

## The samples recoveries from the Hayabusa sample catcher in the past and the future

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### Introduction:

Hayabusa spacecraft returned the first regolith samples from S-type near Earth asteroid 25143 Itokawa in 2010 [1, 2]. It had tried touchdown sampling twice on the largest smooth terrain called Muses Sea regio of the asteroid, although it did not shoot a Ta bullet to excavate its surface at that time [3]. After returning the recovered samples, they have been extracted from a sample container, handpicked one by one, analyzed with an FE-SEM/EDS for identification, and given ID [4]. Note that the samples have not been exposed to the atmosphere, handled in purified N<sub>2</sub> condition and analyzed in low vacuum condition. Here, we describe detail of processes and results of the sample extraction we did and also mention to their future plan and lessons learned from Hayabusa.

### Sample extraction methods from the sample catcher:

The returned samples were situated inside a sample catcher in the sample container. The sample catcher is composed of room A and B (RA and RB) and rotational cylinder (RC) (Fig. 1). Those recovered by the first touchdown should be captured inside the RB, and the second one inside the RA, and both of them should be left inside the RC because it was a passage to both the RA and the RB. So far, samples inside them were extracted by four methods, partially described in [4]. At first, the particles inside the RA were directly handpicked with an electrostatically controlled micromanipulator, although it was so inefficient because of its uneven inner structure (Fig. 1). The next, a specially designed Teflon spatula was used for sample recovery from the RA to be scooped its inner surface and analyzed directly with the FE-SEM/EDS [2]. It was successful in recovering small particles inside the RA, although it was difficult to release them from the spatula because they were stuck to its surface made of Teflon tightly. The third method we tried was to put a quartz glass disk to the opening of the room of the catcher, turn upside down and tap it on its outside in order to let particles inside fall onto the disk. After the tapping, we reversed it to recover the disk by tweezers and place it in a quartz petri dish. We performed this method once for both RA and RB, and also recover the cover of RB, an original part of the catcher, in the same way. Then the particles on the disks were handpicked one by one with the micromanipulator to be analyzed with the FE-SEM/EDS for their initial descriptions. Practically, most of the samples distributed to preliminary examination, NASA and international announcement of opportunity (AO) have been recovered with this method. The total number of those described for RA and RB count up more than 700, and almost 200 particles have been distributed for 51 accepted research proposals in four times of international AOs.

Recently, we developed a metal disk for the sample recovery from the RC. The concept is basically same as the quartz disks, but a good thing about it is to be able to let the disk stay in the upright position, never turn it upside down in the recovery

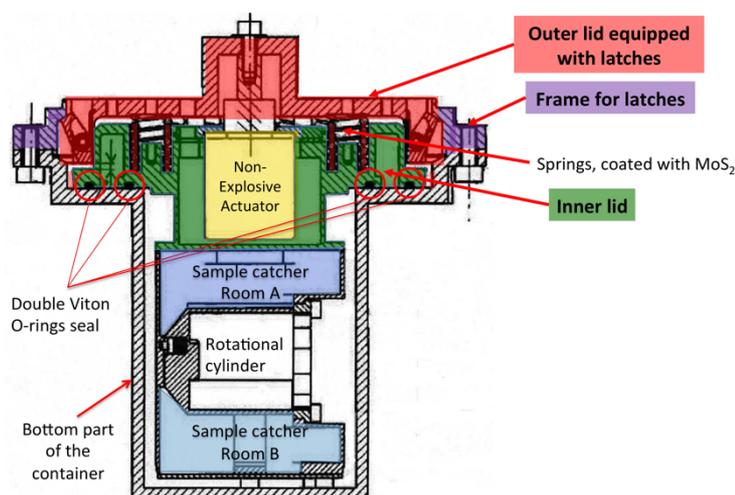


Fig. 1. A cross section of a sample container of Hayabusa. Blown-up samples entering its sampler horn go into a rotational cylinder at first and then captured in either Room A or B of the sample catcher.

process, so that large particles which might fall back into the catcher as it would be reversed must stay on the disk. We are now handpicking particles from the metal disk of the RC and analyzed them with the FE-SEM/EDS.

**Future plan and lessons learned for the sample extractions:**

Now, we are preparing new metal disks for the RA and RB, and will try final recoveries from them in the next year. Then we will continue to handpick from them to finish describing in 2020, until the sample return of Hayabusa2.

In the viewpoint of lessons learned from a series of implements of sample extractions experienced in the Hayabusa mission, we should consider a method to extract samples from a sample catcher in designing a new sampling system for a new spacecraft of a sample return mission. It is partially realized in designing Hayabusa2 sampling system, as three rooms of its sample catcher can be decomposed into each part, which is shaped like a container. However, detail processes of the sample extraction, which is partially mentioned in [5], was not discussed in its designation. Ideally, a whole sample extraction processes after its return to the Earth must be discussed and designed in developing a sample recovery system for the future sample return mission, such as the Martian Moons Exploration, MMX [6].

**References:**

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# Readiness of Receiving and Curation facility for Hayabusa2 Asteroid Sample Return Mission

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**Introduction:** Astromaterials Science Research Group (ASRG), established in 2015, is continuing curatorial work for Hayabusa returned samples and developing the curation facility for Hayabusa2 returned samples. JAXA curation facility of Extraterrestrial Sample Curation Center (ESCuC) was completed in 2008 for Hayabusa returned samples acceptance. Its conceptual examination was started in 2005, and its specification was decided in 2007 by the advisory committee of the Curation Facility [1]. After receiving the Hayabusa returned samples and curatorial work for them, we are going to research using these samples, such as international announcement of opportunity.

**Special feature of JAXA curation facility:** The feature of JAXA curation facility is the ability to be able to observe, and take out and keep a precious return sample scientifically, without being exposed to the atmosphere. Thereby, for example, noble-gas analysis and space weathering observation were enabled while they are difficult in the meteorite research due to the influence of terrestrial contamination. Moreover, in this facility the handling of the 10-micrometer sized particle is also possible using electrostatically controlled micromanipulation system installed in a clean chamber under N<sub>2</sub> atmosphere. The curation facility in which handling of such small samples without exposing to the atmosphere is available is the only one in the world [1].

**Hayabusa2 mission:** Hayabusa2 spacecraft will bring back surface samples of the near-Earth C-type asteroid (162173) Ryugu at the end of 2020. Because the C-type asteroids, of which reflectance spectra are similar to carbonaceous chondrites, are highly likely to record the long history of the solar system from the beginning to planet formation including the supply of volatiles to terrestrial planets, the main scientific goals of the Hayabusa2 mission are the investigations of (a) the origin and evolution of the solar system, and (b) the formation process and structure of the asteroid.

**Curatorial work of Hayabusa2 returned samples:** After receiving the returned samples of the Hayabusa2 mission, prior to the initial analysis, the phase-1 curation (sample description) will be done at the JAXA receiving and curation facility. Along with the initial analysis, the phase-2 curation of returned samples will be done for integrated thorough analysis and description of samples to build a sample database and to obtain new scientific perspective from thorough analysis of samples. The phase-2 curation will be done both in JAXA and also in several research institutes outside JAXA led by the JAXA curation facility.

**Preparation of receiving and curation facility for Hayabusa2:** We have started examination of receiving facility of Hayabusa2 returned sample in 2015. Since Hayabusa2 is a sample return mission from C-type asteroid, it is necessary to ensure recovery of the volatile matter from the samples containing an organic components and water. Moreover, since recovery of the mm-sized particles which was not able to be performed by Hayabusa is expected, the technical development for the description and the handling method for large particles is required.

In Hayabusa2 mission, more attention is paid to contamination control than Hayabusa mission. Final cleaning of the sample catcher is executed in the curation facility and cleaning level is known. Moreover, the contamination coupon is monitoring the contaminant during the construction of the sampling devices.

**Conceptual design of clean chamber for Hayabusa2:** After examination of receiving facility for Hayabusa2, we had fixed the specification and conceptual design of the clean chambers for Hayabusa2 in this year. The clean chambers are consisted of mainly two part. One is CC3 in vacuum environment, the other one is CC4 in ultra-pure nitrogen gas environment. CC3 is separated to 3 rooms, one is used for opening sample container, second one is used for sampling in high vacuum environment, and third one is used for sample storage. CC4 is separated to 2 rooms, one is micrometer-size samples handling and sealing of sample holders similar to Hayabusa CC2 clean chamber, second one is millimeter-size samples handling.

**Schedule until receiving of returned samples:** We have started the production of clean chambers and clean room for the receiving facility from this year. Clean room had already been completed in this summer and the clean chambers will be installed by the next summer. After the manufacturing of the curation facility for Hayabusa2, we will execute the rehearsal of the operation to succeed the curatorial work of the returned samples of Hayabusa2 until the return of the Hayabusa2 spacecraft to the Earth.

## References

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# A REPORT ON THE PREPARATION STATUS OF THE CURATION PROTOCOL FOR HAYABUSA2 SAMPLE

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We present an interim report on the returned sample curation protocol of Hayabusa2 project.

Hayabusa2 spacecraft was launched in 2014, and currently en route to a C type asteroid, called Ryugu, that is expected to be rich in organic compounds and water-bearing minerals. Hayabusa2 is the second asteroid sampling project of JAXA and has the following scientific and engineering objectives. The scientific objectives are to investigate chemical characteristics of the C type asteroid, especially the mineral – water – organic interactions by researching and analyzing its subsurface materials, and thereby to gain insight into its internal structure and reaccumulation process in its formation history. The engineering objectives are to mature the technology, which had been developed for the past Hayabusa mission, by improving its robustness, reliability and operability, and to execute the first impact experiment on the asteroid surface [1]. In 2018, Hayabusa2 will begin remote-sensing observations over the surface of Ryugu, fire metal impactors to excavate its surface and perform touchdowns for collecting its surface and/or subsurface materials. Hayabusa2 will leave Ryugu by 2019 and carry the sample, stored in vacuum-tight containers, back to Earth in December 2020. Later, the containers will be transported to the Extraterrestrial Sample Curation Center (ESCuC) in JAXA.

ESCuC is fully responsible for curating all the returned sample of Hayabusa2 and contribute to the Hayabusa2 project through the curation work. We believe that the curation of extraterrestrial samples is a critical interface between sample return missions and international science communities [2]. To accomplish our role, we have set following goals in our curation protocol:

- Handling the returned sample without any contamination as possible;
- Providing primary information about bulk returned sample and Ryugu grains obtained in the curation for the Hayabusa2 project researchers and other scientists;
- Creating the database of collected Ryugu grains.

The first goal is obvious, but is most important for ensuring a correctness and maximum output of scientific information about the asteroid to be obtained from the returned sample. Especially so, since the source of the sample is identified unambiguously unlike meteorites, which is an utmost advantage of the sample return mission. The goal depends seriously on the curating work in ESCuC. Therefore, the curation protocol must reduce risk of terrestrial contamination as possible, as well as prepare for every conceivable contingency.

Primary information about the returned sample, including the total weight and the size distribution of Ryugu grains and their physical and chemical states are very important for scientists to properly plan their researches and request suitable samples. In case any contamination was detected in the returned sample, the level of contamination and when it happened is critical not only to the scientists but also to the engineers who designed the spacecraft to improve the sampling system for future missions. The chemical and physical properties of Ryugu sample are necessary information for us to optimize the allocation procedure of the sample and would be interesting and informative to the scientists when they are designing research plans. We are planning to use 5% of the returned sample for preliminary examination to obtain necessary data to characterize physical and chemical properties of the returned sample. The sample allocation on request will also inform researchers of the size, weight and surface state (e.g., IR spectra) of the requested samples. We have just started selecting analytical instruments and designing analytical procedures in our curation protocol. Part of the analysis should be consistent with the Goal-1 defined previously and/or ensure no interruption in the allocation process.

As already noted, we are responsible for curating all the returned Ryugu sample. We are now developing a nomenclature for pieces of the sample or grains that are collected from the container. We will create a database for the grains, including necessary information such as their names, physical properties and histories of removing procedure that occurred during curation and after allocation as well. Such database would facilitate management of the collected grains and allow scientists to access all information they need.

