itokawa grains also experienced micrometeoroids impact. Microimpact craters are reported on the surfaces of Itokawa grains [23], which results in melt splashes and adhering particles [24] and even secondary submicrometer craters distributed on their surfaces, assuming their exposure time as $10^2$ to $10^4$ years [25, 26].

**New insights of S-type asteroid:** Itokawa samples bring us new insights of S-type asteroid. For example, ~1 mole% enrichment of water and hydroxyl on the surface of olivine in Itokawa samples, which is caused by continuous exposure of solar wind to the asteroid surface, indicating ubiquitous presence of such water on airless bodies. They further assume a part of potential sources of Earth's ocean in the early solar system [27]. Concerning about water, euhedral NaCl crystals and KCl, which should have formed by water-rock interaction in Itokawa or its precursor body, were discovered on the surface and interior of Itokawa grains and nanoscale NaCl grains were discovered in an Itokawa grain, indicating S-type asteroid might have once contained certain amount of water and provided water to ancient Earth [28, 29, 30]. S-type asteroids are thought to be poor in organic matters as ordinary chondrites, but indigenous organic matters were discovered from carbon-rich Hayabusa grains [30, 31]. They discovered nanocrystalline graphite and disordered polyaromatic hydrocarbon in carbon-rich grains recovered from the Hayabusa sample canister, showing D- and $^{15}$N-enrich isotopic compositions. In another report, they discovered non-protein amino acids, racemic β-aminoisobutyric acid and β-amino-n-butyric acid in carbon-rich grains, indicating their non-biological, non-terrestrial origins.

**Concluding remarks:** As mentioned above, Itokawa samples continue providing new and striking scientific results. Even though we have (will have) other new returned asteroid samples like Ryugu from C-type asteroid [32] and Bennu from B-type asteroid [33], Itokawa samples remain important because they are still the only S-type asteroid samples for human being.

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# Summary of Hayabusa2 and Status of JAXA curation

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Japan Aerospace Exploration Agency (JAXA) has a strategic small-body sample return program to understand the formation, evolution, and migration of planetary building blocks, water, and organics in the early solar system. The JAXA's sample return program started with Hayabusa for S-type asteroid Itokawa in 2010, followed by Hayabusa-2 for C-type asteroid Ryugu in 2020, and the future mission of Martian Moons eXploration (MMX) for Phobos in 2029. My presentation covers the recent achievement of Hayabusa 2 curation and sample analysis. I also present an overview of MMX, particularly how we leverage the Hayabusa 2 experience to develop the MMX curation and sample science.

Hayabusa 2 team has completed the initial curation and sample analysis of the Ryugu samples. The Hayabusa 2 curation/sample analysis is unique in having a role as a "bridge" between the remote sensing and the sample analysis communities. Along with the conventional curation tools (e.g., optical microscope and balance), JAXA installed remote sensing instruments (e.g., ONC: Optical Navigation Camera) in the curation facility for ground truthing. Moreover, a flight spare of MicrOmega (infrared hyperspectral microscope) detected important minor phases (clays, carbonates, organics) in the apparently black Ryugu samples in the early stage of the curation. Following the initial sample analysis/curation activity, Ryugu samples are now publicly available <https://jaxa-ryugu-sample-ao.net/>.

JAXA plans a Phobos sample return mission MMX in 2024-2029. The MMX spacecraft is scheduled to be launched in 2024, orbit Phobos and Deimos (multiple flybys), and retrieve and return >10 g of Phobos regolith to Earth in 2029. The Phobos regolith represents a mixture of endogenous Phobos building blocks and exogenous materials that contain solar system projectiles (e.g., interplanetary dust particles and coarser materials) and ejecta from Mars and Deimos. The MMX Sample Analysis Working team started designing the curation and sample analysis protocol to identify Phobos' fragments with different origins. Under the condition that remote sensing observations guarantee the representativeness of the sampling sites in the geologic context of Phobos, laboratory analysis of the returned sample will provide crucial information about the moon's origin: the capture of an asteroid or in-situ formation by a giant impact.

# Future perspective of sampling and curation for extraterrestrial materials in JAXA's small body exploration

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*Introduction*

Japan Aerospace Exploration Agency (JAXA) successfully completed the sample return planetary exploration missions for the small bodies Itokawa (Hayabusa; 2003–2010) and Ryugu (Hayabusa2; 2014–2020). JAXA is preparing to receive the next return samples to Institute of Space and Astronautical Science (ISAS) and planning new missions for the next decade. I introduce the concept and tentative plan for the curation of the Bennu sample returned by Origins, Spectral Interpretation, Resource Identification, Security, Regolith Explorer (OSIRIS-REx; NASA), the Phobos sample collected by Martian Moon Exploration (MMX; JAXA), and the comet sample collected by Next-Generation Small Body Sample Return (NGSR; JAXA). The concept of curation in the future is threefold: ground truthing of remote-sensing and in-situ data, certification for the curation data, and in-house contamination control. Subsequently, I introduce the scientific scopes and the key techniques for sampling the comet materials in the NGSR mission.

*Curation*

**Ground truthing of remote-sensing and in-situ data**. Ground truthing for remote-sensing and in-situ analysis data obtained by the mission instruments should be done to complete the mission objectives in the sample return mission. The curation phase of the return samples is the chance for ground truthing without any sample biases. In the MMX curation, the initial description will be done with the ToF-type mass spectrometer, visible/infrared spectral imager, and Raman spectrometer, corresponding to the mission instruments in the MMX spacecraft [1]. In addition, the simulator of Optical RadiOmeter composed of CHromatic Imagers (OROCHI), an optical camera of the MMX spacecraft, will be installed in the Bennu clean chamber to help plan the MMX's curation strategy [2].

**Certification for the curation data**. Whereas the observation in the clean chamber is useful to characterize the bulk-scale return sample, the analytical method is limited to a totally non-destructive way. For instance, we estimated the bulk density of Ryugu grains with the information from the weight and optical image [3]. To confirm the accuracy of the curation data within the clean chamber, we will conduct the coordinated analysis for the return sample (e.g., Ryugu, Bennu) outside the clean chamber, such as X-ray Computed Tomography (XCT) and Scanning Electron Microscope- Energy Dispersive Spectroscopy (SEM-EDS). This dataset is available as additional information for outreach and allocation in the Announcement of Opportunity (AO).

**In-house contamination control.** Regular monitoring for the contamination of clean environments is essential to maintain cleanliness levels. We newly introduce the method for sampling the metal particles within clean rooms and chambers by Gas Exchange Device- Inductively Coupled Plasma- Mass Spectrometer (GED-ICP-MS). We can count the number of metal particles without any biases in the sample preparation. We can attain the cross-check for possible contamination in the return samples by mass spectrometric techniques developed with in-house contamination control.

*Next-generation sample return mission*

**Scientific scopes.** Following small-body explorations such as the Hayabusa and Hayabusa2 missions, we should explore more primitive targets in the Solar System. Our target for the next sample return is a comet, which potentially possesses the record of the early Solar System and "presolar" system in the Milky Way Galaxy, avoiding the secondary alteration within the parent body. Kurokawa et al. [4] will report the scientific concept of NGSR in detail.

**Subsurface sampling**. The surface of a comet should have non-primitive layers such as recondensed and/or consolidated surfaces up to ~1 m depth [5]. Therefore, subsurface sampling for the comet is critical to attain the scientific objectives in NGSR. We are developing the subsurface sampling system using a Small Carry-on Impactor (SCI) and bullet-system sampler.

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# Updates on OSIRIS-REx: Return journey to Earth and the sample from Bennu

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NASA's OSIRIS-REx (Origins, Spectral Interpretation, Resource Identification, Security and Regolith–Explorer) spacecraft explored B-type near-Earth asteroid (101955) Bennu from December 2018 to May 2021. [1]. The spacecraft data indicated that Bennu's surface material contains hydrous silicates, carbonates, magnetite, and organic matter [2-4], suggesting that it experienced aqueous alteration within a parent body. In October 2020, the spacecraft collected a sample of surface material from a site nicknamed Nightingale within the 20-m-diameter Hokioi crater. The in-flight inspection of the sample with the SamCam imager showed that millimeter- to centimeter-sized particles were successfully collected [5]. Analysis of various telemetry data from before and after sample collection yielded an estimated sample mass of 250 ± 101 g, well above the mission goal (60 g) [5]. The spacecraft will fly by Earth and drop the Sample Return Capsule (SRC) into the Utah desert in the western United States on September 24, 2023. As of writing (September 21, 2023), the spacecraft is on track targeting Earth. After retrieval, the SRC will be delivered to the NASA Johnson Space Center (JSC) to be curated in a new cleanroom dedicated to the Bennu sample [6]. At the symposium, we will report updates on the SRC retrieval operation, curation processes at JSC, and the sample.

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# Developing European Curation for MMX Samples

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Curation of extraterrestrial samples is imperative for maximizing science return. Despite Europe's established meteorite and overall museal curation expertise, it currently lacks specialized infrastructure for samples directly returned from space. An opportunity to enhance capabilities in this area is provided by the Martian Moon eXploration (MMX) mission. MMX is led by the Japan Aerospace Exploration Agency (JAXA) and is planned to return >10g of core and regolith material from Phobos to Earth in July 2029 [1, 2].

Cooperative discussions between partnering space agencies and European institutions regard possible transfer of a portion of the anticipated MMX sample collection for long-term curation in European institutions, following the period of initial description at JAXA and the initial scientific analysis conducted by the MMX Science Sub-Teams (i.e., post-2030). Leading this initiative are the Centre National d'Études Spatiales (CNES) and the Museum National d'Histoire Naturelle (MNHM) in France and the German Aerospace Center (DLR) in Germany. Both are actively engaged in designing advanced curation facilities to receive, curate, and handle Phobos samples.

The Centre National de la Matière Extraterrestre (CNME, National Center for Extraterrestrial Materials) is a joint program supported locally by the National Museum of Natural History (MNHN), Sorbonne University and the Institut de physique du globe de Paris (IPGP) and, at the national level, by the French spatial and scientific research agencies (CNES and CNRS). The CNME will be built in the historical Geology and Mineralogy Gallery of MNHN in the center of Paris. The CNME will be designed to ensure long-term curation of unrestricted extra-terrestrial samples allocated to France from past and future space missions such as MMX, together with existing major collections of extra-terrestrial samples including: the national meteorite collection from MNHN, large polar micrometeorites collections and terrestrial analogues from the geology/mineralogy collections. The CNME will consist in a clean-room infrastructure, divided in separated modules with ISO7 to ISO5 environments, together with an adjacent laboratory for sample preparations and experiments not requiring a cleanroom environment. The CNME curation team will work under the supervision of CNES on the recently funded MARCUS project to build a dedicated apparatus for small sample (solid and gas) handling under restricted conditions (pure nitrogen glove boxes) and bio-contained environment. Instrumentation in the CNME will focus on acquisition of the basic properties on samples (from µm to cm scales), including optical 2D and 3D microscopy and imaging, weighting, magnetic susceptibilities, scanning electron microscopy, Raman and infrared (IR) microspectroscopy, XRD, with a dedicated suite of instruments to achieve initial characterization and cataloging of samples before allocation.