We are still considering the best way to curate the returned sample of Hayabusa2 and recognize that there is room for further improvement in the current curation protocol.

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## Initial analysis of Ryugu samples

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Hayabusa2 spacecraft will bring back surface samples of a near-Earth C-type asteroid Ryugu late 2020. The Hayabusa2 returned-samples will be classified into (1) millimeter-sized coarse grains, (2) <100 µm-sized fine grains, and (3) volatiles components that will be extracted from the sample container prior to its opening [1–3]. After the first characterization at the curation facility of Institute of Space and Astronautical Science (ISAS), JAXA, the initial analysis of Ryugu samples will be done by the Hayabusa2 mission to maximize the scientific achievement of the project for 12 months to prove the potential of the samples.

Initial analysis of returned samples will focus on revealing the formation and evolution of Ryugu in the early Solar System. The scientific objectives of sample analysis are listed in the following table, which covers from the presolar history to the current geological activity of the near-Earth asteroid [1].

The initial analysis team will consist of six sub-teams for 1) chemistry (elements and isotopes), 2) petrology and mineralogy of coarse grains (mm-sized grains), 3) petrology and mineralogy of fine grains (<100 µm-sized grains), 4) volatiles, 5) macromolecular organics (insoluble organic matter), and 6) organic molecules (soluble organic matter).

Each sub-team will be an international analysis team led by a researcher who can have a research base in Japan at least a year before the delivery of the samples (the end of 2020) and throughout the initial analysis phase (2021–2022). The sub-team leaders will make an analysis and work flow plan in their sub-teams with the IAT members to make the best effort in fulfilling the scientific goals of the mission through integration of analytical results from each sub-team and on-site remote-sensing data.

The Hayabusa2 project opened a call for nomination of the sub-team leaders in October 2016. All the nominations were thoroughly reviewed by the Hayabusa2 Sample Allocation Committee (HSAC). The HSAC recommended candidates of the sub-team leaders to the Hayabusa2 Joint Science Team (HJST) for approval. The initial analysis plan of Ryugu samples will be presented with the names of approved sub-team leaders at the symposium.

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# Advanced Curation Activities at NASA: Preparing to Receive, Process, and Distribute Samples Returned from Future Missions

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**Introduction:** The Astromaterials Acquisition and Curation Office (henceforth referred to herein as NASA Curation Office) at NASA Johnson Space Center (JSC) is responsible for curating all of NASA's extraterrestrial samples. Under the governing document, NASA Policy Directive (NPD) 7100.10F JSC is charged with curation of all extraterrestrial material under NASA control, including future NASA missions. The Directive goes on to define Curation as including documentation, preservation, preparation, and distribution of samples for research, education, and public outreach. Here we briefly describe NASA's astromaterials collections and our ongoing efforts related to enhancing the utility of our current collections as well as our efforts to prepare for future sample return missions. We collectively refer to these efforts as advanced curation.

**NASA Curation:** The NASA Curation Office presently curates nine different astromaterials collections: (1) Apollo samples, (2) Luna samples (Soviet Union), (3) Antarctic meteorites, (4) Cosmic dust particles, (5) Microparticle Impact Collection [formerly called Space Exposed Hardware], (6) Genesis solar wind atoms, (7) Stardust comet Wild-2 particles, (8) Stardust interstellar particles, and (9) Hayabusa asteroid Itokawa particles (JAXA).

In addition, the next missions bringing samples back to Earth are Hayabusa 2/ asteroid Ryugu (JAXA) and OSIRIS-Rex/ asteroid Bennu (NASA), in 2021 and 2023, respectively. We currently house contamination knowledge (CK) witness plates for OSIRIS-REx, and we will soon begin curating CK witness plates for the Mars 2020 mission, which is going to collect and cache martian samples for possible future return to Earth.

**Advanced Curation at NASA:** The NASA Curation Office plans for the requirements of future collections in an "Advanced Curation" program. Advanced Curation is tasked with conducting research to develop, invent, integrate, test, and evaluate new and innovative technologies for sample collection, contamination control, clean handling, characterization, analysis, and curation of astromaterials collected by human and non-human explorers – protecting the scientific integrity of each sample from the point of mission inception through long-term preservation and distribution on Earth. As each new sample collection is returned, new facilities are added to accommodate them.

Advanced Curation at NASA is founded as a cross-disciplinary field of advanced research and development under the auspices of the Astromaterials Acquisition and Curation Office at NASA Johnson Space Center. Advanced curation conducts research, explores and invents new innovative technologies and techniques for collection, handling, characterization, analysis, and curation of astromaterials that could be used in next generation human and robotic space exploration missions and current collections. Advanced Curation has a primary goal of expanding the sample processing and storage capabilities of NASA's astromaterials curation facilities to prepare for future sample return missions as well as maximizing the science returns of our existing sample collections. In addition, the program integrates, tests, and evaluates new technologies and operational procedures for future sample return missions through human and robotic analog studies. These goals are aimed at improving our core curation functions of protecting the scientific integrity of NASA's astromaterials collections and serving as responsible distributors of astromaterials to the global community of sample scientists and educators in a fair, timely, and professional manner. The primary result of advanced curation is to reduce contamination to astromaterials and preserve the scientific integrity of all samples from mission inception and through ATLO, sample collection, preliminary examination on Earth, curation, and secure delivery of the samples to Earth-based laboratories for in-depth scientific analyses.

Curation starts at the inception of a sample return mission, and Advanced Curation is an ever-evolving field with specific foci that start at the inception of a sample return concept. If we look only at improving upon our current curation capabilities, we will not be prepared when returned samples require care that is very different from those within our current collections. At present, most of the samples we curate are geologic in nature, with the exception of the Genesis solar wind atoms that are implanted within a number of inorganic substrates. All of the samples are kept close to room temperature, and we do not curate gases, liquids, ices, or biologic materials. However, future sample return missions may bring back samples that require storage and handling conditions outside of our current capability, so we must prepare for such instances. Additionally, many of our samples, when kept in the pristine environments of our labs, will maintain their fidelity indefinitely. Returned samples from future missions – ices, for example – may have certain properties that have a short "shelf-life", and hence curation will need to determine such shelf lives for particular types of analyses through analog studies so that we can prioritize the order in which science questions are answered from a particular collection. Another aspect of advanced curation is expanding our ability to document samples, analyses, and sample histories.

**Concluding Remarks:** The return of every extraterrestrial sample is a scientific investment, and the curation facilities and personnel are the primary managers of that investment. Our primary goals are to maintain the integrity of the samples and ensure that the samples are distributed for scientific study in a fair, timely, and responsible manner. It is only through the long-term stability and support of curation facilities, coupled with the infusion of technological advances realized through new advanced curation initiatives that the maximum returns on that scientific investment are achieved. In the coming decades, sample return missions will increase in their complexity with respect to sample storage and sample handling requirements. Our advanced curation efforts today ensure we will be poised to curate and handle these samples upon return.

## Curating NASA's Past, Present, and Future Extraterrestrial Sample Collections

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**Overview:** As codified in NASA Policy Directive (NPD) 7100.10F, the Astromaterials Acquisition and Curation Office at NASA Johnson Space Center (hereafter JSC Curation) is charged with curation of all extraterrestrial material under NASA control, including future NASA missions. The NPD defines Curation as including documentation, preservation, preparation, and distribution of samples for research, education, and public outreach. Here we briefly describe NASA's astromaterials collections, the physical infrastructure involved in the curation process, as well as our plans for future facilities to house our emerging astromaterials collections.

**Current Facilities:** JSC Curation curates all or part of nine astromaterial collections in seven clean room suites, comprising 22 different rooms: (1) Apollo Samples (1969; ISO 6-7), (2) Luna Samples (from USSR; 1972; ISO 7), (3) Antarctic Meteorites (1976; ISO 7), (4) Cosmic Dust (1981; ISO 5), (5) Microparticle Impact Collection (formerly called Space Exposed Hardware; 1985; ISO 5), (6) Genesis Solar Wind Atoms (2004; ISO 4); (7) Stardust Comet Particles (2006; ISO 5), (8) Stardust Interstellar Particles (2006; ISO 5), (9) Hayabusa Asteroid Particles (from JAXA; 2010; ISO 5). We also curate spacecraft coupons and witness plates for multiple past and current missions (e.g. Stardust, OSIRIS-REx, as well as upcoming missions (e.g., Mars2020). Thus, we currently curate large rock samples (Apollo, Meteorites), bulk regolith and core samples that are intimate mixtures of particles ranging from submicron to 1 cm (Apollo), micron-scale individual particles (Cosmic Dust, Hayabusa), micron-scale particles embedded in aerogel (Stardust), atoms of the solar wind implanted in various materials, physical pieces of spacecraft that have astromaterials embedded in them (Microparticle Impact Collection), and materials that capture contamination knowledge for returned extraterrestrial samples (Genesis, Stardust, OSIRIS-REx). In addition to the labs that house the samples, we have installed and maintained a wide variety of facilities and infrastructure required to support the clean-rooms: >10 different HEPA-filtered air-handling systems, ultrapure dry gaseous nitrogen systems, an ultrapure water (UPW) system, and cleaning facilities to provide clean tools and equipment for the labs. We also have sample preparation facilities for making thin sections, microtome sections, and even focused ion-beam (FIB) sections to meet the research requirements of scientists. To ensure that we are keeping the samples as pristine as possible, we routinely monitor the cleanliness of our clean rooms and infrastructure systems. This monitoring includes: daily monitoring of the quality of our UPW, weekly airborne particle counts in the labs, monthly monitoring of the stable isotope composition of the gaseous N<sub>2</sub> system, and annual measurements of inorganic or organic contamination in processing cabinets. Additionally, each delivery of liquid N<sub>2</sub> is monitored for contaminants (typically <6 ppm Ar, and <1 ppm all others combined). We also track within our databases the current and ever-changing characteristics (weight, location, destructive analysis spots) of >250,000 individual samples across our various collections (including the 19,141 samples on loan to 433 Principal Investigators in 24 countries). Similarly, there are 100s of thousands of images associated with the samples that are stored on our servers. We also have the sample processing and sample handling records (often hand written) for our older collections.

**Future Facilities:** The next sample return missions are Hayabusa2 and OSIRIS-REx, in 2020 and 2023 respectively. Details of the curation plans for each mission can be found in [1,2]. The designs for a new state-of-the-art suite of clean rooms to house these samples at JSC have been finalized. This includes separate ISO class 5 clean rooms to house each collection, a common ISO class 7 area for general use, an ISO class 7 microtome laboratory, and a separate thin section lab. Additionally, a new cleaning facility is being designed and procedures developed that will allow for enhanced cleaning of cabinets and tools in an inorganically, organically, and biologically clean manner. We are also designing a large multi-purpose Advanced Curation laboratory [3] that will allow us to develop the techniques necessary to fully support the Hayabusa2 and OSIRIS-REx missions, as well as future possible sample return missions (e.g., Lunar Polar Volatiles, Mars, Comet Surface). A micro-CT laboratory dedicated to the study of astromaterials has come online this summer within JSC Curation, and we plan to add additional facilities that will enable non-destructive (or minimally-destructive) analyses of astromaterials in the near future (e.g., micro-XRF, confocal imaging Raman Spectroscopy). These facilities will be available to: (1) develop sample handling and storage techniques for future sample return missions, (2) be utilized by PET for future sample return missions, (3) for retroactive PET-style analyses of our existing collections, and (4) for periodic assessments of the existing sample collections.