At the DLR Institute for Planetary Research in cooperation with the Museum für Naturkunde in Berlin, the Sample Analyses Laboratory (SAL) and its extension, the Sample Curation Facility are currently being setup [3]. The target date for completion is in the summer of 2024. It is mainly dedicated to the analyses of unrestricted extra-terrestrial materials from sample return missions. SAL will focus on spectroscopic, geochemical, mineralogical analyses at microscopic level. The instrumentation includes a Malvern Panalytical Empyrean X-ray diffraction (XRD), a JEOL iHP200F Field Emission - electron microprobe analyzer (FE-EMPA), a Field Emission - scanning electron microscope (FE-SEM), Keyence VHX-7000 3D microscope, and a vis-IR-microscope (Bruker Hyperion 2000), all housed in a clean room that is currently being built. Samples will be processed, handled and analyzed in pure nitrogen or vacuum conditions to minimize alteration and contamination.

Within the European Centre for Space Applications and Telecommunications (ECSAT) site of the European Space Agency (ESA), the recently established Vulcan Analogue Sample Facility (formerly SACF) is actively involved in the development of a robust European network dedicated to both existing and prospective extra-terrestrial analogue sample procurement, production, and supply chain management. The Vulcan Facility is further oriented towards advancing the scientific investigation of planetary analogues encompassing lunar, Martian, and other celestial bodies. This is accomplished through the provision of state-of-the-art benchtop instrumentation for fundamental analyses encompassing geochemical, mineralogical, and crystal lattice properties (SEM-EDS, XRD, FTIR and Raman). Additionally, the Vulcan Facility offers geotechnical property characterization capabilities (ViseSize particle size analyser, pycnometer, and TGA). Concurrently, Vulcan lends support to the curation of extra-terrestrial materials and associated technology development initiatives (glovebox systems and a Double-Walled Isolator [DWI] with robotic arm equipped with a micromanipulator). The strategic focus of Vulcan on analogue samples is anticipated to play a pivotal role in addressing the curation and research challenges associated with upcoming and future extraterrestrial sample return missions.

Between partners of any joint sample return activity, a tightly-coordinated approach on curation protocols, and mutually high level of technical proficiency and training, is fundamental to achieving the main goal of long-term curation: preparing for techniques that have yet to be conceived, enabling testing theories that have not yet been developed, and catering for the ideas and needs of future scientists.

The implications of capability development in Europe for handling returned samples extend beyond the MMX mission. Establishing these curation facilities and developing a collaborative framework for distributed long-term curation will increase the readiness of European involvement in future sample return missions. In particular, developments in sample handling and curation infrastructure may be synergistic with that required by the long-term curation of Martian samples that are planned to be returned by the NASA/ESA Mars Sample Return (MSR) campaign.

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# The DLR Sample Analysis Laboratory – the final countdown

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Laboratory measurements of extra-terrestrial materials like meteorites and ultimately materials from sample return missions can significantly enhance the scientific return of the global remote sensing data. This motivates the ongoing addition of a dedicated Sample Analysis Laboratory (SAL) to complement the work of well-established facilities like the Planetary Spectroscopy Laboratory (PSL) and the Planetary Atmosphere Simulation LABoratory (PASLAB) within the Department of Planetary Laboratories at DLR, Berlin. SAL is being developed in preparation to receive samples from sample return missions such as JAXA Hayabusa 2 and MMX missions, the Chinese Chang-E 5 and 6 missions as well as the NASA Osiris-REX mission. SAL is focusing on spectroscopic, geochemical, mineralogical analyses at microscopic level with the ultimate aim to derive information on the formation and evolution of planetary bodies and surfaces, search for traces of organic materials or even traces of extinct or extant life and presence of water.

SAL is currently being set up at the Institute for Planetary Research at the DLR location in Berlin-Adlershof in Germany. The cleanroom environment is on the ground floor of the main DLR building in Berlin-Adlershof with a room for support infrastructure in the basement below.

Procurement of the instruments is almost complete and first instruments are already been delivered. SAL will be equipped with a vis-IR-microscope (Bruker Hyperion 2000), a Malvern Panalytical Empyrean X-ray diffraction (XRD) system with Bragg-Brentano geometry which can be switched to parallel beam geometry, equipped with a Cu Kα source, 1Der detector and automated incident beam optics, a Field Emission – scanning electron microscope (FE-SEM), a JEOL iHP200F Field Emission – electron microprobe analyzer (FE-EMPA), petrographic and stereo microscopes, Keyence VHX-7000 3D microscope and a set of gloveboxes.

The Bruker Hyperion 2000 and the Keyence VHX-7000 3D microscope are already in operation at PSL and PASLAB and have been used recently to study Ryugu sample A0112. The JEOL iHP200F is currently setup at JEOL in Freising, Germany. Acceptance tests were successfully completed in March 2023. Commissioning, calibration, testing and initial training was completed in summer of 2023. The instrument has been used recently for work on meteorites and will be transferred to DLR in early 2024 with an additional delta commissioning planned after final installation. The X-ray diffraction system has been delivered in December 2022 and is currently in storage and will be setup as soon as the cleanrooms are ready. SEM procurement is currently under way with a delivery expected in summer of 2024.

In collaboration with the Natural History Museum (MfN) in Berlin, SAL will also have the expertise and facilities for carrying out curation of sample return material which will be made available for the whole European scientific community. DLR is already curating a 0.45 mg of Lunar regolith collected from the Luna 24 Soviet mission and the first analyses of the material are being planned.

Currently, the curatorial expertise is being developed on the existing expertise from the Meteorite Collection based at the MfN and in collaboration with the JAXA and NASA curation facilities. Current curators, together with the younger generation are being trained and working on skillset exchange

# Curation of Extraterrestrial samples in France and the future center for extraterrestrial materials in Paris.

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The coming decade will witness important developments in curation facilities dedicated to pristine samples from space missions. The return of samples from asteroid Bennu by the OSIRIS-REx NASA-led mission [4] is imminent and, on a longer term, samples will be returned from the Martian moon Phobos by the MMX JAXA-led mission [5]. After 2030, samples from the Martian surface are expected to be returned to Earth by the NASA/ESA Mars Sample Return (MSR) mission [6]. Advanced curation studies are on-going [9, 10] in major curation facilities at JAXA and NASA [7-9] while others facilities are currently into construction, such as the SAL in Berlin [see e.g. 11 and this meeting]. Many laboratories in France have experience in handling samples from spatial missions or from existing collections of extra-terrestrial materials (meteorites, micrometeorites, IDPs…). These experiences cover a whole range of expertise from curation itself to dedicated samples handling (e.g. micromanipulation, fragmentation…), first-order characterization by non-invasive or non-destructive techniques and dedicated sample preparation (e.g. thin and ultra-thin sections, polished sections, …) in clean-room environments.

The CNME project was launched in 2022 to build a national curation facility for extra-terrestrial materials at MNHN. This project is supported, at the national level, by the French spatial and scientific research agencies (CNES and CNRS) and will be supported locally by the National Museum of Natural History (MNHN), Sorbonne University and the Institut de physique du globe de Paris (IPGP). This project will benefit from the local experience in curation of existing collection of meteorites and micrometeorites and from expertise developed in other French laboratories. A key objective of CNME will be to ensure the long-term curation of a fraction of samples from the future MMX JAXA-led mission [5]. As a result of on-going agreements between JAXA and the French space agency CNES and ESA, a fraction of Phobos (MMX) samples are expected to be transferred to the CNME at MNHN and 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). In the long-term, the CNME will be designed to allow the reception of un-restricted samples from MSR mission, i.e. once they will be out of the Sample Receiving Facility.

The design of CNME will be modular to allow flexible configuration of different environments for the curation of samples from different space missions. The CNME clean-room infrastructure will be divided in separated modules (ISO7 to ISO5 [24]) environments, together with a laboratory dedicated to sample preparations. It will contain secured cabinets and glove boxes under controlled atmospheres (dry and purified $N_2$, Ar, vacuum, …). In the long-term perspective of MSR, the CNME team is involved in the MARCUS project to study, under the supervision of CNES, a dedicated apparatus for small sample (solid and gas) handling in clean and bio-contained (BSL4-like) environment. The CNME will include a dedicated space for rehearsal activities on the MARCUS apparatus (before operation in BSL4-like laboratories). Instrumentation in CNME will focus on acquisition of the basic properties on samples with sizes going from µm up to cm scales, including optical 2D and 3D microscopy and imaging, weighting, magnetic susceptibility measurements, scanning electron microscopy, XRD, Raman and infrared (IR) micro-spectroscopy with a dedicated suite of instruments, to achieve initial characterization and cataloguing of samples. The control of terrestrial contamination within CNME cleanrooms will be achieved by real-time monitoring of inorganic, organic and biological contamination.

The CNME will include instruments and advanced storage facilities developed by several French laboratories. The magnetic environment of the samples and the magnetic properties of the handling tools will be monitored to ensure preservation of the original paleomagnetic record of the samples. The CNME will develop research programs to improve existing curation techniques and new technological solutions for the mid to long-term curation of volatile elements contained in samples collected by future space missions, e.g. ice and gas from cometary objects or planetary atmospheres (see G. Avice et al. this meeting). 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 of samples. The analysis will be fully non-destructive and non-invasive with no need for specific sample preparation, it will be performed within a dedicated bench in a controlled atmosphere (e.g., $N_2$). Other setups for samples preparation and/or first-order charaterization are currently in study in French laboratories with the aim to built a national network of experts in curation-related activities. At the international level, the CNME team will develop in-depth collaboration with other teams currently managing major curation centers in Europe and on a world-wide scale (see A. Hutzler et al this meeting).

The CNME will ensure the long-term curation of the MNHN historical meteorite collection that include a rich panel of Martian samples (Shergottites, Chassignites, Nakhlites) [17] and several emblematic primitive chondrites (e.g. Orgueil CI-chondrite). The MNHN meteorite collection is actively used for cosmochemistry research projects and is constantly growing with new additions every year, thanks to collections performed by a joint team from CEREGE and MNHN in Atacama Desert (see e.g. [14]). The CNME will also have the responsibility for the long-term curation of micrometeorite collections recovered from both Greenland and Antarctica [15] including the Concordia micrometeorites collection (currently in a dedicated curation cleanroom at IJCLab) that contains thousands of micrometeorites with minimal terrestrial weathering [16]. Beside these collections, CNME will also ensure the long-term curation of samples from the Chinese mission Chang'e5 recently donated to France.