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## Sample curation in support of the OSIRIS-REx asteroid sample return mission

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The OSIRIS-REx asteroid sample return mission launched to asteroid Bennu Sept. 8, 2016. The spacecraft will arrive at Bennu in late 2019, orbit and map the asteroid, and perform a touch and go (TAG) sampling maneuver in July 2020. After sample is stowed and confirmed the spacecraft will return to Earth, and the sample return capsule (SRC) will land in Utah in September 2023. Samples will be recovered from Utah [2] and then transported and stored in a new sample cleanroom at NASA Johnson Space Center in Houston [3]. The materials curated for the mission are described here.

a) Materials Archive and Witness Plate Collection: The SRC and TAGSAM were built between March 2014 and Summer of 2015, and instruments (OTES, OVIRS, OLA, OCAMS, REXIS) were integrated from Summer 2015 until May 2016. A total of 395 items were received for the materials archive at NASA-JSC, with archiving finishing ~30 days after launch (with the final archived items being related to launch operations)[4]. The materials fall into several general categories including metals (stainless steel, aluminum, titanium alloys, brass and BeCu alloy), epoxies, paints, polymers, lubricants, non-volatile-residue samples (NVR), sapphire, and various miscellaneous materials. All through the ATLO process (from March 2015 until late August 2016) contamination knowledge witness plates (Si wafer and Al foil) were deployed in the various cleanrooms in Denver and KSC to provide an additional record of particle counts and volatiles that is archived for current and future scientific studies. These plates were deployed in roughly monthly increments with each unit containing 4 Si wafers and 4 Al foils. We archived 128 individual witness plates (64 Si wafers and 64 Al foils); one of each witness plate (Si and Al) was analyzed immediately by the science team after archiving, while the remaining 3 of each are archived indefinitely. Information about each material archived is stored in an extensive database at NASA-JSC, and key summary information for each will be presented in an online catalog.

b) Bulk Asteroid sample: The Touch and Go Sampling Mechanism (TAGSAM) head will contain up to 1.5 kg of asteroid material. Upon return to Earth, the TAGSAM head with the sample canister will be subjected to a nitrogen purge and then opened in a nitrogen cabinet in Houston. Once the TAGSAM head is removed from the canister, it will be dis-assembled slowly and carefully under nitrogen until the sample can be removed for processing in a dedicated nitrogen glovebox. Bennu surface samples are expected to be sub-cm sized, based on thermal infrared and radar polarization ratio measurements [1]. The upper limit on material collected by the TAGSAM head is ~2 cm. Therefore, we will be prepared to handle, subdivide, and characterize materials of a wide grain size (from ~10  $\mu\text{m}$  to 2 cm), and for both organic (UV fluorescence) and inorganic (SEM, FTIR, optical) properties. Representative portions of the bulk sample will be prepared for JAXA (0.5 %; see also [5]) and Canadian Space Agency (4%), with the remaining divided between the science team (<25%) and archived for future studies (NASA) (>75%).

c) Contact Pad samples: The base of the TAGSAM head contains 24 contact pads that are designed to trap the upper surface layer of material and thus offer an opportunity to study asteroid samples that have resided at the very top surface of the regolith. Asteroid material is trapped on the pads in spring steel Velcro hooks, and material will have to be removed from these pads by curation specialists in the lab.

d) Hardware: Some canister and SRC hardware items will contain information that will be important to understanding the collected samples, including the canister gas filter, temperature strips, flight witness plates, and the TAGSAM and canister parts that might have adhering dust grains.

Some challenges remaining for both bulk sample and contact pad samples include: i) working with intermediate size range (200 to 500  $\mu\text{m}$ ) samples – a size range NASA has not previously worked in such detail; ii) techniques for removal of contact pad material from the spring steel hooks, iii) static electrical effects of dust sized particles during sample handling and curation is likely to be significant, and iv) the TAGSAM head and associated canister hardware will undoubtedly be coated with fine adhering dust grains from Bennu. In the case of collection of a large bulk sample mass, the adhering dust grains may be of lower priority. If a small sample mass is returned, the adhering dust may attain a higher priority, so recovery of adhering dust grains is an additional challenge to consider. In the year leading up to sample return we plan a variety of sample handling rehearsals that will enable the curation team to be prepared for many new aspects posed by this sample suite.

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# The European Space Agency Exploration Sample Analogue Collection (ESA<sup>2</sup>C) and Curation Facility – progress update

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**Introduction:** Since 2014, the Natural History Museum (NHM) has been the prime contractor to the European Space Agency (ESA) for defining and initiating the development of a Sample Analogue Collection and Curation Facility in support of the Robotic Exploration mission preparation programme. The ESA Sample Analogue Collection (ESA<sup>2</sup>C) will support the ongoing or future technology development activities that are required for human and robotic exploration of Mars, Phobos, Deimos, C-Type Asteroids and the Moon. The long-term goal of this work is to produce a useful and useable resource for engineers and scientists developing technologies for ESA missions.

**Analogue Sample Collection:** The complex mission architectures and diverse target bodies of interest means that a variety of different analogue materials are required to test all systems that come into contact with the target body, whether these be part of the spacecraft system, such as landing and/or roving systems (e.g. wheels), sample collection systems (e.g. drills or scoops) or scientific payload. The analogue materials must replicate as far as possible the expected ‘geological’ environment of the target body in terms of both physical/mechanical properties and chemical/mineralogical properties. In addition to ensuring that the samples as accurately as possible represent the physical and chemical properties of the target bodies of interest, it is important to select materials that can be readily obtained both now and in the future, in enough volume that will ensure a sustainable collection. As is the case for the existing NASA lunar and martian analogues (JSC-1A and JSC-Mars-1A) [1] we have selected samples that are available from commercial suppliers to mitigate the risk of materials becoming unavailable and to ensure large quantities can be sourced if necessary. Additionally, as our chosen suppliers provide materials to a number of industries we are confident in the quality control procedures in operation during material production, which should allow for good reproducibility in sample properties over time.

Samples selected include a variety of aggregates from the olivine-rich basalts from the Upper Lava Formation of the Paleogene Antrim Lava Group of Northern Ireland and clay samples from Cyprus, Spain and Senegal. During 2016 and 2017 we carried out a detailed characterisation of the analogue samples’ physical and chemical properties [2,3]: *Chemical properties:* Whole-rock chemistry – major, minor and trace element analyses by ICP-AES and ICP-MS. Mineralogy – analytical SEM, EPMA and XRD (whole-rock). *Physical properties:* Grain size and shape – sieving and visual inspection, X-ray micro-CT. Bulk density and porosity – mass-volume measurement and helium pycnometry, X-ray micro-CT. Shear strength (aggregate and powder samples) – shear box apparatus. Compressive and tensile strength – UCS testing and Brazilian indirect tensile method.

**Sample Analogue Curation Facility:** This unique venture will build on the Robotic Exploration mission preparation programme by establishing methodologies and protocols/procedures for curating the ESA<sup>2</sup>C, as well as defining and validating the distribution mechanisms and information exchange protocols for the analogue materials. Underpinning the work will be the development of the ESA<sup>2</sup>C database that is currently being developed. Samples will be available to suitable qualified PIs and we welcome requests for information on the samples we have already acquired and characterized and dialogue with colleagues who are also working on analogue samples as part of mission development e.g. JAXA’s Martian Moons eXploration (MMX) mission [4].

As part of ongoing work, further samples have been acquired for the ESA<sup>2</sup>C - anorthosite blocks from a Norwegian quarry and basaltic sand/gravel and basaltic/hyaloclastite blocks were collected from the Askja Region in Iceland. Additionally, sample mixtures will be made up using the characterised clays and basalts for varying grain sizes and clay:basalt ratios to better replicate the Phobos/Deimos/C-Type Asteroids and Martian regoliths. We will continue to seek sources of new materials for potential acquisition and subsequent characterization to enhance the initial collection. A critical part of our work is to actively collaborate with our colleagues in the space mission engineering and planetary sciences communities to ensure that the ESA<sup>2</sup>C is a relevant and practical resource for technology development.

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## NASA Sample Return Missions: Recovery Operations

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The Utah Test and Training Range (UTTR), southwest of Salt Lake City, Utah, is the site of all NASA unmanned sample return missions. To date these missions include the Genesis solar wind samples (2004) and Stardust cometary and interstellar dust samples (2006). NASA's OSIRIS-REx Mission will return its first asteroid sample at UTTR in 2023.

The reason for recovery operations at UTTR is many fold, but the simple reason is that it is the largest contiguous block of restricted airspace in the continental United States. This airspace covers over 9,000 square kilometers of land and is under the jurisdiction of the U.S. Air Force. Hill Air Force Base (AFB) is responsible for the operation of the range and supports thousands of test and training exercises each year. This valuable test experience coupled with its robust radar tracking assets is another attractive feature of NASA's chosen landing site. Grounding missions due to weather are uncommon, in fact the Hill AFB On-Scene Commander reviewed a sub-set of data earlier in 2017 from the last three years of missions and none were grounded due to weather – just one was delayed by an hour. Temperature lows during their winter months (December, January and February) are typically below freezing which could be attractive for a future cold sample return. The soft clay on the range is of particular interest to sample return capsule (SRC) designers because it offers a landing surface that might save precious spacecraft mass if padding on the SRC is reduced. As a U. S. military base, non-U. S. citizen visitors must be escorted at all times, but this did not deter international Genesis or Stardust team members from participating in recovery operations. However, it does require more planning due to the approval process for foreign visitors.

Two risk items at UTTR are worth noting for future sample return mission managers: (1) the range contains zones where the SRC cannot be recovered. In comparison to the large landing footprint the range offers, these prohibited zones are small but should be factored into a mission's risk posture; and (2) due to the nature of testing conducted on the range, unfired ordnance is a hazard to visitors of the range. For this reason, no one from NASA goes on the range without military escort, and a military On-Scene Commander led both recovery teams during all training and actual recovery events. It is expected that this protocol would be followed for any future sample recovery operation.

Once recovered in the field, UTTR has facilities to accommodate sample assessment. Genesis and Stardust (and OSIRIS-REx in 2023) took advantage of this by setting up a modular ISO Class 7 cleanroom. After initial investigation in Utah, the SRC was flown from the UTTR's military airfield directly to Ellington Field, 12 kilometers from NASA's Johnson Space Center (JSC) where the Curation facility resides. Upon arrival at JSC, the Genesis and Stardust samples were initially assessed and prepped for transfer to their dedicated Curation Facility in an ISO 7 hardware cleanroom. Once transferred to the dedicated Curation Facility (housed within the same building as the hardware cleanroom, these Curation Facilities are ISO Class 4 and 5, respectively); preliminary examination of the samples by the Science Team began.

The excitement from a sample return is hard to predict. Upon arrival at JSC for Genesis and Stardust, the media, science team, fellow JSC scientists and even the surrounding community's interest were overwhelming. This excitement can lead the team to work fast. Try to avoid this and stick with the rehearsed plan. Designate a person or two to talk with outsiders so that the mission team can focus on what's important – protecting the samples.

## Sample return and the Canadian Space Agency: Ongoing activities and avenues for international collaboration

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**Canadian Planetary Exploration Overview:** Broadly, the Canadian Space Agency's (CSA) planetary exploration program consists of participating in ongoing missions and conducting preparatory activities for missions yet to come. CSA's science goals are developed in conjunction with the Canadian academic community, and follow two general themes: (i) understanding the origin and evolution of planetary bodies within the solar system, and (ii) habitability and life detection. As these goals are squarely aligned with a variety of current and future sample return efforts, CSA – in collaboration with its international partners – has become increasingly involved in sample return mission operations and planning.

**OSIRIS-REx:** CSA's first formal participation on a sample return effort is with the NASA-led Origins Spectral Interpretation Resource Identification Regolith Explorer (OSIRIS-REx) mission. OSIRIS-REx aims to return at least 60g of material from asteroid Bennu, a primitive carbon-rich B-type asteroid believed to contain organic materials [1]. Canada's hardware contribution to the mission is the OSIRIS-REx Laser Altimeter (OLA) instrument (Fig. 1), built by MDA Corporation and led by Principal Investigator Dr. Mike Daly of York University. OLA is a scanning lidar that will provide high-resolution 3D topographic information about the asteroid, helping provide geologic context for the spacecraft's spectral instruments and aiding selection of a site where samples can be collected safely [2].



Figure 1: The OSIRIS-REx Laser Altimeter  
(Image credit: NASA / Goddard / Debora McCallum)

In return for its contribution of OLA and support of a number of mission Science Team members, Canada will receive 4% of the returned sample. A Canadian OSIRIS-REx Sample Advisory Committee is being targeted to assist in evaluating the appropriate curation partner and to review the proposed Curation Plan. This committee would seek input from international partners who have heritage in astromaterial curation. Upon successful return of the samples, Canada also aims to maximize the scientific use of its sample allocation, and would thus welcome discussions on potential sample access opportunities with interested parties.

**Mars Sample Return – Mission Architecture and Science Management:** Mars Sample Return (MSR) remains one of the highest priorities of the international planetary science community. Because MSR is likely too large an endeavor to be taken on by any individual country or space agency, international cooperation will be paramount to reaching this goal successfully. Several agencies throughout the world are evaluating possible contributions to this multi-mission endeavor, with coordination efforts discussed through the International Mars Exploration Working Group (IMEWG).

In 2014, IMEWG tasked the international Mars Architecture for the Return of Samples (iMARS) working group to define a mission architecture that could successfully achieve MSR and to outline a science management plan for the returned samples. Canada played a lead role in this effort, co-chairing both the science and engineering sub-teams. Over two years, the working group developed an extensive set of findings and recommendations, some of which have already been implemented. A summary presentation was presented at the Mars Exploration Payload Analysis Group (MEPAG) meeting in 2016 [3], with the full report expected to be published in fall of 2017.

**Mars Sample Return – Caching and Retrieval:** One of the key findings from the iMARS team was that a minimum of three flight missions would be required to achieve MSR: (i) sample collection and caching; (ii) sample retrieval, and; (iii) Earth return. A number of open scientific, technical, and operation questions remain open regarding the execution of the surface elements, (i) and (ii). With international cooperation coordinated via IMEWG, Canada led robotic field deployments near Hanksville, Utah (USA) to start answering some of these questions (Fig. 2).

Science operations for the sample cache mission were conducted over four weeks spanning 2015 and 2016. The mission team conducted operations using a combination of rover-integrated sensors and hand-held instruments, successfully capturing eight scientifically-selected samples and developing an environmental reconstruction of the “landing site”. Additionally, a two week deployment in 2016 utilized the rover in its sample retrieval configuration, demonstrating successfully the adaptive caching approach currently preferred by the Mars 2020 mission [4]. These efforts have advanced international readiness for an eventual MSR campaign and paved the way for future deployments to further reduce risk.



Figure 2: Sample collection and retrieval configurations of CSA's Mars Exploration Science Rover (MESR) prototype (Image Credit: CSA)

**Science Opportunities for the Future:** As human presence expands through the solar system, the Canadian planetary science community is also interested in evaluating new opportunities for science enabled by human exploration of the Moon and Mars. In addition to developing potential rover concepts, CSA is conducting science definition work in support of a Human Lunar Exploration Precursor Program lunar sample return mission. With its international partners, terrestrial field demonstrations are anticipated in the coming years.

Moreover, a number of open competitions are seeking proposals for sample return missions from various destinations in the solar system. Although Canadian hardware contributions to these campaigns are not currently anticipated, in many cases Canadian scientists have been sought to provide expertise in a key mission roles. Depending on the outcome of the competitions, it is possible that science support will be enabled by CSA through a competitive co-investigator program.

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## In the Cold: The Future of Astromaterials Curation?

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**Introduction:** Astromaterials, including meteorites, lunar samples, solar wind, cometary dust, asteroidal regolith and interplanetary dust, provide a unique record of the conditions that prevailed during the formation of our solar system, and the subsequent processes involved in the evolution of a variety of planetary bodies. However, the majority of astromaterials formed in environments not found at the Earth's surface [1]. Therefore, curation is a critical component in the planning of sample return missions [1] (and can be captured in the question: Why spend billions to bring samples back if they become contaminated during sample handling and curation?).

Modern curation facilities have as their primary goal the isolation of astromaterials from the terrestrial environment [1]. Airborne particulate contaminants are mitigated using HEPA filtration systems, as well as recognized clean room practices (e.g., use of gloves, gowns, boots, etc.). Due to the relative abundance of organic compounds at the Earth's surface, organic contamination is particularly problematic, and may be mitigated by specialized handling practices to limit the transfer of terrestrial organics to the samples, and cleaning procedures and methods for identifying and monitoring contaminants [e.g., 2]. However, astromaterials can be compromised in ways other than simple sorption of non-indigenous compounds on exposed surfaces, or via mixture with airborne dust. Oxidation and hydrolysis are a type of invasive contamination as both processes permanently chemically alter the intrinsic compounds and minerals in the sample; for this reason, inert atmospheres are utilized in curation to limit reaction of the indigenous organics and minerals with atmospheric water and molecular oxygen gas. However, the recognition of volatile and/or reactive organic species in carbonaceous chondrites [e.g., 3] necessitates considerations of curation at low temperature, in order to prevent the loss of intrinsic volatile species.

**Insights from Tagish Lake:** The Tagish Lake meteorite fell January 18 2000 onto a frozen lake surface in northern British Columbia, Canada. Samples of the meteorite were recovered within a week of the fall and kept frozen and untouched by hand (the so-called "pristine specimens"). Studies of the Tagish Lake meteorite demonstrate that it is an ungrouped Type 2 carbonaceous chondrite with affinities to CI and CM chondrites [4]. Tagish Lake is among the most enriched in carbon of all chondrites, containing up to ~6 wt% total C, of which approximately half is organic [5]. The soluble organic component, while relatively small (~2 % of organic C), contains several classes of compounds of prebiotic interest, including some which are particularly volatile (e.g., formic acid) [6-8]. Systematic study of different lithologies within Tagish Lake demonstrate variation in organic matter characteristics that correlate with mineralogy and petrology [9]; these variations are thought to represent a record of the effect of parent body alteration on the structure and composition of the organic matter [10]. Further details on intrinsic and contaminant organic species found in the Tagish Lake meteorite are summarized by [11].

**Cold curation in practice:** The pristine specimens of Tagish Lake necessitated the development of a facility that would enable the documentation, processing and storage of astromaterials under cold, inert conditions. The Subzero Curation Facility for Astromaterials at the University of Alberta is designed with these considerations in mind, within the limitations of funding available. At the heart of the facility is an Ar gas glove box (MBraun, Inc.), housed within a controlled environment chamber capable of maintaining temperatures between -30 and -10 °C (Fig. 1). The glove box consists of a single user station made of brushed 304 stainless steel with radius corners, with a polycarbonate window with chemical and scratch resistant coating (Fig. 1c). Integrated into the window is a binocular microscope (Leica, Inc.), fitted with a camera adapter (Fig. 1c). An adjustable stage sits beneath the microscope, within the glove box. On the right side of the main box is a secondary, storage box made of the same materials as the main box (Figure 1c); separated from the main box by a sealable door, this box allows for temporary storage of samples while experiments (e.g., involving solvents) are being carried out in the main box. The atmosphere within the glove box is maintained using an MB 20 G gas purifier (MBraun, Inc.); once charged with high-purity oxygen-free (99.998%) argon, the system continuously recirculates the argon through a purification system, which removes airborne contaminants and maintains O<sub>2</sub> and H<sub>2</sub>O to < 1 ppm. HEPA filters on gas inlets also reduce any particulate matter that may be otherwise be circulated into the glove box. An activated carbon filter unit on the gas outlet for the main glove box removes any volatile organic compounds that might contaminate the materials used within the purifier; this feature also allows for organic solvents (e.g., chlorinated solvents such as dichloromethane) to be used within the glove box, either for cleaning purposes or to

carry out organic extractions on samples within a purified inert atmosphere at low temperature. A Class 1000 clean room (Lasco Services, Inc.) serves as a room temperature anteroom to the freezer chamber (Fig. 1a). This anteroom was established to provide a source of clean air for the freezer chamber, since HEPA filtering of the freezer chamber air was not practicable. The anteroom also provides improved storage for the University of Alberta Meteorite Collection. Further details are provided in [11], including methods and results pertaining to commissioning of the facility.



Figure 1. The Subzero Curation Facility at the University of Alberta, consisting of a Class 1000 room temperature anteroom (A), and a walk-in freezer (B) in which an Ar glove box is housed (C).

**Insights into cold curation for future sample return:** Processing of Tagish Lake specimens now occurs on a routine basis within the Subzero Curation Facility for Astromaterials. To date, no significant levels of organic contaminants have been observed in any meteorite samples, although the use of witness plates is planned but not yet implemented. In practicality, the facility accomplishes the purpose for which it was built, i.e., to enable the processing of Tagish Lake specimens under clean, cold conditions in an inert atmosphere (although Tagish Lake specimens remain in storage in air, [11]). The two main limitations encountered thus far in the use of the facility include mitigation of a glove box leak and user comfort – the low temperature of the freezer chamber compounds the challenges associated with glove box work. As with any cold environment work, standard operation involves donning insulated clothing (under the clean room smocks), working with a partner, and limiting exposure to the cold – typically 15-20 minutes at a time. The main advantage of the facility is the reduced risk to specimens once they are transferred into the glove box, allowing for frequent user breaks (to warm up). However, in the case of a sudden leak or atmospheric contamination event, rapid mitigation of the problem can be hampered by the cold, especially if the user has already been working in that environment before the problem is noticed.

**Conclusions:** In spite of the challenges, cold curation provides significant advantages over room-temperature curation, including: the retention of intrinsic volatiles; the suspension or inhibition of microbial activity; the minimization of outgassing of glovebox components; and the reduction in reaction rates of oxidation and hydrolysis of intrinsic organic compounds and minerals. Therefore cold curation is recommended for future sample return from any parent body in which volatile components are anticipated (e.g., organic-rich asteroids, cometary nuclei, Mars). The optimal design of a cold curation facility will need to balance the parent-body-specific conditions required to preserve the sample with those which maintain user comfort. In practice, this will most likely require the ultra-cold ( $\sim -80^{\circ}\text{C}$ ) storage of specimens and the handling and processing of specimens under cold ( $\sim -15^{\circ}\text{C}$ ) conditions. Notably, micromanipulation of small samples under cold conditions has yet to be tested, and is an important consideration for future sample return mission planning.

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# Amino Acids in Returned Samples and other Solar System Materials

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## Introduction:

The organic contents of asteroids and comets reflect early solar system chemistry, as well as the physical and chemical processes that have occurred in the past 4.5 billion years. Both returned samples and meteorites present an opportunity to understand these organic contents. Meteorites provide samples from a diverse selection of solar system bodies, while returned samples have the advantage of context, known parent bodies, and minimal contamination.

Among the most well-studied of the organic compounds present in these extraterrestrial materials are amino acids. Amino acids are of particular interest to astrobiology and astrochemistry research for several reasons: (1) they are essential to life on Earth; (2) they are a structurally diverse group of compounds; and (3) some of them possess large enantiomeric excesses of extraterrestrial origin. Amino acids have been detected in a variety of meteorites, as well as in materials collected from NASA's Stardust mission to Comet Wild-2 and in lunar samples returned by NASA's Apollo missions. Observations by the ROSINA mass spectrometer also identified glycine in the coma of 67P/Churyumov-Gerasimenko. The abundances, relative distributions, enantiomeric ratios, and stable isotopic composition of amino acids in extraterrestrial materials can be used to understand formation histories and contamination of these materials.

## Amino acids in meteorites:

We have examined the abundances, structural distributions, stable isotopic ratios, and enantiomeric compositions of amino acids in meteorites from all eight carbonaceous chondrite groups (CI, CM, CR, CO, CV, CK, CH, and CB), as well as representatives of other meteorite classes [1]. Analytical techniques include liquid chromatography coupled with fluorescence detection and time-of-flight mass spectrometry (LC-FD/ToF-MS) to sensitively measure abundances, and gas chromatography coupled with mass spectrometry and isotope-ratio mass spectrometry (GC-MS/IRMS) to measure compound-specific isotopic ratios. These studies show a wide diversity in the amino acids present across these samples. This diversity highlights the potential roles of parent body processes and composition on the organic content of these bodies, as well as the potential for a variety of formation mechanisms and organic reservoirs in the solar system. In addition, the observed large L-enantiomeric excesses of some proteinogenic amino acids in certain meteorites (up to ~60%) may be relevant to understanding the origin of homochirality in life on Earth, although the potential mechanisms leading to these enantiomeric excesses are currently poorly understood.