In this presentation, I will summarize the general landscape of curation activities in France and present the current status of the CNME project.

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# Mars Sample Return: curation activities and planning.

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Curation of extra-terrestrial samples is a multifaceted process that aims to balance the conservation of a collection with its efficient use. Therefore, a robust curation plan will maximize the science conducted in the first years after sample return while ensuring a representative collection remains available to enable science for decades.

The Mars Sample Return (MSR) campaign, initiated in 2020 with the launch of the Perseverance Rover, represents an international collaboration between the United States National Aeronautics and Space Administration (NASA) and the European Space Agency (ESA) for the purpose of bringing Martian geological samples back to Earth for scientific investigations. This ambitious undertaking marks the first instance of sample return from another planet and the first return classified as Restricted since Apollo 14. The Restricted classification requires rigorous backward planetary protection requirements (BPP), which impacts how samples can be curated and analysed.

NASA and ESA have agreed to jointly proceed on science and curation and are in the formulation phase of the joint NASA/ESA Sample Receiving Project (SRP). After the sample arrive on earth and are transported to the Sample Receiving Facility, initial characterization begins. The aim on initial characterization is to generate a robust catalogue, which is a mandatory element to the allocation process. Sample requests for scientific research accomplished in the first years after sample return will be openly competed and jointly selected by ESA and NASA; this includes allocations for objective science completed within the SRP (first planned AO nominally in 2026) as well as opportunity science outside of the SRP. Proposals from a consortium of institutions proposing a coordinated analysis plan will be encouraged, to ensure efficiency and accountability.

While the Martian samples are expected to be back as soon as 2033, preparatory activities for protocols, hardware and infrastructure are underway. NASA and ESA have selected several working groups from the scientific community to advise on: 1) measurements to be conducted on the samples, 2) appropriate contamination control parameters, and 3) necessary requirements for handling and analysing the collection. Several curation and engineering teams in the United States and in Europe, coordinated by the NASA/ESA Joint Curation Office (JCO), are in close interaction with the NASA/ESA Joint Science Office and are working on developing hardware and strategies for the Sample Receiving Facility. The JCO is developing a curation plan following guidelines from the NASA NPR 7100.5 [1] (pending validation by NASA and ESA upcoming agreements).

The JCO is also considering long-term curation of the collection, separate from the SRP as part of their planning. It is expected that long-term curation might not require high-containment, and that while only one Sample Receiving Facility is planned, there might be several MSR curation facilities.

Latest updates on curation, science, and R&D planning will be shared, with an emphasis on synergies between the MSR curation team and the science community.

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# Mars Sample Return: Considerations for the Curation of Astromaterials from a Restricted Planet

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The joint NASA/ESA Mars Sample Return (MSR) campaign is underway. The Perseverance Rover has already collected a returnable sample suite currently cached at Three Forks and the pairs to these samples are stored on the Rover with more compelling samples planned to be collected. The MSR collection would represent the most geologically diverse astromaterial collection ever returned and should provide information on topics ranging from Martian geological and biological history to Martian environmental hazards and in situ resource utilization to support potential human exploration [1]. Although Jezero Crater and the surrounding area are not Mars special regions, the scientific opinion is that Mars as a whole is of significant interest to the process of chemical evolution and/or the origin of life. Therefore, due to possibility, however remote, that the samples could contain extraterrestrial life, MSR is classified as a Category V: Restricted Earth Return mission by the NASA Planetary Protection Office. As a result of this classification, a MSR Sample Receiving Facility (SRF) must not only provide a pristine environment to ensure samples are protected from terrestrial contamination for scientific investigations, but it must also provide high-containment to isolate the samples from Earth's biosphere until the samples are deemed safe for release and/or sterilized.

The SRF is first and foremost a curation facility, however it will be utilized for an array of tasks and scientific objectives, including:

- Receive the flight hardware containing the sample collection (e.g., Earth Entry System, Orbiting Sample)
- Deintegrate the sample tubes from the hardware and put in a stable state
- Characterize the sample tubes (Pre-Basic Characterization)
- Open the sample tubes (e.g., collect headspace gas, extract samples while maintain stratigraphy)
- Perform initial sample characterization and cataloging
- Conduct a sample safety assessment
- Execute preliminary examination of samples for science
- Enable select competed/early science
- Prepare, sterilize, and distribute samples for science outside of the SRF
- Sample isolation/storage

The SRF is not intended to be the long-term curation facility for Martian samples. The nominal utilization period for the SRF is anticipated to be 2-5 years. However, to account for possible delays in schedule or the identification of extant life, this anticipated period of time must be flexible to accommodate schedule extensions and contingency plans. Due to the high-containment requirements, a traditional receiving/curation facility cannot be utilized for MSR.

As a result of the complexity of designing, constructing, and operating a contamination-controlled high-containment facility, NASA initiated an assessment of current technologies. Personnel toured both contamination-controlled and high-containment facilities around the world, exploring the implementation of new technology and standard practices. The report, entitled: "Tours of High-Containment and Pristine Facilities in Support of Mars Sample Return (MSR) Sample Receiving Facility (SRF) Definition Studies" compiles the knowledge of experts in their fields and offers recommendations for the best path forward [2]. NASA and ESA have used this data, as well as outputs from numerous MSR science working groups, to perform the Mars SRF Assessment Study (MSAS) and the European Extraterrestrial Sample Infrastructure (EETSI) System Study.

While EETSI investigated the preliminary design, costs, and schedules for new, traditionally built fixed SRF and Sample Curation Facilities (SCF), MSAS was a scoping study, designed to assess the feasibly of utilizing traditional versus more novel infrastructure, specifically:

1. Lease and renovation of existing space
2. Construction of a new, traditional fixed facility
3. Construction of a modular facility (new or within an existing building)

4. Construction or renovation of a hybrid facility to address requirements with multiple modalities that may include a combination of modalities 1-3.

The assessment also considered the following aspects of the SRF for each modality:

- Ability to meet requirements
  - Regulatory
  - Planetary protection
  - Contamination control
  - Science and curation
- Ability to meet changing needs for equipment, timelines, and facility use
- Timelines for design, construction, commissioning, installation of equipment, testing, training, and operational readiness drills
- Cost for construction and operation, including those associated with hazard resilience
- Ease of access for international users
- Decommissioning, repurposing, sale, or lease following use of the facility
- Uncontained preparatory laboratory spaces
- Uncontained ancillary spaces
- Waste management

The outputs for MSAS and EETSI have been critical to understand the potential trades and identify priorities for the SRF. However, while options were able to be refined, a second phase (MSAS2) will develop high-concept designs at multiple locations in order to optimize the technical capabilities, cost, and schedule of the SRF. As part of the next steps in planning, the NASA/ESA Mars Sample Receiving Project (SRP) Joint Curation Office (JCO) is developing a curation plan following guidelines from the NASA NPR 7100.5 [3] and supporting the Measurement Definition Team (MDT). The MDT is chartered to evaluate the measurements and instrumentation needs for the SRF. Outputs from this team, as well as the Sample Safety Assessment Protocol (SSAP) Tiger Team, will be critical for SRF design. Upon completion of MSAS2, the SRF design concepts would be utilized to inform site-specific design but the location of the SRF will not be finalized until NASA's completion of the National Environmental Policy Act (NEPA) process.

Every sample return mission offers scientists and engineers unique challenges and opportunities, MSR is certainly not an exception. While differences in robotics and spacecraft are often apparent, differences in the approach for the curation of a given collection are usually more nuanced. NASA's Astromaterial Acquisition and Curation Office, and other international space agency partners, have developed strong foundations of best-practices and lessons learned. Although MSR represents the first Restricted Earth return in five decades, the knowledge gained from the development and operations of the Lunar Receiving Laboratory are informing the potential curation strategies for MSR. Whether the SRF is reutilized by NASA for another Restricted Earth return after the MSR samples are deemed safe or turned over to a partner for other types of high-containment work, the knowledge gained during technology development, SRF design, construction, and operations will lay the foundation for sample return missions for the next five decades.

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# Fostering future missions and curation: fine-particle simulant characterization for a lunar highland testbed (ESA, European Astronaut Centre - EAC)

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In the framework of the European Centre for Space Applications and Telecommunications (ECSAT), the UK site of the European Space Agency (ESA), the Vulcan Analogue Sample Facility is actively engaged in the establishment of a robust European network devoted to the acquisition, production, and management of extraterrestrial analogue samples (or simulants), both existing and prospective. The Vulcan Facility is primarily oriented towards advancing scientific inquiries into planetary analogues, encompassing celestial bodies such as the Moon and Mars. This pursuit is facilitated through the deployment of benchtop instrumentation for fundamental property analyses, and support for the curation of extraterrestrial materials and the development of associated technologies. European simulant priorities were determined following a user survey and simulant supplier workshop in 2022 (**Table 1**).

As part of supporting the European simulants network, Vulcan's role encompasses choosing the optimal fine-particle highland feedstock option for the ‘Dust Chamber’ [1] of the Luna Analogue Sample Facility in Cologne, Germany (EAC, ESA). The selection process entails a comprehensive exploration of the European network of simulant providers and both commercial and academic laboratories, entailing an exhaustive evaluation of the availability and logistical aspects of materials accessible in the market. This consideration encompasses critical factors such as loading times and associated costs. Furthermore, a rigorous assessment of simulant properties is conducted, including but not limited to particle size distribution, shape, and abrasivity. These parameters hold significant importance in the context of primary geotechnical and geomechanical objectives within the ‘Dust Chamber’.

Nonetheless, these deliberations serve to refine the pool of potential highland simulants obtainable in Europe. Ultimately, the most suitable simulant candidate will be meticulously chosen to facilitate comprehensive testing of geotechnical and engineering-related activities within the Dust Chamber. It comprises due diligence of the full simulant supply chain (including assessment of the source site, excavation and processing methods, and quality control). Consequently, discerning selection process aims to contribute substantively to the accumulation of essential knowledge, thus enhancing our readiness for the upcoming sample return and human lunar surface missions in this decade.

**Table 1.** Priority activities, among 36 simulant users surveyed in 2022 (35 European-based, 1 Japan-based), centring around exploration hardware and resource extraction studies. Red: 25-28%; Yellow: 11-16%; Green: 3-8%; Grey: No data.

| | Lunar | Martian | Asteroids / Meteorites | Other |
|---|---|---|---|---|
| Spacecraft, instruments and/or software | Red | Yellow | Green | Yellow |
| ISRU (Resource extraction) | Red | Green | Grey | Green |
| ISRU (Additive manufacturing) | Yellow | Green | Grey | Green |
| ISRU (Unspecified) | Green | Green | Grey | Green |
| Planetary Science Research | Green | Yellow | Green | Green |

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# Nanoscale infrared characterization (AFM-IR) of Ryugu samples returned by the Hayabusa-2 space mission


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The distribution of chemical bonds in organic matter (OM) of interplanetary samples (meteorites and micrometeorites) can be efficiently and non-destructively characterized using infrared vibrational spectroscopy (FTIR) [1]. Conventional FTIR microscopy provides a global view of the dust grain physico-chemical composition but remains spatially limited by the diffraction. In state-of-the-art synchrotron-based FTIR microscopy, the typical spot sizes in the mid-IR range can, at best, sample a few µm. This spatial resolution limitation often hampers a direct comparison with complementary techniques such as isotopic imaging with NanoSIMS, transmission electron or X-ray microscopy. Such IR diffraction limitation can be circumvented using AFM-IR microscopy [2]. AFM-IR is now a well-established microscopy technique in the vibrational field, combining an atomic force microscope (AFM) and a tunable IR illuminating source to detect photo-thermal effect and access chemical information. This technique is applied in a wide diversity of scientific fields [3] and we recently used it to analyze various extraterrestrial samples [4-8]. For this study the tunable IR illuminating source is a QCL laser with a spectral range from 1900 $cm^{-1}$ – 900 $cm^{-1}$ with a top-down illumination. This configuration allows two modes of acquisition. In the first one, the wavenumber is fixed and the tip moves along the surface, allowing to acquire simultaneously AFM topography and an IR absorption map of the sample at the selected wavenumber. In the second one, the tip position is fixed on a sample position and the IR laser is tuned to explore the whole available spectral range of the QCL laser, giving access to local IR spectra at the point of interest.

Ryugu samples from chamber A (surface) and chamber C (sub-surface) were received from the “IOM” and “Stone” Hayabusa2 initial analysis teams. Several samples from chambers A and C were prepared by crushing small fragments on diamond windows, down to a thickness of ~1 µm. Because of the high resolution of AFM-IR (tens of nanometers), regions of interest were first localized and selected using synchrotron-based FTIR microscopy [8].

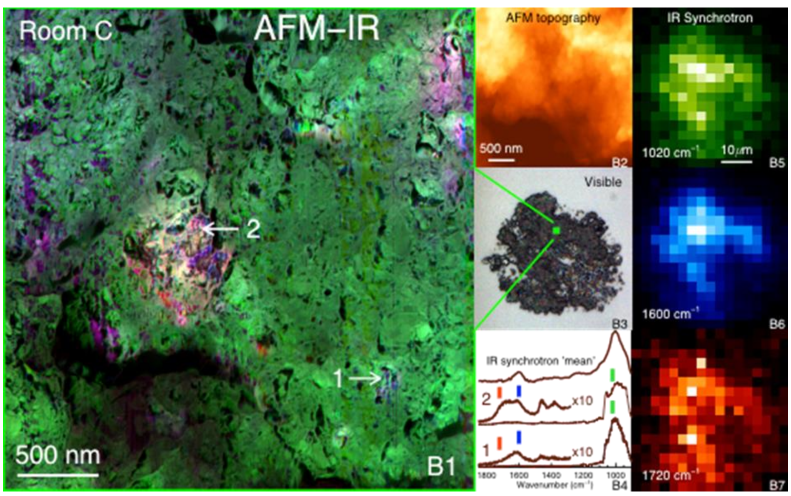


Figure 1: Study of chamber C sample C109-04. B1: 3 x 3 µm RGB composite image combining the AFM-IR absorption mapping obtained at different wavenumbers corresponding to the absorption of Si-O silicates (1020 $cm^{-1}$, green), C=C (1600 $cm^{-1}$, blue) and C=O (1720 $cm^{-1}$, red). The size of the image here corresponds to the size of one pixel in the synchrotron maps - B2: AFM topography of the 3 x 3 µm area studied in AFM-IR - B3: optical image - B4: from top to bottom : average IR synchrotron spectra obtained on the whole sample, local spectra obtained by AFM-IR highlighting the presence of OM with and without a C=O signature at 1720 $cm^{-1}$, on the locations highlighted by arrows in B1. The red, blue and green dashes indicate the wavenumber positions of the IR mapping with the same color - B5-B7: IR maps obtained by transmission synchrotron µFTIR at same wavenumber (and corresponding colors) as the AFM-IR maps. Adapted from [7]

A large-scale map (20 µm x 20 µm) was first recorded to characterize the main components' distribution within the sample with a spatial resolution of ~75 nm [8]. As the OM contribution in the IR spectra is weaker than that of minerals, highly spatially resolved maps of 3 x 3 µm in size were acquired with a lateral spatial resolution of ~25 nm. It was then possible to localize OM inclusions in the samples (Fig.1 – B1) by comparing the signal from the Si-O of the silicates (Fig. 1 – B1 in green) and that from the OM contributions of the C=C absorption (Fig. 1 – B1 in blue) and C=O absorption (Fig. 1 – B1 in red). On the larger OM inclusion displayed in Fig. 1 – B1, the OM signal is a mix between C=C and C=O (which appears in purple), but chemical heterogeneities are observed at small scales: parts of the inclusion seem to exhibit local enrichment in C=O (redder) or in C=C (bluer). Local AFM-IR spectra were recorded on these spots, showing locally different C=C and C=O contributions (Fig.1 – B4) [7].

Based on this first measurement, a more complete analysis of various samples was conducted either on whole-rock samples or on IOM extracted from chambers A and C samples [9]. The results obtained not only confirmed the heterogeneity of the OM distribution already observed but also highlight the fact that OM is mainly distributed in two phases, a diffuse organic component intimately mixed with the mineral matrix and nanoglobule-like organic particles (Fig. 2). These particles are texturally resembling nanoglobules present in primitive meteorites and were identified in both whole-rock and IOM samples from chambers A and C Ryugu samples. The local IR spectra of nanoglobule-like particles also clearly show enhanced carbonyl (C=O) and CH contributions with respect to the diffuse organic matter in Ryugu whole-rock and IOM residue (Fig. 2 – (c)). Such spectra are compatible with that of organic residues formed from UV or ion irradiated ices at low temperatures, simulating the environment of the outer regions of the protoplanetary disk, or in the protosolar cloud.

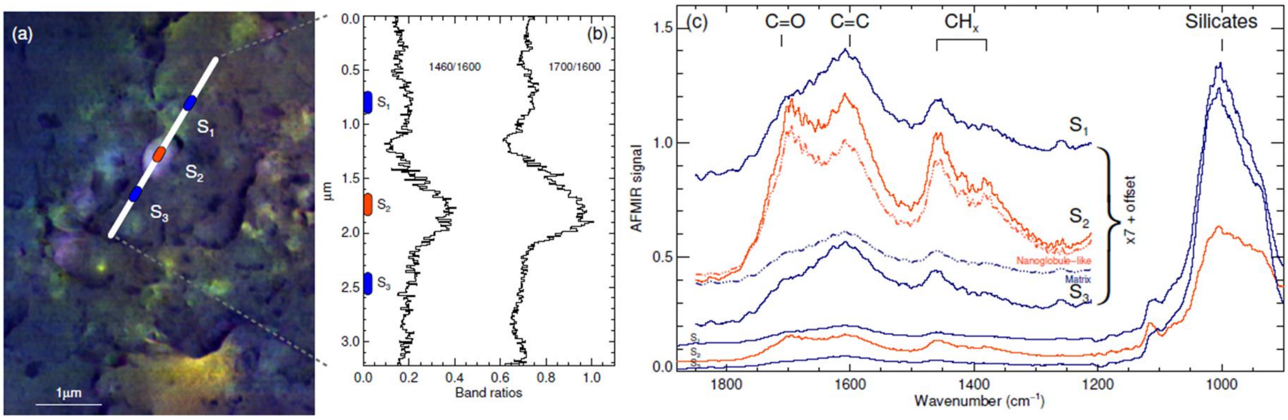


Figure 2: Whole-rock Ryugu sample A0108-19. (a) RGB image of the region including an organic nanoglobule-like particle (C=O at 1720 $cm^{-1}$ in red, C=C at 1600 $cm^{-1}$ in green, $CH_X$ at 1460 $cm^{-1}$ minus 1520 $cm^{-1}$ in blue). The white line shows the location of individual AFM-IR spectra taken across the nanoglobule-like feature. The colored dots (S1 to S3) correspond to average spectra taken on each side (S1 and S3 in blue) and on the nanoglobule-like feature (S2 in red). (b) Intensity ratios corresponding to $CH_X$/C=C (1460 $cm^{-1}$/1600 $cm^{-1}$) and C=O/C=C (1700 $cm^{-1}$/1600 $cm^{-1}$) along the white line shown in (a). The location of the S1 to S3 spectra is recalled on the left axis. (c) Average spectra on each side (blue, S1 and S3) and on the nanoglobule-like feature (red, S2). The red dot-dashed line spectrum labelled 'Nanoglobule-like' is obtained by scaling the average of S1 and S3 spectra to the same silicate band intensity as in the S2 spectra, and by subtracting this scaled spectrum from S2. The resulting 'Nanoglobule-like' spectrum is thus freed from the matrix contribution underneath the globule. The nanoglobule-like spectrum shows elevated $CH_X$ signal (intense methyl and methylene deformation modes at ~1460 $cm^{-1}$ and ~1370 $cm^{-1}$), as well as high carbonyl contributions around 1700 $cm^{-1}$. The blue dot-dashed line spectrum labelled 'Matrix' corresponds to the expected contribution from the matrix for equivalent probe depth as for the nanoglobule-like spectrum. Adapted from [9].

AFM-IR measurements demonstrate the presence of organic inclusions intimately mixed with minerals in Ryugu samples at the sub-micron scale. Focusing on the OM-rich zones of Ryugu samples it is possible to unveil, without any chemical treatment, the IR signature in the chemical bondings of chemical OM heterogeneities as well as the sub-micrometric spatial distribution of the different components. This study shows that OM exists in (at least) two forms in Ryugu samples, as a diffuse phase in the minerals matrix, and as isolated inclusions resembling nanoglobules.