## Amino acids in returned samples:

Analysis of bulk comet-exposed materials from the Stardust collector by LC-FD/ToF-MS revealed several amines and amino acids, including glycine, methylamine and ethylamine [2]. The origin of these compounds could not be firmly established by LC-FD/ToF-MS data alone, although the distinctive 1:1 ratio of methylamine to ethylamine suggested a cometary origin for those compounds. Subsequent GC-MS/IRMS analyses measured the stable carbon isotopic ratios of glycine and determined its likely extraterrestrial origin for glycine, representing the first detection of a cometary amino acid [3]. The in-situ measurements of glycine in the coma of 67P/Churyumov-Gerasimenko supported the presence of cometary amino acids [4].

Lunar regolith samples returned by NASA's Apollo missions were investigated almost immediately after their return, but these studies yielded inconclusive identifications about the origins of detected amino acids (e.g. [5,6]), in part due to analytical limitations. It was not possible to determine if the detected amino acids were indigenous to the lunar samples or the result of terrestrial contamination. More recently, we applied modern analytical techniques to determine the abundances, distributions, and carbon isotopic ratios of amino acids in lunar regolith from the Apollo 16 and 17 missions. We observed amino acids in low concentrations in all samples. Isotopic and abundance data suggested that terrestrial biological contamination was a primary source of the observed amino acids, but that some contribution from meteoritic infall was also present [7].

The material returned by JAXA's Hayabusa mission from asteroid Itokawa was examined for organic materials, including amino acids. Five individual particles were extracted with organic solvents, but analyses of these extracts showed amino acids

present only at levels below those seen in a procedural blank [8]. Future studies with hot-water extraction may be possible, but the small sample sizes available from this returned material may preclude any compound-specific amino acid identification.

#### **Future plans for amino acid studies of returned samples:**

Both the samples to be returned by NASA's OSIRIS-REx mission to asteroid Bennu and JAXA's Hayabusa2 mission to asteroid Ryugu are expected to be analyzed for amino acids and other organic materials. Asteroid Bennu is a B-type carbonaceous asteroid whose spectra most closely match those of CI and CM chondrites. A comparison of the amino acid content of the Bennu regolith with previous carbonaceous chondrite studies will help in understanding the potential relationship of these meteorites to asteroid parent bodies. Asteroid Ryugu is a Cg-type asteroid that may preserve some of the most pristine material in the solar system and studies of its organic content and amino acid inventory will add to our knowledge of extraterrestrial organic formation, distribution, and preservation.

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# The origin and evolution of organic matter in the solar system: the amino acid content of interstellar ices and the primitive carbonaceous chondrite Paris

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The organic matter present in carbonaceous chondrites reflects the physical and chemical reactions that occurred in the interstellar medium, solar nebula, and/or on their parent bodies [1, 2]. It is possible that organic matter synthesized in the initial molecular cloud survived the protosolar disk phase, was incorporated into planetesimals that would later form comets and asteroids, and finally experienced (aqueous or thermal) alteration on the parent body of carbonaceous meteorites [3]. Therefore, laboratory produced interstellar ice analogues, as well as primitive carbonaceous meteorites are precious samples that allow studying key steps into the origin and evolution of organic matter in the solar system. Amino acids, as well as many other complex organic molecules may be formed from ultraviolet irradiation and thermo-processing of interstellar icy grains, accreted into the parent bodies of meteorites [4-6], and finally witness aqueous alteration, which seems to influence their distribution and relative abundance [7-11].

In this study, we have analysed the amino acid content of laboratory organic residues produced by simulated photo- and thermo-processing of icy mixtures [12]. These have been considered as analogues for the organic material synthesized in interstellar or circumstellar icy grains [13-17]. We have also analysed the amino acid content of one of the most primitive CM chondrites, the Paris meteorite [6]. This meteorite is one of the least aqueously altered CM chondrites analysed to date [18-23]. Our results show that Paris has the lowest relative abundance of  $\beta$ -alanine/glycine ( $0.15 \pm 0.02$ ), which is the smallest  $\beta$ -alanine/glycine ratio observed in CM chondrites [6]. The relative abundance of  $\beta$ -alanine/glycine increases with increasing aqueous alteration, from the CM2.7/2.8 Paris to the CM2.0 MET01070. The isovaline detected in the Paris meteorite is racemic (corrected D/L = 1.03). This is a good indication that aqueous alteration may be responsible for extending an initial L-enantiomeric excess (Lee) of isovaline [6], but not responsible for creating an isovaline asymmetry [24-31]. Furthermore, our data shows that the laboratory organic residues have relative distributions of 4-carbon amino acids in agreement with that of the Paris meteorite, and that the relative  $\beta$ -alanine/glycine ratio is similar to that of Paris [12]. The analysis of the soluble organic content of carbonaceous meteorites and laboratory organic residues analogue to interstellar ices helps to increase our knowledge on the origin and evolution of organic matter in the solar system. It also shows that interstellar ice evolution may be an important source for organic matter in the solar system. This helps to build links between the different contributions for the formation of complex molecules, i.e. interstellar precursors, solar nebula, the incorporation in asteroids, and finally meteorite parent body alteration.

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## Sugars and its related compounds in space and on the early Earth

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Sugars are essential components of life, employing as substrates in nucleic acid formation and working as energy resource in numerous biological reactions. The distribution of sugars, particularly bio-important pentoses and hexose, in space including the Earth would be important for the origin of life.

Carbonaceous chondrites contain many bio-important molecules such as amino acids and nucleobases [e.g., 1,2]. Thus, they were a source of building blocks of life on the prebiotic Earth. The detection of glucose, mannose, arabinose, and xylose by paper chromatography in carbonaceous and enstatite chondrites was originally reported in 1960's [3,4]. However, the paper chromatography has not sufficient resolution to identify any sugar isomers, and these reports were not clear proof on their extraterrestrial origin. Thus, a review concluded that the origin of these reported sugars were terrestrial contamination [5]. More recently, Cooper's group have intensively investigated sugars and their related compounds in Murchison and Mary carbonaceous chondrites. They found 3-carbon sugar, dihydroxyacetone, several sugar acids, and several sugar alcohols by gas chromatography/mass spectrometry (GC/MS) (Fig. 1) [6,7]. Some of the detected compounds were confirmed on those extraterrestrial origins by compound-specific carbon isotope analysis. However, the presence of meteoritic bio-important sugars remained unclear.

The formose-like reaction is a plausible process to form sugars in meteorite parent bodies, on interstellar dusts, and on the prebiotic Earth. In the Formose reaction, the condensation of formaldehyde forms numerous sugars, simultaneously. Ribose is an intermediate product of this reaction. However, characterization of the product "formose" remained insufficient so far, which causes ambiguity in the potential availability of sugars in space.

We developed a protocol to effectively extract sugars from mineral assemblages. Then, we found multiple sugars in carbonaceous chondrites with GC/MS. The carbon isotopic composition of individual sugars in meteorite extracts was determined by gas chromatography/isotope ratio mass spectrometry (GC/IRMS). For comparison, we analyzed the products of typical Formose reaction simulating meteorite parent bodies. Insoluble organic matter (IOM) was extracted from the same chondrites by demineralization with inorganic acids, and the carbon and nitrogen isotopic compositions of bulk chondrite and IOM were determined. These carbonaceous chondrites were also investigated by scanning electron microscopy (SEM) to evaluate the aqueous alteration levels. In this talk, we will present our preliminary results of these analyses for sugars in carbonaceous chondrites as well as in several experimental Formose reaction products, and will discuss the availability of sugars in space including Earth.

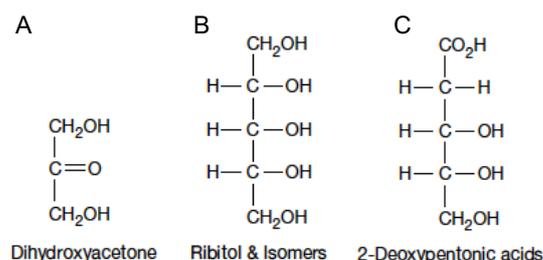


Fig. 1: Structures of sugar, sugar acids and sugar alcohols detected in meteorites. A) dihydroxyacetone, B) ribonic acid, and C) 2-Deoxypentonic acid. Cooper *et al.*, 2001.

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# Constraining Mineralogical Composition of Asteroid Ryugu with Ground-Based Observations

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In preparation for the arrival of the Japanese Space Agency's (JAXA) Hayabusa2 sample return mission to near-Earth asteroid (NEA) (162173) Ryugu, we took the opportunity to characterize the target with a ground-based telescope. We observed Ryugu using the SpeX instrument in Prism mode on NASA Infrared Telescope Facility (IRTF) on Mauna Kea, Hawaii, on July, 12 2016 when the asteroid was 18.87 visual magnitude, at a phase angle of 13.3°. The NIR spectra were used to constrain Ryugu's surface composition, determine meteorite analogs and study spectral affinity to other asteroids. We also modeled its photometric properties using archival data. Using the Lommel-Seeliger model we computed the predicted flux for Ryugu at a wide range of viewing geometries as well as albedo quantities such as geometric albedo, phase integral, and spherical Bond albedo. Our computed albedo quantities are consistent with results from Ishiguro et al. (2014). In previous work, Ryugu's visible spectrum revealed that it can be classified as a C-type object. In addition, not all previous ground-based observations of Ryugu detected the 0.7  $\mu\text{m}$  absorption feature due to the presence of phyllosilicates. Our spectrum of Ryugu has a broad absorption band at 1  $\mu\text{m}$ , a slope change at 1.6  $\mu\text{m}$ , and a second broad absorption band near 2.2  $\mu\text{m}$ , but no well-defined absorption features over the 0.8-2.5  $\mu\text{m}$  range. The two broad absorption features, if confirmed, are consistent with CO and CV chondrites. We computed the Reflectance Factor (REFF) of Ryugu at 550 nm, which is consistent with the reflectance measured for the CM and CI carbonaceous chondrite groups. Samples of CO and CV chondrites are usually brighter and less red sloped than Ryugu. It is interesting to note that recent work suggested space weathering could darken and redden the spectra of carbonaceous chondrites. Our spectrum of Ryugu is different from previously published spectra showing a more neutral spectral slope, however, this is not the only object with this kind of spectral shape. The shape matches very well those of NEA (85275) 1994 LY and Mars-crossing asteroid (316720) 1998 BE7, suggesting that their surface regolith have similar composition. With a semi-major axis of  $\sim 1.9$  AU, and NEA 1994 LY may come from the inner part of the main asteroid belt. Asteroid 1998 BE7, with a semi-major axis of  $\sim 3$  AU, probably formed far in the outer part of the main belt. The differences observed between the spectra of these asteroids could be explained by differences in composition, grain size, space weathering, and phase angle. We also compared the spectrum of Ryugu with that of main belt asteroid (302) Clarissa, the largest asteroid in the Clarissa asteroid family, suggested as a possible source of Ryugu by Campins et al. (2013). We found that the spectrum of Clarissa shows significant differences with our NIR spectrum of Ryugu. Our analysis shows Ryugu's spectrum best matches two CM2 carbonaceous chondrites, Mighei and ALH83100. Previous work suggested CM and CI carbonaceous chondrites are the most consistent with Ryugu's spectra. We expect the surface regolith of Ryugu to be altered by a range of factors including temperature, contamination by exogenic material, and space weathering, posing challenges to link spacecraft and ground-based data, and sample site selection.