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# Sampling and curation of volatile elements in the new era of sample return missions

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The scientific community has been entering a new era of sample return missions with the successful Hayabusa 1&2 (JAXA) and future OSIRIS-REx (NASA) missions, the future missions of samples return from Mars (Mars Sample Return mission, NASA and ESA) and its moon Phobos (MMX, JAXA). Other than their inner scientific values, sample return missions are of key scientific importance as they trigger the development of suites of state-of-the-art analytical techniques in terrestrial laboratories to conduct exhaustive characterization of the returned samples (petrography, mineralogy, chemical analyses etc.). Among these investigations, measuring the elemental and isotopic composition of volatile elements in extraterrestrial samples is a high priority scientific target as they can be used to understand the origin of planetary atmospheres and of water in terrestrial planets (*e.g.*, [1]). More broadly, such measurements could provide answers to the question: Why is the Earth habitable? Such investigations rely on the ability to conduct a proper curation of the samples containing volatile elements. A recent study highlighted the need for developing advanced curation techniques for volatile-rich samples [2] and a recent experiment developed by US-based scientists opened lunar core containers returned to Earth by the Apollo astronauts in order to sample volatile elements (see ref. 3). Developing new curation techniques is also one of the goals of the future curation center CENAME (a Center National for Extraterrestrial Materials) which will be built at the French Musée National d'Histoire Naturelle (MNHN, Paris, France) in collaboration with the Institut de physique du globe de Paris (IPGP, France) (see J. Duprat et al., *this meeting*). This is also one goal of the project MARCUS led by CNES (PI. C. Mustin) and which is part of the new French initiative PEPR Origins: from planets to life.

In 2019, the Hayabusa2 mission successfully sampled over 5 grams of solid samples from the surface and subsurface of the asteroid Ryugu. The preliminary scientific investigations revealed that Ryugu samples are similar to primitive carbonaceous material similar to Ivuna-type meteorites but with less alteration than identified in these meteorites [4]. Having pristine samples from carbon-rich asteroids also allows to put new constraints on the role of these bodies in the delivery of volatile elements to Earth [5]. Recent measurements of the D/H ratio of hydrogen contained in Ryugu samples revealed that carbonaceous-type material could have delivered up to 3% of Earth's water [6]. Importantly, the sealing technique adopted for closing the sample capsule consisted in an aluminum metal seal [7], maximizing the chances to retain extraterrestrial volatile-rich elements such as noble gases. A quick recovery of the sample capsule followed by careful onsite curation protocols [8] allowed to recover the gas originally contained in the sample capsule. Results obtained by a preliminary study reveal that, despite a certain degree of contamination by the Earth's atmosphere, the gas sampled during the mission is extraterrestrial with a clear contribution from solar-wind derived gases [9]. Investigations also revealed that the Al-seal partially re-opened during Earth's entry due to the strong deceleration when the parachute deployed.

The technical developments and sample handling protocols used before, during and after the return of samples by the Hayabusa2 mission are the best and most recent examples of advanced curation techniques for volatile-rich elements collected during space missions [8,9]. Therefore, they represent a reference starting point for improving the current curation protocols and developing new solutions. Ryugu samples are thus providing perfect opportunity to assess the quality of the current techniques of curation of volatile-rich extraterrestrial samples. In this presentation we will show how Hayabusa2 samples have the potential to provide key information on the state-of-the-art of curation techniques and possible improvements.
Gas samples from Ryugu allocated by the JAXA curation center will be delivered to IPGP in fall 2023. Noble gases (Ne, Ar, Kr and Xe) elemental and isotopic composition will be immediately measured in order to : i) evaluate if the different samples prepared by the curation team have the same composition (NT1 vs NT2 sample) ; ii) compare with published data (*e.g.*, [9]) for NT1 sample and evaluate if the composition of the gas has evolved since the preliminary investigations. Samples will then be stored in distinct conditions (closed and exposed to room pressure and temperature for one sample, closed and attached to a turbo molecular pumping station for another sample, closed and exposed to moderate vacuum for another sample). New measurements will then be conducted after 6-9 months to assess which storage conditions is the most appropriate. Results will be shared and discussed with the JAXA curation team the international community concerned on this aspect of the curation of extraterrestrial samples.

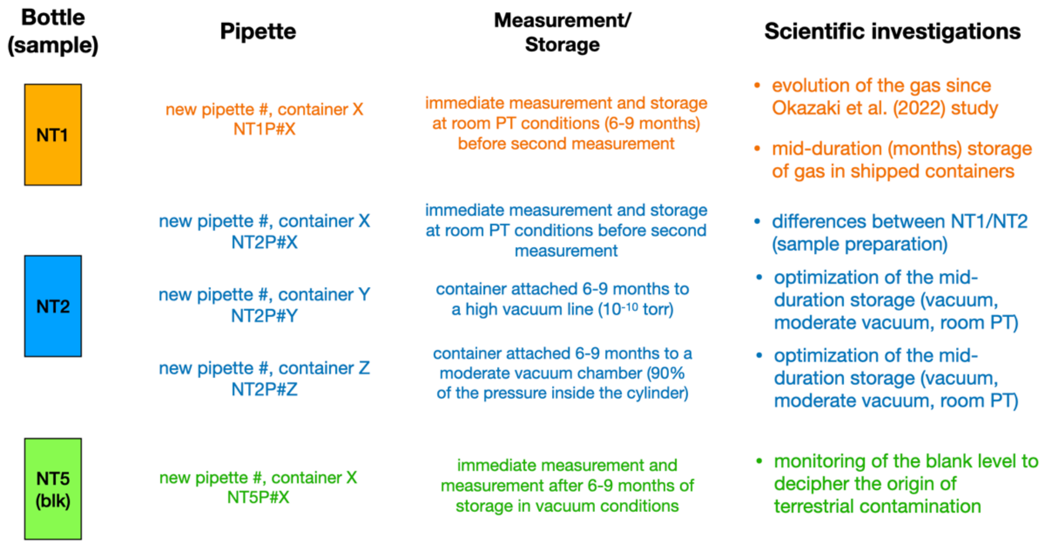


Figure 1: Summary of the sample allocated by the JAXA curation center. The original samples NT1, NT2 and NT5 (bottles, ref. 8) are identified as well as the three different pipettes to be drawn from the bottle by the JAXA curation team. Samples will be measured at different times and stored in different conditions to evaluate curation techniques.

In this presentation we will also describe future long-term developments for the curation of volatile-rich samples. One development will involve testing new materials for the sample containers (*e.g.*, TiN covered Titanium coupons used for the preparation of Perseverance sample tubes and gently provided by colleagues from JPL). We will also improve curation protocols (short- and long-term monitoring) and develop new solutions for vacuum containers.

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# Machine Learning Data Analyses for Asteroid and Micrometeorite Samples

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We have developed and trained Machine Learning (ML) convolutional network models on aerogel-captured meteoroid samples of the Tanpopo [1] missions onboard the International Space Station using new camera, recording, and processing techniques that greatly speed and automate their identification and classification. This technique moves beyond datasets that have already been laboriously centred, focused, scaled, imaged, and classified to various types by human researchers, and builds on prior systems [2] to open the door to automated transits by microscope across the Tanpopo aerogel panels at approximately 500x500 pixel increments, at different focal lengths, with images then fed directly into core ML Object Detection programme. The programme then uses its object detection/localisation capabilities to automatically draw bounding boxes around the object or objects of interest in each image, and to automatically run a confidence prediction of which classification of the types it might be, displayed both on the image and as a searchable table [3].

The time-and-manpower gains that can be affected by ML became clear with its further application to the Ryugu A0180 sample. Hundreds of nano-CT scans were conducted to create segmented images [4] whose cross-sections helped reveal characteristic micro-features within the sample such as voids, cracks, and micro-chondrules of particular interest. For an example, human-eye examination of void evidence and 3D distribution in cross-section allowed re-integration of the images to reveal the voids in full dimension. This manual process of identifying and classifying evidence of voids in cross-section is ripe for ML identification, classification, and reintegration using the methods we have developed. Moreover, the data gained by manual imaging of A0180 now forms a robust training data set for applying to more porous and aggregate samples such as unmelted micrometeorites collected in the terrestrial environment.

Thus, 3D optical images, nano-CT data, and external and internal SEM images of Ryugu asteroid samples returned by Hayabusa2 can be archived at international research institutions to create further training data for searching the diversity among different groups of asteroid samples and for practically comparing characteristic micro-structures with the wider suite of micrometeorite collections. In this manner, it may also be possible for the ML modelling to connect evidence found in the Ryugu samples to the potential underrepresentation of particular meteoritic constituents in terrestrial collections.

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# Characterization of Mg-Fe carbonates in the Ryugu returned samples with MicrOmega

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The Ryugu samples brought back by the Hayabusa2 spacecraft in December 2020 have been delivered to the JAXA Extraterrestrial Curation Center [1]. Bulk samples and then sub-bulks and individual grains have been picked up and stored into sapphire dishes, weighed, and analyzed with an optical microscope, FTIR spectroscopy, and MicrOmega hyperspectral imaging [2] for initial description within the curation facility [1]. 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 × 5 mm, with a resolution of ~22.5 µm/pixel in the focal plane. It covers the spectral domain from 0.99 µm to ~3.6 µm. Its capabilities enable the identification of organic matter and different minerals in the returned samples [3]. In particular, carbonates can be detected and characterized in the MicrOmega spectral domain primarily through a strong absorption band at 3.3-3.5 µm, together with shallower specific bands at 2.5 and 2.3 µm, and for some carbonates a large absorption band around 1 µm.

A recently published study [4] based on the analysis of MicrOmega data of ~180 extracted individual grains (a few mm in size) and 14 aggregate samples (all observed with MicrOmega within the Curation Center in 2021) has shown that carbonates are distributed in two main populations. Those populations are different in composition and size/morphology: most detections are made on small grains and inclusions (<100 µm large) with a spectrum similar to dolomite $CaMg(CO_3)_2$, while for the largest detections, although less numerous, spectra similar to breunnerite $(Mg,Fe)CO_3$ dominate.

Dolomite is present in many grains as inclusions, and in many aggregate samples, and many occurrences have been reported in recently published studies analyzing some grains in detail [e.g., 5-11]. Breunnerite occurrences have been listed only in studies accessing a larger volume of samples [e.g., 10-13]. However, the large size of breunnerite occurrences [4] makes them a significant component of the returned Ryugu material, showing that it is important to understand when and how they formed compared to the dolomite, and what was the source of Fe and C for this population of carbonates.

The largest breunnerite inclusion was found 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" described in [5]. This carbonate inclusion shows a complex morphology with three branches, 100s µm long, around a main area, that could point to a formation in a fracture or between grains. In addition, several detached grains of breunnerite, 100s µm long, have been detected in several aggregate samples, indicating possibly many other large inclusions from which those grains were separated.

MicrOmega did not detect any obvious spatial transition from dolomite to breunnerite within a carbonate detection at the surface of grains, which would have indicated a possible gradient during a single formation event, although one observation of dolomite in contact with breunnerite has been made through SEM observations [10]. To better understand formation processes, we are investigating spatial heterogeneity of carbonate composition with a more systematic technique at small scale (few 10s µm) in the MicrOmega data to check for gradients in Mg or Fe content for example: to achieve this, we check for shifts in NIR absorption band positions and shapes at the MicrOmega pixel level. We have also succeeded in extracting one loose grain of breunnerite (in collaboration with the Phase 2 curation Kochi team) and studying it with different techniques (imaging IR spectroscopy, Raman spectroscopy, EDS) that will enable us to check for heterogeneities in carbonate composition of the grain or the presence of other minerals or molecules within the grain at a smaller scale (<10 µm).

The two main populations of carbonates question the formation process or processes that occurred on Ryugu's parent body/bodies, and their respective age of formation. To our knowledge, only one attempt of Ryugu's breunnerite dating has been published so far [6] that does not conclude on a noticeable difference in age of formation between breunnerite and dolomite. More studies of breunnerite occurrences are required to better constrain their age, formation, and carbon sources.

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# Heterogeneity of Ryugu samples due to space weathering effects: near-infrared spectroscopy and fitting analysis

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## Introduction

Hayabusa2 brought back about 5.4 g of Ryugu samples (chamber A: surface samples, chamber C: excavated samples) from the C-type asteroid Ryugu in 2020, and the initial description of the returned samples is ongoing at the Curation Center of the Institute of Space and Astronautical Science (ISAS), JAXA [1][2]. In the initial description, measurements with a near-infrared hyperspectral microscope MicrOmega and spectral analysis are ongoing, and we have developed a fitting analysis method for the asymmetric absorption bands [3].

MicrOmega is a near-infrared hyperspectral microscope developed by the Institut d'Astrophysique Spatiale (IAS) in France, characterized by its ability to acquire spectral data over an area of approximately 5 mm square with a resolution of 22.5 μm/pix at 0.99-3.65 μm [4]. The measurement results to date have indicated a relatively deep absorption band at 2.7 μm which is thought to originate from the OH group and a slope around 2.0 μm, as common features of most of the Ryugu samples [2].

## Methods

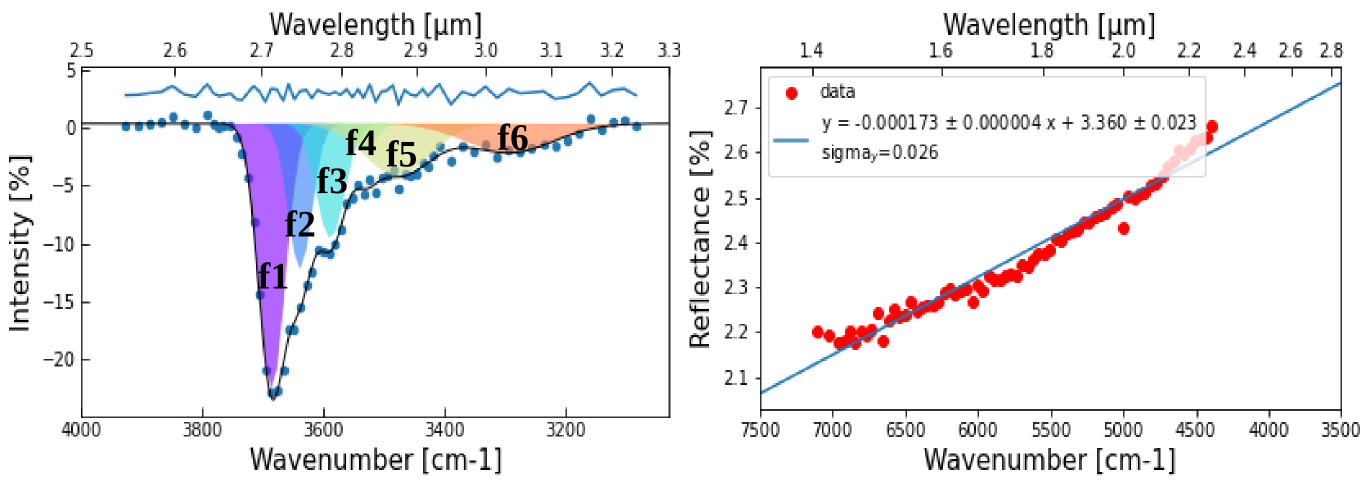
In our previous work [3], we developed a fitting analysis method with four Gaussian functions to achieve a more physically accurate analysis for the characteristic 2.7 μm asymmetric absorption band of Ryugu samples. In this study, we applied a fitting analysis with six Gaussian functions after applying baseline estimation and smoothing where necessary [5]. We also applied a fitting analysis with linear functions to the slope around 2.0 μm, which is a characteristic of Ryugu samples, to determine the magnitude of the slope [6].

The spectroscopic data were used in the MicrOmega-Curation DARTS Server (chamber A: 95 spectra, chamber C: 62 spectra).

## Results

The results of the fitting analysis are shown in Figure 1 (left) with each Gaussian function, composite waveform, and residuals for the asymmetric absorption band of Ryugu sample A0007 at 2.7 μm. Each of the six Gaussian functions is named f1 to f6 from the short wavelength side, where their peak wavelengths are f1: 2.713 μm, f2: 2.748 μm, f3: 2.786 μm, f4: 2.831 μm, f5: 2.874 μm, and f6: 3.036 μm, respectively.

The results of the fitting analysis using linear functions are shown in Figure 1 (right) for the slope around 2.0 μm.




[Figure 1: Results of fitting analysis of spectral data measured by MicrOmega with Ryugu sample A0007 (left: fitting analysis by six Gaussian functions for the asymmetric absorption band at 2.7 μm, right: fitting analysis by linear functions for the slope around 2.0 μm)]

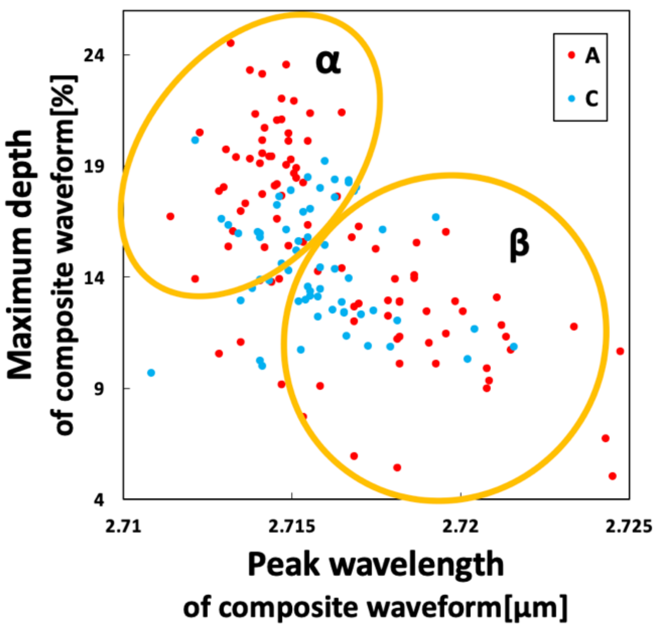
**Discussion**

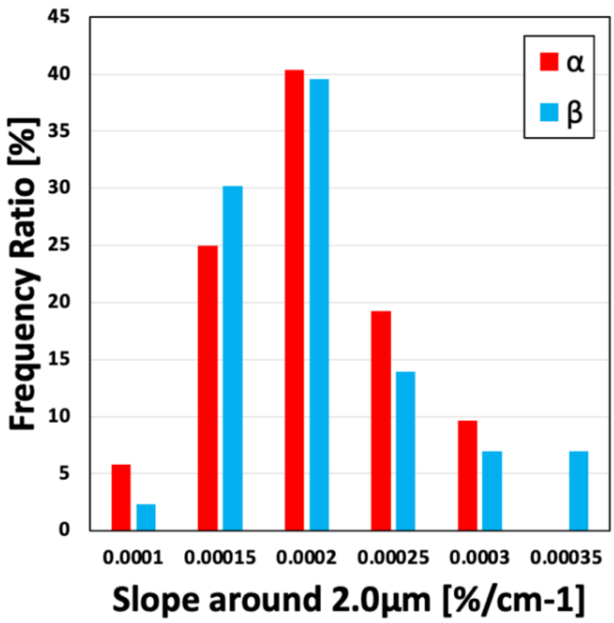
The relationship between peak wavelength and depth of the 2.7 μm absorption band (Figure 2 left) shows that the chamber A sample is split into two groups: α, with a shorter peak wavelength and greater depth, and β, with a longer peak wavelength and smaller depth. In contrast, the chamber C sample does not exhibit a clear tendency for such division into two. This dichotomous distribution for the chamber A sample is also present for f1, f2, and f4. Therefore, f1, f2, and f4 are considered to be derived from the same functional OH group. On the other hand, f3, f5, and f6, which do not exhibit dichotomous distribution in the chamber A sample, may be derived from carbonate, carbonyl, and NH groups, respectively, based on the position of the peak wavelengths [2][4][8].

Based on the results of the slope analysis around 2.0 μm, β tends to have a larger absolute value of slope than α, despite within the standard error range, as shown in Figure 2 right (α: $(1.79 \pm 0.501) \times 10^{-4}$ [%/cm$^{-1}$], β: $(1.84 \pm 0.576) \times 10^{-4}$ [%/cm$^{-1}$], C: $(1.81 \pm 0.496) \times 10^{-4}$ [%/cm$^{-1}$]). Since the slope of the spectrum is considered to reflect the effect of space weathering, β may be affected by greater space weathering than α [9].

Therefore, in the relationship between peak wavelength and depth in the 2.7 μm absorption band (Figure 2 left), the longer wavelength and smaller depth of the peak position for β compared to α may be due to the greater effect of bond scission related to the OH group caused by space weathering.

In summary, the Ryugu return samples that were measured by MicrOmega were classified into three major groups: α and β in chamber A, and C in chamber C. Also, each of them is considered to be affected by greater space weathering in the order of α < C < β, respectively.




[Figure 2: Left: Relationship between peak wavelength and depth of the composite waveform in the 2.7 μm absorption band, right: slope magnitude around 2.0 μm (chamber A sample: α and β only) versus Frequency ratio]

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# NH-rich grains detected by MicrOmega in the Ryugu returned samples

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NH-rich compounds have been reported on Ceres [1, 2], Comet 67P [3, 4], and other primitive asteroids [5, 6] thanks to NIR observations. The proposed compositions include ammonium salts, ammoniated phyllosilicates, and ammonia-bearing organics. Investigating their composition and relation with other components can tell us information on how they were formed, what was the environment, and may also indicate the transfer of some volatiles in the Solar System. Similarly, NIR observations of the Ryugu samples obtained at the millimeter scale showed that they exhibit a ~3.06 µm shallow feature that was tentatively attributed to NH-rich compounds that would be present at a small scale and spread over the collection [7, 8]. However, one grain (a few hundred microns in size) exhibited a much stronger ~3.06 µm feature, coupled with additional features such as ~3.24 µm and ~2.72 µm bands [7]. Its reflectance (~10%) was also much higher than that of the typical matrix (2-3%). Here we report on our latest analyses to identify grains/inclusions with similar properties (both showing 2.7 µm and 3.06 µm absorptions).