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## 3- $\mu\text{m}$ SPECTROSCOPY OF WATER-RICH METEORITES AND ASTEROIDS: NEW RESULTS AND IMPLICATIONS

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**Introduction:** Ground-based observations of water-rich asteroids are important to constrain many questions related to the abundance and distribution of volatiles in the early Solar System, and to the evolution of many diverse Solar System bodies. Recent studies have revealed that several airless bodies, including the Moon and asteroid Psyche ([1], [2], [3], [4]), show spectral indications of hydration on their surfaces. Absorption features at  $\sim 3.0 \mu\text{m}$  are particularly indicative of aqueous alteration. These absorptions are likely due to hydroxyl and/or water-bearing materials (OH/H<sub>2</sub>O) (e.g., [5], [6]), but could also be due to surficial OH implanted from solar wind or exogenic sources like those seen on Vesta [7]. We are observing and studying 60 new water-rich asteroids in the 3- $\mu\text{m}$  region using NASA Infrared Telescope Facility (IRTF) and Gemini North telescopes, in addition to the 50 water-rich asteroids previously observed by [6] and [8]. We are also studying additional carbonaceous chondrite meteorites (e.g., CI, CM, CO, CV, CR, CH, and CB) by measuring their 3- $\mu\text{m}$  spectra under asteroid-like conditions to determine their mineralogical and spectral indicators. Applying these spectral analyses of carbonaceous chondrites to water-rich asteroids in the 3- $\mu\text{m}$  region has been challenging because chondrite spectra have generally been acquired in ambient terrestrial environments, and hence are contaminated by atmospheric water. In this work, however, chondrite IR reflectance spectra are measured under asteroid-like conditions (i.e., vacuum and elevated temperatures) to eliminate the adsorbed water that affected previous analyses. This investigation is important for matching the observed water-rich asteroids to specific chondritic groups for better understanding of the origin and evolution of our Solar System. Results from this work will also help analyze and characterize the returned carbonaceous samples from asteroids Bennu (OSIRIS-REx's target) and Ryugu (Hayabusa2's target), putting these returned samples into a wider perspective and broader Solar System context.

**Methodology:** Ground-based spectra of water-rich asteroids were measured using the long wavelength cross-dispersed (LXD: 1.9-4.2  $\mu\text{m}$ ) mode of the SpeX spectrograph/imager at the NASA IRTF and the cross-dispersed mode of the Near InfraRed Spectrograph (GNIRS) spectrometer at Gemini North, following the methodology of [6]. New 3- $\mu\text{m}$  bi-directional reflectance spectra (*incidence* = 15°, *emission* = 45°, *phase angle* = 60°) of carbonaceous chondrites (CVs, COs, and CIs) have been collected at the Johns Hopkins University Applied Physics Laboratory (JHU APL) under vacuum-desiccated conditions, following the methodology used in [9].

**Results:** [8] found that CM (and CI) chondrites are possibly the meteorite analogs for water-rich asteroids with the sharp 3- $\mu\text{m}$  band, attributed to phyllosilicates. The sharp

spectral group contains asteroids that are located in the  $2.5 < a < 3.3$  AU region. No meteorite match was found by [8] either for the rounded group, Ceres-like group, or asteroid Europa-like group. These three spectral groups are located farther from the Sun ( $3.0 < a < 4.0$  AU). Here we present new 3- $\mu\text{m}$  spectra of water-rich asteroids, including 212 Medea, 690 Wratislavia, 372 Palma, 259 Aletheia, 114 Kassandra, 701 Oriola, 360 Carlova, 747 Winchester, 386 Siegena, 356 Liguria 233 Asterope, 135 Hertha, 87 Sylvania, and 142 Polana. Asteroid Polana, which is the main asteroid in the New Polana Family [10], is thought to be the probable source of primitive near-Earth asteroids including Bennu and Ryugu [11]. The new 3- $\mu\text{m}$  spectra are grouped according to the classification scheme of [6]. We will also present new 3- $\mu\text{m}$  spectra of carbonaceous chondrites, which will be used to interpret ground-based, and eventually space-based, spectra of water-rich asteroids. We will then compare the new spectra of meteorites and asteroids to determine new possible matches on the basis of the 3- $\mu\text{m}$  band.

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## Hayabusa2 landing site selection (LSS) training: Summary report of scientific evaluation

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The Japanese C-type asteroid sample return mission, Hayabusa2, was launched on December 3, 2014. The spacecraft is scheduled to arrive at the near Earth asteroid Ryugu on July 2018. During its 18-month stay, remote-sensing observations will be carried out by the on-board instruments, Optical Navigation Camera (ONC), Near Infrared Spectrometer (NIRS3), Thermal Infrared Imager (TIR), and Light Detection and Ranging (LIDAR). Based on the observation data, the collection of the asteroid samples from three sites at maximum will be performed. We will carry out the landing site selection (LSS) within a month after the arrival to Ryugu, for the first touch down and for the release of MASCOT, a small hopping rover developed by DLR and CNES on October 2018.

It is therefore very important that scientists from remote sensing, MASCOT, and sample analyses are mingled to work out a landing site selection strategy by sharing the common picture of the multi-scale asteroid science. During this June-August 2017, we carried out the LSS training by using the asteroid Ryugu analog model “Ryugoid”. Beginning of shape modeling, the data products such as surface temperature, thermal inertia, grain sizes, visible and near infrared spectra, and spectral parameters (albedo, UV slope) were obtained from the Box A (at 20 km in altitude), Box C and mid-altitude (at 5 km in altitude) observations by TIR, ONC, NIRS3, and LIDAR teams. Then, six potential landing sites (zones A, B, C, D, D2, and E, in figure) were indicated by the system side. Based on the products, scientific evaluations (e.g., compositions and distributions of hydrate minerals, relative abundance of organic carbon, thermal metamorphism degree, space weathering degree, and number density of boulders) of these zones were conducted in order to prioritize the first landing site. This training has made us prepare for the actual LSS next year, to determine the most scientifically valuable site, that is, water-rich region.

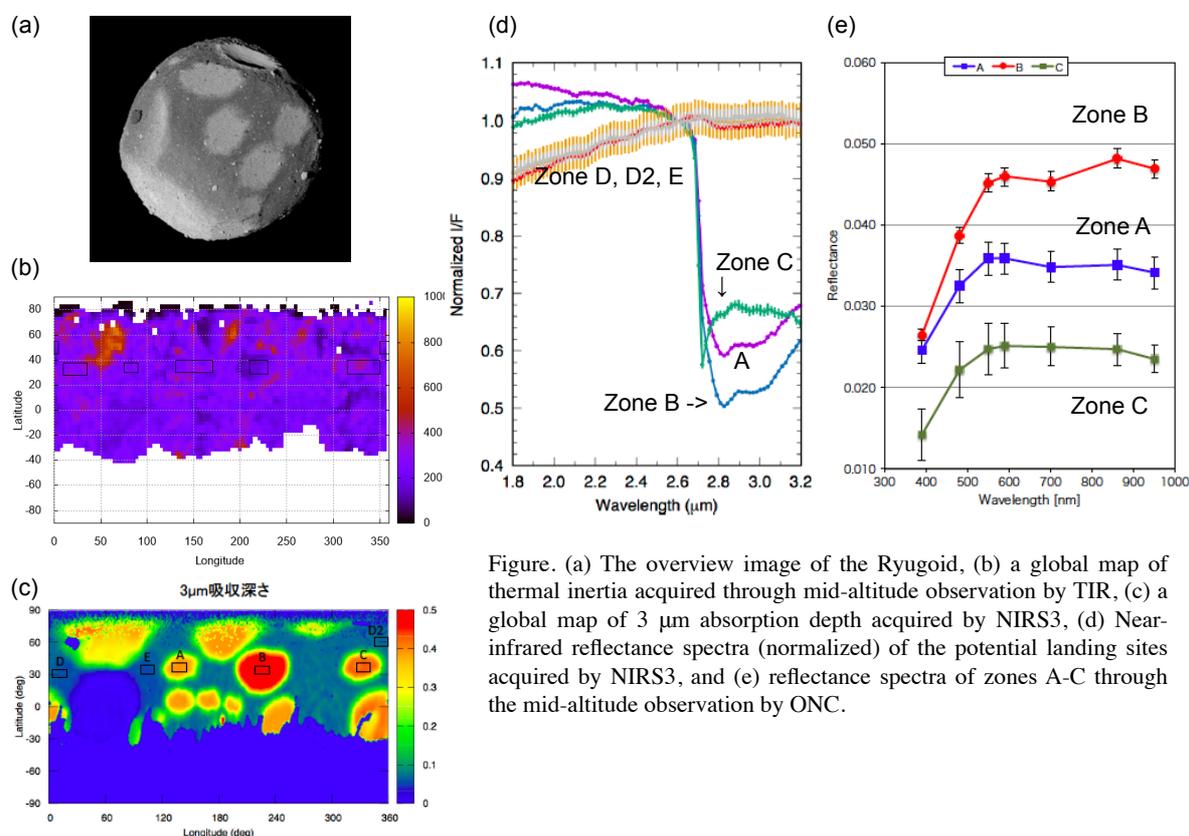


Figure. (a) The overview image of the Ryugoid, (b) a global map of thermal inertia acquired through mid-altitude observation by TIR, (c) a global map of 3 μm absorption depth acquired by NIRS3, (d) Near-infrared reflectance spectra (normalized) of the potential landing sites acquired by NIRS3, and (e) reflectance spectra of zones A-C through the mid-altitude observation by ONC.

## Measuring Shock Stage of Itokawa Regolith Grains by Electron Back-Scattered Diffraction and Synchrotron X-ray Diffraction

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We have been analyzing Itokawa samples in order to definitively establish the degree of shock experienced by the regolith of asteroid Itokawa, and to devise a bridge between shock determinations by standard light optical petrography, crystal structures as determined by electron and X-ray diffraction techniques [1,2,3,4]. We are making measurements of olivine crystal structures and using these to elucidate critical regolith impact processes. We use electron back-scattered diffraction (EBSD) and synchrotron X-ray diffraction (SXRD). We are comparing the Itokawa samples to L and LL chondrite meteorites chosen to span the shock scale experienced by Itokawa, specifically Chainpur (LL3.4, Shock Stage 1), Semarkona (LL3.00, S2), Kilabo (LL6, S3), NWA100 (L6, S4) and Chelyabinsk (LL5, S4). In SXRD we measure the line broadening of olivine reflections as a measure of shock stage. In this presentation we concentrate on the EBSD work. We employed JSC's Supra 55 variable pressure FEG-SEM and Bruker EBSD system. We are not seeking actual strain values, but rather indirect strain-related measurements such as extent of intra-grain lattice rotation, and determining whether shock state "standards" (meteorite samples of accepted shock state, and appropriate small grain size) show strain measurements that may be statistically differentiated, using a sampling of particles (number and size range) typical of asteroid regoliths.

Using our system we determined that a column pressure of 9 Pa and no C-coating on the sample was optimal. We varied camera exposure time and gain to optimize mapping performance, concluding that 320x240 pattern pixilation, frame averaging of 3, 15 kV, and low extractor voltage yielded an acceptable balance of hit rate (>90%), speed (11 fps) and map quality using an exposure time of 30 ms (gain 650). We found that there was no strong effect of step size on Grain Orientation Spread (GOS) and Grain Reference Orientation Deviation angle (GROD-a) distribution; there was some effect on grain average Kernel Average Misorientation (KAM) (reduced with smaller step size for the same grain), as expected. We monitored GOS, Maximum Orientation Spread (MOS) and GROD-a differences between whole olivine grains and sub-sampled areas, and found that there were significant differences between the whole grain dataset and subsets, as well as between subsets, likely due to sampling-related "noise". Also, in general (and logically) whole grains exhibit greater degrees of cumulative lattice rotation. Sampling size affects the *apparent* strain character of the grain, at least as measured by GOS, MOS and GROD-a. There were differences in the distribution frequencies of GOS and MOS between shock stages, and in plots of MOS and GOS vs. grain diameter. These results are generally consistent with those reported this year [5]. However, it is unknown whether the differences between samples of different shock states exceeds the clustering of these values to the extent that shock stage determinations can still be made with confidence. We are investigating this by examination of meteorites with higher shock stage 4 to 5.

Our research will improve our understanding of how small, primitive solar system bodies formed and evolved, and improve understanding of the processes that determine the history and future of habitability of environments on other solar system bodies. The results will directly enrich the ongoing asteroid and comet exploration missions by NASA and JAXA, and broaden our understanding of the origin and evolution of small bodies in the early solar system, and elucidate the nature of asteroid and comet regolith.