MicrOmega is an infrared hyperspectral microscope installed inside the Hayabusa2 Curation Facility. It covers the spectral range 0.99-3.65 µm with a pixel size of ~22.5×22.5 µm², and a total field of view covering ~5×5 mm². From 2021 to July 2023, MicrOmega has measured almost half (in weight) of the Ryugu returned samples in the form of aggregates (~50) (small subsets extracted from the bulks, a few tens of mg each) and individual (mm-sized) grains (>500). Here we focus on the aggregate samples, which give access to a large number of grains spread as a thin layer in the sample holders. We use the average spectrum of the grain from the first NH-rich detection in [7] as a reference. After removing the continuum from 2.5 to 3.2 µm, we calculate the similarities between the reference spectrum and spectra from each pixel, then select the enriched regions with high similarity (strong 3.06 µm and 2.7 µm bands) and check for consistency at different orientations to avoid biases.

The detections of such areas are quite rare: among all the aggregate samples, we have detected 10 regions of interest (ROIs). The reflectance of the ROIs is generally higher than that of the surrounding material, mostly ranging from ~5% to ~10% but can be up to 15%. The size of the ROIs varies from ~100 µm to ~400 µm, their shape can be from relatively rounded to elongated. Figure 1 shows an RGB image (R 2.01 µm, G 2.72 µm, B 3.45 µm) of an aggregate sample, the pink color area is the ROI, and its average spectrum shows very strong 2.7 µm absorption (~50%) and 3.06 µm feature (~10%). We will report on the spectral heterogeneity within the ROIs at pixel scale and between different ROIs, in particular their variations in band position, depth, and shape. Since most of the ROI are present as inclusions instead of isolated grains, we will also present their relationship with the surrounding materials.

Such detections highlight the presence of a few particular grains in the Ryugu returned samples that may contribute to understanding the origin and evolution of the N-bearing material in Ryugu's parent body.

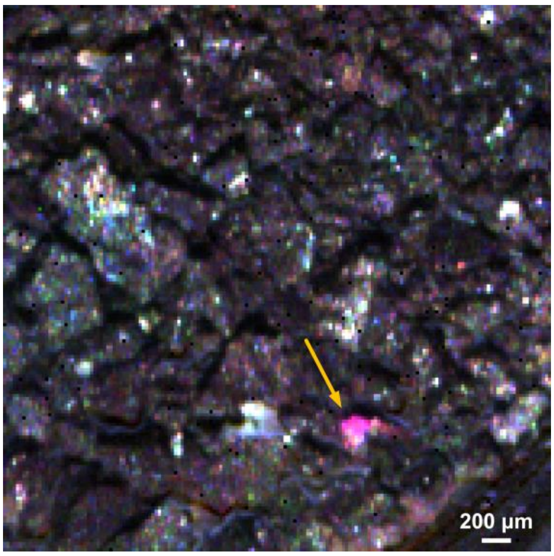


Figure 1. RGB image of an aggregate-sample (Sample ID: A0481). R 2.01 µm, G 2.72 µm, B 3.45 µm. The pink region pointed by the yellow arrow is the NH-rich ROI.

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## Nanoscale spectroscopic and microscopic investigation of Ryugu samples

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Carbonaceous asteroids are leftover materials from the early solar system. Having escaped harsh planetary processes, they provide clues to understanding the planet formation processes as well as the origin and evolution of the early solar system. The Hayabusa2 spacecraft returned the first samples from the carbonaceous asteroid Ryugu [1,2]. In addition to abundant phyllosilicates (~64–88 vol%;), carbonates, sulfides, and magnetite [3], the returned samples provide uncontaminated pristine organic compositions Macromolecular insoluble [4] and soluble organic matter as well as presolar silicate grains [6,7] have been reported in the Ryugu particles. Extraterrestrial organic matter is typically submicron in size (50-500 nm), and most organic compounds are even smaller [8,9]. Conventional IR methods fail to detect spectral signatures of nanoscale organic matter in extraterrestrial samples because of their insufficient spatial resolutions and other technical limitations.

In this study, we investigated the mineralogy and organic matter content of two Ryugu particles, A0030 (from TD1, chamber A) and C0034 (from TD2, Chamber C), using scattering-type near-field optical microscopy (s-SNOM)-based nanoscale Fourier transform infrared (nano-FTIR) spectroscopy, pseudoheterodyne (PsHet) nanoscale imaging, micro-Raman spectroscopic imaging, and synchrotron-based X-ray microprobe analyses.

Our results show that the two Ryugu particles contain different silicate minerals and organic-rich compositions. The spatial distributions of chemical functional groups and their relations with other components also differ in the studied Ryugu particles. Our results indicate various stages of aqueous alteration and thermal metamorphism processes for Ryugu. The identification of abundant nanoscale organic molecules within the Ryugu grains that could not be identified via micrometer-scale investigations emphasizes the importance of using nanoscale nondestructive methods for studying primitive solar system materials, such as Ryugu particles and those that will be returned soon (such as OSIRIS-REx and MMX samples).

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# Spectroscopic Evidence of Parent Body Aqueous Alteration on Ryugu Sample A0112

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The Japanese Hayabusa2 sample return mission successfully retrieved fragments from the near-Earth C-type carbonaceous asteroid Ryugu (162173). These fragments share similarities in composition with the Ivuna meteorite, indicating a potential classification as a primitive CI-type asteroid [1]. Among the collected samples, the piece A0112 was sent for spectral analyses at the Planetary Spectroscopy Laboratories (PSL) at the German Aerospace Center (DLR) in Berlin.
The A0112 piece is a relatively large sample collected from the first touchdown site [1]: it weighs 5,1 mg and is 3046x1823 µm in size. The sample was contained in a nitrogen-filled sample holder, free of any form of terrestrial contamination after its retrieval from the asteroid. In order to preserve the sample from external contamination, such as the atmosphere, the first set of analyses were performed with the grain sealed within its sample holder. These analyses employed micro-infrared spectroscopy and Raman micro-spectroscopy. In addition, High-resolution 3D images were taken of multiple sides of the grain with the digital microscope Keyence VHX-7000 and VHX-7100 observation system, which allowed a global view of its surface morphology and topography. This approach enabled the determination of the sample's bulk composition and mineralogy beneath the glass without being influenced by terrestrial alteration.
More than 50 point-localized infrared spectroscopy measurements were performed on the A0112 grain with the Hyperspectral Bruker Hyperion 2000 MicroFTIR to assess the general mineralogy of the fragment through the glass window of the sample holder. MIR (1.3 – 5 µm) reflectance point measurements consisted of 1000-2000 scans at an optical magnification of 15x and a resolution of 4 $cm^{-1}$. VNIR reflectance spectra were also taken to cover the full spectral range. Raman spectroscopy under neutral atmosphere with the WiTec Alpha 300 confocal Raman microscope [2] was used for organic matter and mineral identification, and to generate elemental maps of the grain.
Through the use of FTIR spectrometers (three identical Bruker Vertex 80V) and a special manufactured sample holder it was possible to measure bi-directional reflectance bulk sample spectroscopy of sample A0112 completely under vacuum in the whole spectral range from UV to FIR (0.25 µm to at least 25 µm spectral range).
From the processed images, the sample can be described as a mostly dark fragment with a few micron-sized, bright inclusions on most of its faces. Micro-FTIR measurements revealed an abundant presence of secondary minerals such as phyllosilicates throughout the sample, with a localized area of approximately 30 µm rich in carbonates. This carbonate-rich region was identified as dolomite due to specific absorbance bands at wavelengths of 1.90, 2.21, 2.73, and 4.4 µm, as well as two distinctive sets of doublets at 3.33, 3.47 µm and 3.81, 3.95 µm [1, 3]. Raman spectroscopy measurements also confirmed the presence of dolomite with spectral bands at 175, 300, 727, and 1098 cm-1. This dolomite inclusion appears to be associated with a vein in the grain. The investigation of hydrated minerals formed through aqueous alteration on the parent body provides valuable insights into the evolution of materials characterizing Ryugu and the protoplanetary disk. The presence of carbonates is particularly significant, suggesting the presence of liquid water within the asteroid, which could potentially play a role in delivering water to Earth or other planets [4]. Furthermore, these results confirm that in-situ point measurements, to localize hydrated minerals and organic matter, are still achievable through the glass window of a sample holder.
The identification of carbonates in the sample provides significant evidence of aqueous alteration processes that occurred on Ryugu's parent body.

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# Nitrogen, neon, and argon analysis of a single Ryugu grain by step-heating

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**Introduction:** Carbonaceous chondrites are primitive, volatile-rich meteorites, considered to originate from C-type asteroids, which may have contributed to Earth's volatile budget. Studying these objects is key to understand the origin of Earth's volatiles, but terrestrial weathering makes it difficult to distinguish between primary and secondary features. In December 2020, JAXA's Hayabusa2 mission returned to Earth 5.4 g of regolith collected on the C-type asteroid (162173) Ryugu, permitting the analysis of material not altered by terrestrial weathering [1]. The first analyses of noble gases and nitrogen were performed by the 'initial analysis volatile team' [2-3], providing key information about Ryugu, especially its formation, composition, and alteration history. Noble gases were found to be mainly of primordial and presolar origin, with variable contributions from solar wind and cosmogenic components. Nitrogen was present in lower abundances (700 to 900 ppm [2-3]) than in typical CI chondrites, with $\delta^{15}N$ values ranging from 0.0±0.4 ‰ [2] up to +43±4 ‰ [4], indicating sample heterogeneity and the presence of at least two carrier phases: a N-rich phase with $\delta^{15}N$ up to +70 ‰ and a N-depleted phase with $\delta^{15}N$ near 0 ‰.

**Sample and experimental method:** For this study, we targeted grain A-0164 (2.6 mg), which was sampled during the first touchdown on the asteroid and corresponds to surface material. The grain was analyzed at the Centre de Recherches Pétrographiques et Géochimiques (CRPG, Nancy, France) by step-heating with a $CO_2$ laser. By performing a large number of extraction steps, various components of nitrogen and noble gases, carried by different phases, can be distinguished. A total of 85 heating steps were performed at increasing laser power to successively analyze the different phases carrying nitrogen and noble gases. Nitrogen, neon, and argon abundances and isotope ratios were analyzed at each step using a Nu Instruments Noblesse HR mass spectrometer, a state-of-the-art instrument for multi-collection, high-precision, static-vacuum analysis.