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# Transmission Electron Microscopy of Plagioclase-Rich Itokawa Grains: Space Weathering Effects and Solar Flare Track Exposure Ages.

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## Introduction

Limited samples are available for the study of space weathering effects on airless bodies. The grains returned by the Hayabusa mission to asteroid 25143 Itokawa provide the only samples currently available to study space weathering of ordinary chondrite regolith. We have previously studied olivine-rich Itokawa grains and documented their surface alteration and exposure ages based on the observed density of solar flare particle tracks. Here we focus on the rarer Itokawa plagioclase grains, in order to allow comparisons between Itokawa and lunar soil plagioclase grains for which an extensive data set exists [1].

## Samples and Methods

Four plagioclase-bearing grains from the JAXA collection were allocated for this study: RB-QD04-0058, RB-QD04-0074, RB-QD04-0090, and RA-QD02-0157. We embedded the particles in low viscosity epoxy and used an ultramicrotome to partly section three of the particles, placing the sections on TEM grids with continuous amorphous carbon support films. Sectioning of the fourth particle is underway. For two of the particles, the epoxy surrounding the particle was trimmed away on three sides to enable further sectioning utilizing a focused ion beam (FIB) instrument [2] (FEI Quanta 3D). The microtome and FIB sections were analyzed in a JEOL 2500SE scanning and transmission electron microscope (STEM) equipped with an energy-dispersive x-ray (EDX) spectrometer optimized for nanometer-scale quantitative x-ray mapping. Brightfield and darkfield images were acquired using both conventional TEM and STEM imaging. Solar flare particle tracks were imaged in STEM mode, and observed track densities were converted to apparent surface exposure ages using our recent calibration [3].

## Results and Discussion

RB-QD04-0090 is an angular  $\sim 40$   $\mu\text{m}$  grain of twinned albitic plagioclase. No shock features are observed. EDX analyses give a composition of  $\text{Ab}_{85}\text{Or}_{5}\text{An}_{12}$ . Solar flare particle tracks occur with a density of  $\sim 5 \times 10^9$   $\text{cm}^{-2}$  which indicates a surface exposure of  $\sim 110,000$  y (Figure 2). The particle is surrounded by a thin continuous amorphous rim  $\sim 50$  nm wide. Quantitative EDX mapping shows that the rim consists of two layers, an inner amorphous layer  $\sim 20$  nm thick with the same composition as the underlying crystal-line host, and an outer amorphous layer  $\sim 30$  nm thick that is Fe-rich and compositionally distinct from the underlying layer and host grain (Figure 1). We interpret the inner layer as a solar wind amorphized layer, and the outer layer as a vapor deposit. Vapor deposits of this thickness are unusual for Itokawa grains, because most grains are typically dominated by solar wind damage [1, 3, 4]. Nanophase Fe grains are present as a thin outermost layer. A few adhering grains (also plagioclase) are attached to the grain surface. In addition, there are numerous  $\sim 0.1$ - $0.3$   $\mu\text{m}$  crystals of NaCl on the grain surface. We also observed a thin continuous rim of NaCl surrounding the grain.

RB-QD04-0074 is an  $\sim 32$   $\mu\text{m}$  irregularly-shaped polymineralic grain. The grain contains major olivine (Fo65), twinned albite ( $\text{Ab}_{85}\text{Or}_{2}\text{An}_{12}$ ), and minor orthopyroxene ( $\text{En}_{65}\text{Fs}_{33}\text{Wo}_2$ ). The olivine and orthopyroxene are more Fe-rich than typical Itokawa grains [5] but consistent with literature data for LL chondrites [6]. The orthopyroxene contains a high density of stacking faults and the olivine contains numerous planar dislocations along (100). The planar dislocations in the olivine grain are consistent with those that develop due to moderate shock. The observed track density  $6 \times 10^7$   $\text{cm}^{-2}$  (corresponding to counting 6 tracks in  $10$   $\mu\text{m}^2$ ) is very low and is approaching the limit that can be reliably counted in a grain this large by TEM methods. The track density implies a short surface exposure of  $\sim 2000$  y. The plagioclase shows a solar wind amorphized outer layer  $\sim 10$  nm wide. The olivine grain appears undamaged and does not show a nanocrystalline solar wind damaged rim like those on olivine-rich Itokawa grains [7]. RB-QD04-0074 is over an order of magnitude younger than the other olivine and plagioclase grains we have analyzed and was either freshly excavated from greater depth in the Itokawa regolith, or possibly had an origin as a relatively fresh fragment of a larger grain due to regolith gardening. This grain also shows surface adhering NaCl particles. We had not previously detected NaCl particles on previous Hayabusa samples analyzed in our lab. Noguchi et al. [8] detected NaCl and KCl particles on Itokawa grains but were unable to determine whether they were indigenous or possible contaminants.

RA-QD02-0157 is an angular ~38  $\mu\text{m}$  grain dominated by albitic plagioclase and minor FeS and olivine. FIB sectioning is underway and here we report preliminary observations from ultramicrotome thin sections. The plagioclase shows twinning and is compositionally similar to the other albite grains in this study. We have not observed solar flare tracks in this particle to date, although there appears to be a thin amorphous layer (<10 nm) that likely represents solar wind damage. Analysis of a FIB section will provide a better constraint on exposure age of this grain. A small FeS grain adhering to the surface shows a damaged, outer layer consistent with our previous work on solar wind damaged sulfide grains in Itokawa samples.

### Comparison to Lunar Plagioclase

We have previously established a relationship between the width of solar wind damaged rims on lunar plagioclase and olivine, and their surface exposure age based on solar flare particle track densities [1]. Although large compositional differences exist between the albitic Itokawa plagioclase grains and the dominantly Ca-rich plagioclase in lunar soils, the solar wind damaged rim widths in Itokawa grains follows the trend for lunar plagioclase. The Itokawa grains show space weathering features typical of immature lunar soil grains.

### Conclusions

We analyzed the space weathering features on three Itokawa plagioclase-bearing grains. Particles RA-QD04-0074 and RA-QD02-0157 are relatively fresh with little surface modification from solar wind damage. The low track density for -0074 suggests a surface exposure age of ~2000y. Particle RA-QD04-0090 has a much longer surface exposure (~110,000 y) and corresponding surface alteration including a 30 nm thick vapor deposit overlying a solar wind damaged layer.

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### Acknowledgement

We thank JAXA for allocating the particles analyzed in this study. This work was supported by a NASA LARS grant (LPK).

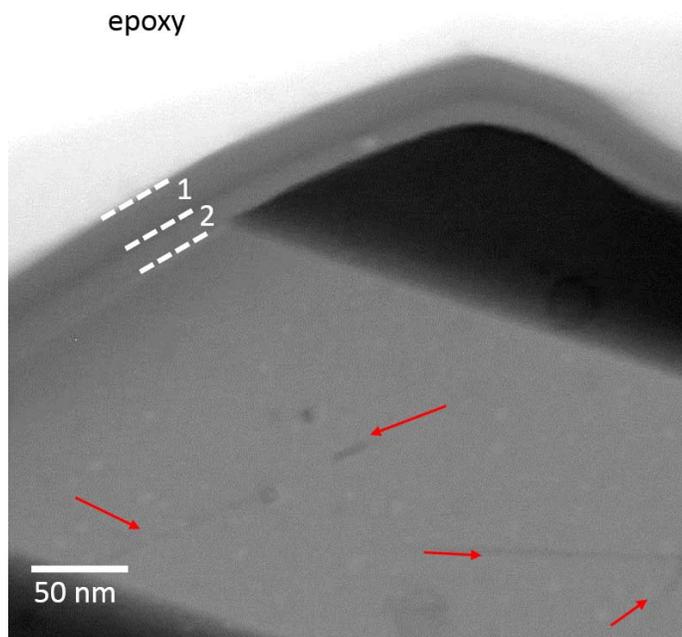


Figure 1. A brightfield STEM image from a FIB section of particle RA-QD04-0090 showing twinning in the host grain, solar flare particle tracks (red arrows), and a space-weathered rim consisting of two distinct layers, a vapor-deposited layer (1) and a solar wind damaged layer (2).

# Microstructures of iron sulfide of Itokawa particles

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## Introduction:

Space weathering has been referred to describe the collective processes that modify the optical properties, chemical compositions, and structures of materials on the surfaces of airless Solar System bodies [1]. Hayabusa spacecraft touched down to a S-type near-Earth asteroid 25143 Itokawa and recovered surface regolith particles, which are consistent with minerals contained in LL5-6 ordinary chondrite [2]. Analysis of Itokawa particles revealed nanoparticle-bearing rim, which are probably the major cause of alteration of reflectance spectra of Itokawa [3]. Prior to Hayabusa mission, the Near-Earth Asteroid Rendezvous (NEAR) mission's orbital study of S-type asteroid Eros revealed that change of reflectance spectra has been developing on Eros's surface similar to Itokawa's surface [4]. NEAR also discovered that Eros's surface appears to be strongly depleted in sulfur compared to ordinary chondrite [4]. However, sulfur depletion has not been obvious on Itokawa from remote-sensing observation and sample analysis so far. Sulfur in Itokawa samples is primarily bound in the form of iron sulfide [1], we investigated microstructures of iron sulfide of Itokawa particles in order to understand behavior of sulfur on airless bodies.

## Experiments:

The four Itokawa particles were fixed with a 5  $\mu\text{m}$ -diameter carbon fiber using glycol phthalate. The surface morphologies of the Itokawa particles were observed using a field-emission scanning electron microscope (Hitachi, SU6600) equipped with an energy-dispersive X-ray (EDX) spectroscopic detector (Bluker XFlash FladQUAD 5060FQ) at the Institute of Molecular Science, Japan. Regions of interest (ROI) were selected based on the FE-SEM observation, and electron-transparent sections including particle surface were prepared from the ROI using a focused ion beam (FEI, Helios G3 CX) at Kyoto University, Japan. The sections were observed using a field-emission transmission electron microscope (JEOL, JEM-2100F) equipped with an EDX system (JED-2300T) at Kyoto University.

## Results:

Iron sulfides are visible as inclusions of olivine grains, adhered particles, and melt-splashes on the Itokawa particles. From surface observation using FE-SEM, we found needle-like structures protruding from the iron sulfide surfaces (Fig.1ab). The lengths of the needles range from several tenth nm to 1  $\mu\text{m}$ . The needles often develop on porous iron sulfide surfaces (Fig.1ab). SEM-EDX analysis shows that the needles are composed of iron and they are deficient in sulfur (Fig.1c). The needles often contain minor nickel. So far, we lifted out FIB sections from a melt-splash of iron sulfide where needle-like structures develop on its surface. The melt-splash is an immiscible mixture of silicate and iron sulfide, covering an olivine grain. Fig. 1 shows a cross section of the melt splash of 50 nm in thickness including the needles. Elemental maps by TEM-EDX analysis clearly shows that the needle consists of iron and lacks in sulfur (Fig.1d). A TEM-selected area electron diffraction (SAED) pattern of the needle (Fig. 1f) indicates that the needle has a structure of body-centered cubic iron ( $\alpha$ -iron). The iron sulfide layer is composed of amorphous structures, except for regions nearby the iron needle. Crystalline pyrrhotite structure is developed in the vicinity of the iron needle. Beneath the iron sulfide layer, vesicular damage rims are developed on olivine surface, which might have been formed due to the implantation of solar wind hydrogen and helium [3]. The existence of vesicular rim indicates that olivine surface has been exposed to the sun over a period of time, before the melt splash attached to the olivine surface.