**Preliminary results:**

*Noble gases*. Neon was mainly released at low temperature steps, whereas Ar was extracted over a wide temperature range. The sample presents a mainly solar wind-like isotopic composition for noble gases, as shown for neon in Figure 1. Step heating allowed us to identify other components, including primordial and presolar components (possibly phase Q and/or HL), as well as a minor cosmogenic contribution.

*Nitrogen.* Nitrogen is present in higher abundance (1219±113 ppm) than in previous studies, with a bulk $\delta^{15}N$ value of +24.4±0.1 ‰, with significant variations during successive extractions (+1.0±1.0 ‰ to +65.8±1.1 ‰), pointing to the presence of at least four N-carrier phases.

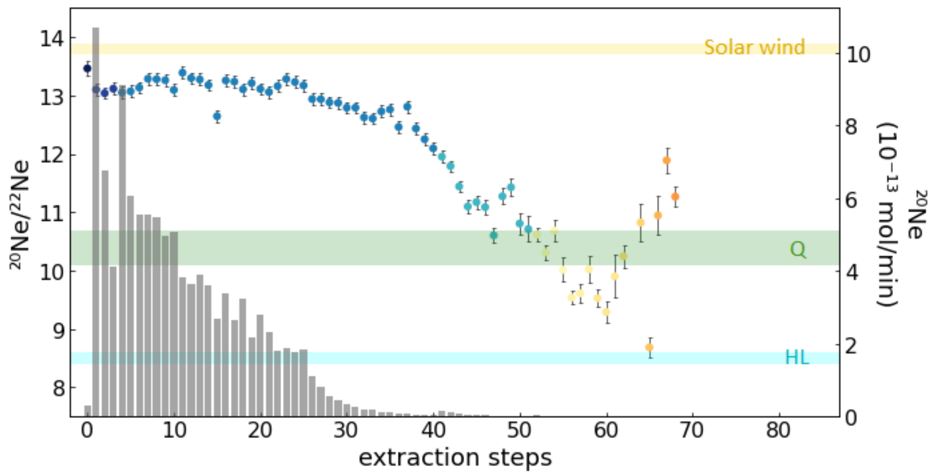


Figure 1. Ne ($^{20}Ne/^{22}Ne$) isotope ratio (colored circles) and $^{20}Ne$ abundance (gray histogram) measured for each of the 85 extraction steps at increasing laser power. The Ne isotopic compositions of the solar wind, Phase Q, and Ne-HL are shown for comparison.

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**Chemical composition and variability of Ryugu samples, CI chondrites and Kainsaz assessed by quadrupole ICP-MS analyses**

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*Introduction.* The similar relative abundances of non-atmophile elements between the Sun and rare CI chondrites suggest that CI chondrites represent the most primordial meteorites available for laboratory analyses. Samples returned from asteroid Ryugu by the Japanese Hayabusa2 mission resemble CI chondrites, were not altered on Earth, but affected by aqueous alteration [1-4].

This study aims to provide additional data on the elemental compositions and variabilities and representative sample masses for CI chondrites, Ryugu and the Kainsaz CO3 chondrite.

*Samples.* Data was obtained for five ~3 mg Ryugu samples from chamber A (1st touchdown), seven ~3 mg chips and 3, 4 and 50 mg bulk powder samples from the Kainsaz CO3 chondrite and ~50 mg powder aliquots from the CI chondrites Ivuna (2 x), Orgueil (3 x) and Y-980115. For quality control, Allende Smithsonian reference powder, JB-2, BHVO-2 and ~3 mg powder test samples from Allende, Ivuna, JB-2 as well as a Perkin Elmer multi element solution were analyzed.

*Methods.* The ~3 mg samples were digested in HF-$HNO_3$ at hotplates. The Ryugu samples and 5 out of 7 chips from Kainsaz were not ground before digestion to avoid material loss. Most 50 mg samples were digested in Parr pressure digestion vessels. Methods for quadrupole ICP-MS analyses and data evaluation are given in [5]. Samples were 4000-fold diluted and Rh and Re were used as internal standards. Most elements were determined in kinetic energy discrimination mode using He as a cell gas with CeO/Ce ~ 0.4%. (1.7% in standard mode). For each sample set, three to seven measurement sessions were run. Outliers were removed if > 4 sd and Ta data was rejected from four sessions that yielded unusual low Ta values. Four-point matrix matched calibration [5, 6] yielded a median correlation coefficient of 0.9999 as calculated from all elements and sessions. Repeatability judged from 121 analyses of Ivuna was 3.2% on average with Mn, Co, Cu, Rb, Y, Sr, Pb < 1.5% and 23% for Be being the worst case. In order to rigorously control blank contributions, seven blanks each were prepared along with the Ryugu and Kainsaz samples and four blanks with the 50 mg CI chondrite samples. Median blanks were subtracted. Maximum blanks for ~3 mg samples were: Ryugu and Ivuna: As, Sn and Sb 2 to 6%; Nb 10%; W 16%; Mo 29%; Kainsaz: Zn, As, Cd and Sn <3%; W 15%; JB-2: Zn, Nb, Sn and W 5 to 6 %; Mo 35%.

*Results.* Most CI chondrite, Allende Smithsonian, JB-2, BHVO-2 and Perkin Elmer solution data agrees within 10 to 20% with reference data [e.g., 7-13]. However, due to problems related to the calibration solutions (as observed in [6]), Sr, Mo, Sb, Ho, Ta, W and Bi are systematically too low. For the basalt reference samples, S, Se, Ag, Ir and Pt were not quantified and Ti, Cr, Ni, Te and As are off by about 20 to 60%. Except for U in Ivuna, results for 3 mg test samples agreed with results for the corresponding 50 mg samples to within better than 10% or within 10 to 20% for Se, Ag, Te (Ivuna), S, Ag, Ir, Pt (Allende) and As and Bi for JB-2 (S, Se, Ag, Ir and Pt not quantified in basalt reference materials). Three mg chips from Kainsaz display some heterogeneity and scatter around the data for the 50 mg bulk sample. However, the 50 mg bulk sample and 3 and 4 mg aliquots from the same powder display fractionated REE. The REE Kainsaz data shows that nugget effects in chondrites can affect larger samples more significantly than small mg samples. The Kainsaz 3 mg chip data displays reproducible, sometimes large enrichments in As, Sb and Pb of unknown origin.

*Discussion.* Ivuna and Mg normalized data reveal the following: Many elements in CI chondrites agree within ~2 %. Two out of three Orgueil samples display 20 to 50% enrichments in some refractory elements, most notably Zr, Hf, Th and Ba while Y-980115 is depleted in Cd, In, Tl and Bi as observed previously [5]. One Ryugu sample matches the CI chondrite REE pattern, the other four samples are enriched in light over heavy REE with variable REE/Mg. Two Ryugu samples are clearly enriched in Ca and Sr, one in Mn and Fe. Only one out of five Ryugu samples displays contamination of Ta from the projectile. Overall, the 3 mg Ryugu samples from chamber A display a clear CI chondrite affinity, but their chemical compositions are obviously affected by aqueous alteration as previously observed. For CI chondrites, Kainsaz and Ryugu, we estimated the representative sample mass needed to obtain elemental abundances to within 5% at the 95% confidence level, using the formula given in [10]: Representative sample mass = test portion mass * (standard deviation / (mean * standard error of the mean))$^2$ * student-t distribution factor.

For CI chondrites (n=4), the median representative sample mass corresponds to 452 mg; for ten elements, including Na, Zr, Hf, Ba, La, Ce and U, the representative sample mass was above 1 g. For Kainsaz, the median representative sample mass equals 74 mg and is above 1 g for S, As, Cd, Sb, Cs and Pb only. The median representative sample mass calculated for Ryugu corresponds to 99 mg with Mn, Ca and P being the least homogeneous elements with calculated representative sample masses of about 300, 400 and 500 mg. A complete table can be obtained from the author.

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# The Mineralogy of Asteroid Ryugu and its Relationship to Highly Altered Extraterrestrial Materials

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The Hayabusa2 mission returned to Earth with ~5.4 g of material collected from two sites on the surface of the Cb-type asteroid (162173) Ryugu [e.g., 1]. In hand specimen, Ryugu particles are dark, often highly friable, and have bulk densities in the range of ~1.2 – 1.8 gcm$^{-3}$ [2–4]. Most Ryugu particles examined to date are breccias consisting of an abundant (~80 – 90 vol.%) fine-grained (<1 μm) matrix of phyllosilicates (interlayered serpentine and saponite) in which coarser (~10's – 100's μm in size) grains, fragments, and clusters of oxides (~4 vol.%), sulphides (~3 vol.%), carbonates (~3 vol.%), and phosphates (<1 vol.%) are embedded [2–6]. Several CAI-like fragments (<30 μm) have been identified, as have small (<10 μm), rounded objects with characteristics, such as barred textures, related to melting and crystallisation in chondrules [e.g., 4, 7]. The mineralogy, petrography, and physical properties of Ryugu particles are consistent with them being having formed through near-complete, low temperature (<50°C) water-rock reactions during the first few million years of the Solar System [2–6].

If samples of Ryugu were to land on Earth as meteorites, we could classify them as petrologic type 1 [8]. Such materials were completely altered to secondary mineral assemblages by aqueous processing and contain various phyllosilicates, carbonates, sulphides, and magnetite. Type 1 materials are represented in four meteorite groups (CI, CM, CR, and CY), a handful of ungrouped chondrites (e.g., Flensburg [9]), as xenoliths within meteorites [e.g., 10], and as fine-grained micrometeorites [e.g., 11] and interplanetary dust particles (IDPs) [e.g., 12]. The mineralogy and chemistry of Ryugu particles are closely related to the CI1 ("Ivuna-like") carbonaceous chondrites, except for the presence of sulphates and ferrihydrite in the latter, which are most likely terrestrial weathering products [13, 14]. However, type 1 samples exhibit a remarkably high diversity of starting materials and alteration conditions, with variations in mineralogy, textures, and oxygen isotopic compositions pointing towards multiple parent bodies. Despite type 1 materials being relatively rare in our collections, in part due to their fragile nature hindering survival during atmospheric entry, highly altered bodies appear to be common throughout the Solar System. These bodies could include primitive asteroids that accreted within the inner and/or outer Solar System, or transition objects such as Main Belt comets or D-type asteroids. Characterising the sources of type 1 materials through laboratory analysis of meteorites and Ryugu particles is therefore an important step towards understanding volatile reservoirs in the early Solar System.

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