## Discussions:

Remarkable surface morphology of iron sulfide such as iron needles have not been reported in previous analysis of Itokawa particles. On the other hand, prior observation of pyrrhotite grain of Itokawa particles reported that the outer 10-nm-wide zone is sulfur-depleted, including metallic iron grains (<5 nm) [5]. Mineral surfaces exposed to the space environment can be modified through space weathering by solar wind irradiation and impacts of micrometeorites. In previous studies, the feasibility of alteration of iron sulfide by space weathering effects have been examined experimentally [6, 7]. Laboratory studies on the chemical alteration of troilite by 4keV He ions simulating exposure to the solar wind and by nanosecond laser pulses simulating evaporation by micrometeorite impact showed that sulfur is depleted from troilite by these both effects [6] and iron layer of 2-3 nm in thick is identified after He ion implantation [7]. However, these experiments have not produced metallic iron needles as observed in this study. Prior experiments of heating troilite at near its eutectic temperature under  $\text{H}_2$  gas flow showed that sulfur evaporates from troilite and iron residue is formed through incongruent evaporation [8]. This experiment showed that iron exists as irregular rods or sheet of micron meter in size. This could suggest that heating events such as meteoroid impacts together with implantation of solar wind hydrogen cause metallic iron needles on iron sulfide of Itokawa particles.

These heating events and ion implantation may lead to preferential loss of sulfur from Itokawa. X-ray fluorescence observations of Itokawa by the Hayabusa spacecraft did not find evidence for a large sulfur depletion on this S-class asteroid, as seen on Eros, though errors are large due to low solar activity during the orbital phases of the Hayabusa mission [9]. The microstructures of iron sulfide observed in this study could suggest that sulfur depletion processes are ongoing on Itokawa.

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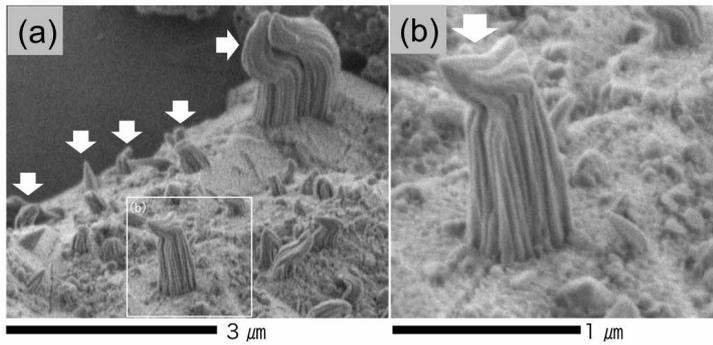
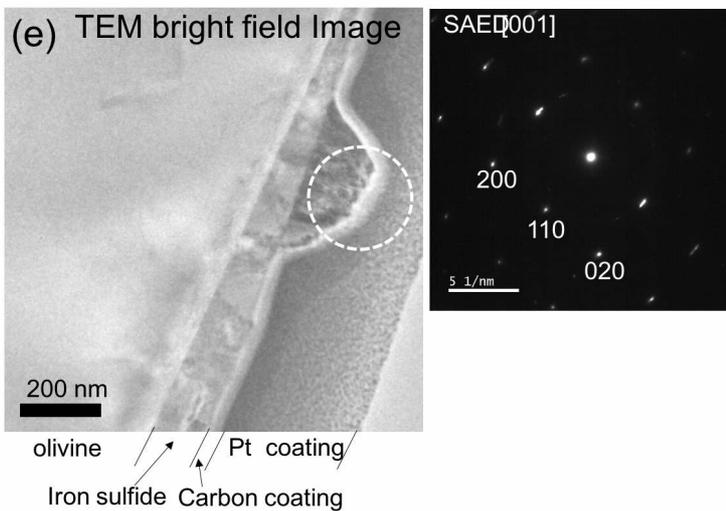
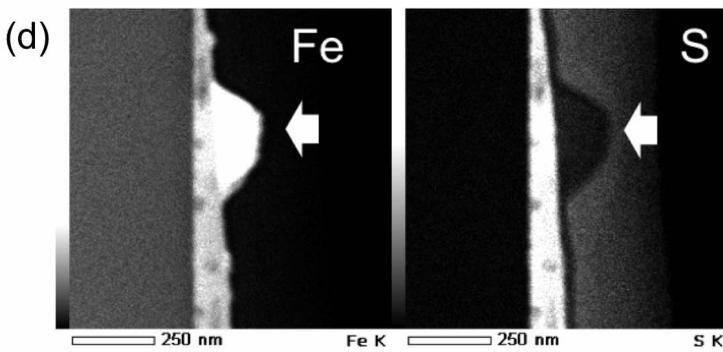
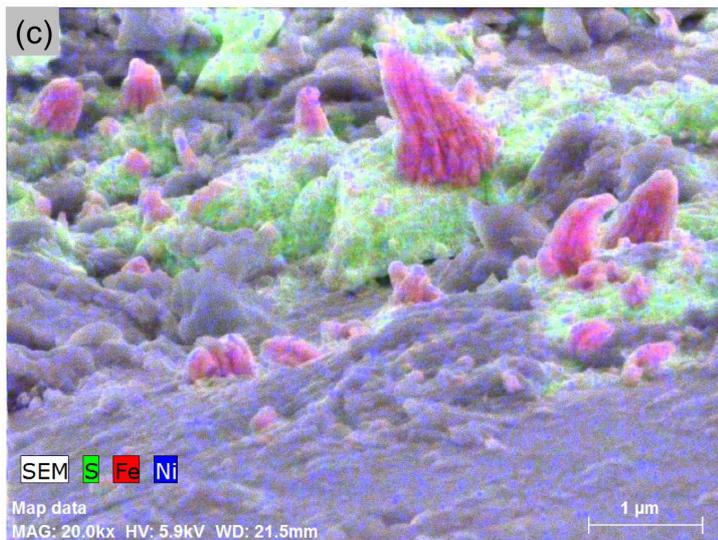


Figure 1 (a) (b) Secondary electron images of iron sulfide. Needle-like structures are indicated by arrows. (c) A SEM-EDX image of iron sulfide grains on olivine surfaces. (d) STEM-EDX images of a cross section of splash melt on olivine particle. A needle-like structure is indicated by arrows. (e) A TEM image and A SAED pattern of a needle-like structure.



## FTIR Micro-tomography of five Itokawa Particles

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Primitive extra-terrestrial materials (asteroidal and cometary particles, meteorites, IDPs) are characterized by a large mineralogical and compositional heterogeneity at different scales (from nm to mm) [1], which witnesses the complexity of the pre-accretional (solar nebula) and post-accretional (parent bodies) processes undergone by the small bodies of our solar system [2]. This heterogeneity has been observed by different techniques such as infrared (IR) micro spectroscopy mapping which is a powerful tool as it is (a) non-destructive and allows (b) comparison with astronomical observations of primitive Solar System small bodies (asteroids, comets, TNOs) [3] and (c) access both to the mineral and carbonaceous phases.

Thanks to Focal Plane Array (FPA) detector, 3D hyperspectral micro-tomography, can be performed to access structural information on intact samples [4, 5]. So far, this technique has never been applied to Hayabusa-1. Here, we will present the first 3D infrared reconstruction of five particles of Itokawa (RA-QD02-0214, RA-QD02-0223, RA-QD02-0232, RA-QD02-0156 and RB-QD04-0046). The FTIR micro analyses are performed at the SMIS beamline of the Synchrotron SOLEIL using a FPA detector with its Globar intern source. It is complementary to the X-ray micro-tomography previously performed on Hayabusa-1 particles [6]. Novel numerical methods have been developed to deal with a huge quantity of hyperspectral infrared data and we were able to obtain the 3D spatial distribution of chemical/mineralogical components (low/high calcium pyroxene, olivine, and plagioclase).

Another analysis was performed on grains of the Paris meteorite, one of the most primitive carbonaceous chondrite [7], to study the spatial correlation between the organic and mineral phases at scales down to  $\sim 3 \mu\text{m}$ . X-rays tomography was also performed on the same Paris particles, at the PSICHE beamline of the synchrotron SOLEIL, to obtain complementary information about the physical properties of the grains (shape, fractures, porosity ...). By combining X-ray and FTIR data we could obtain a physico-chemical description of precious grains in a non-destructive way and thus gives information about the formation and evolution of asteroids.

Performing FTIR micro-tomography on extraterrestrial samples rich in organic matter, is an important step in view of the sample return of dust particles from carbonaceous asteroid Ryugu by the Hayabusa-2 mission. In the sequence of analyses, micro-FTIR 3D spectral imaging coupled with X-rays tomography can provide a first, powerful non-destructive characterization of whole grains, in order to identify areas of interest and provide useful information before subsequent destructive analyses.

### Acknowledgments

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## Asteroid 25143 Itokawa Dust Particles: Mineralogy and Chondrite Affinities

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In the third international announcement of opportunity (AO3) for Hayabusa mission sample investigation, we received three dust particle samples. Two specimens are polished sections of post-analyzed particles embedded in resin: RA-QD02-0011-02 (~30  $\mu\text{m}$ ) and RA-QD02-0048 (~20  $\mu\text{m}$ ) with Au- and C-coatings, respectively (Figure 1). The third sample is a pristine particle, RB-CV-0083 (~95  $\mu\text{m}$ ). Particle RA-QD02-0011-02 was originally described to be mainly composed of olivine, low-Ca pyroxene, high-Ca pyroxene, and plagioclase [1-4]. In this study, the morphology and composition of the particles were inspected by means of (1) field emission scanning electron microscopy (FESEM), and associated energy-dispersive X-ray microanalysis (EDS) and electron back-scattered diffraction (EBSD) using an Hitachi SU-70 with Schottky type field emission gun, and (2) micro-Raman spectrometry at the Planetary and Space Science Centre (PASSC), University of New Brunswick, Canada.

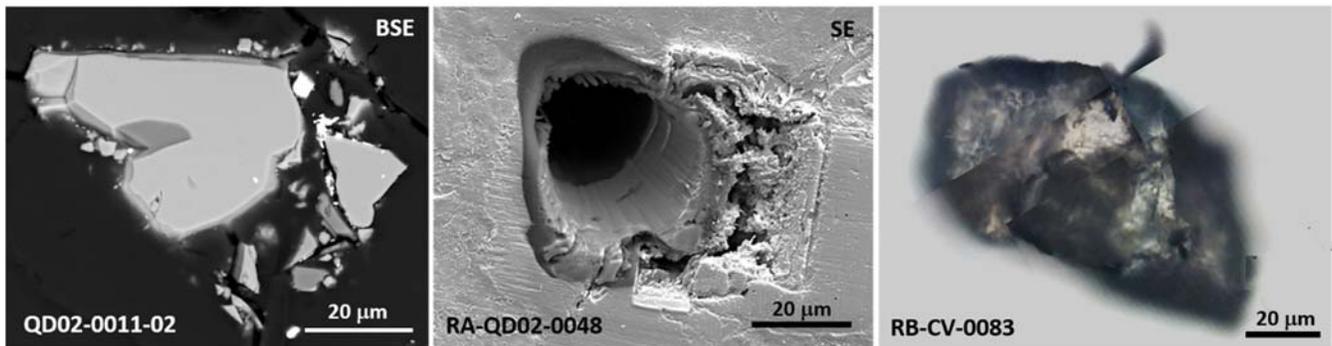


Figure 1. The three assigned Itokawa dust particles RA-QD02-0011-02 (~30  $\mu\text{m}$ ), RA-QD02-0048 (~20  $\mu\text{m}$ ), and RB-CV-0083 (~94  $\mu\text{m}$ ) provided by the Japan Aerospace Exploration Agency (JAXA) Hayabusa asteroidal sample return mission for this study.

The particles were collected from the surface of the S-type asteroid 25143 Itokawa. The particles comprise olivine, pyroxene and plagioclase. Fe-Ni metal, troilite (FeS), and chromite are also present. Energy dispersive spectrometry reveals that the olivine is  $\text{Fo}_{70}$ , and the plagioclase is  $(\text{Ab}_{81}\text{An}_{13}\text{Or}_6)$ . The plagioclase is interstitial to the olivine. The EBSD pattern of the  $(\text{Mg,Fe})\text{SiO}_4$  phase in RA-QD02-0011-02 matches well with the pattern of the orthorhombic crystal structure of forsterite with space group *Pbmn*. The unit cell dimensions are  $a = 4.76 \text{ \AA}$ ,  $b = 10.21 \text{ \AA}$ ,  $c = 5.98 \text{ \AA}$ ,  $\alpha = 90.0^\circ$ ,  $\beta = 90.0^\circ$ ,  $\gamma = 90.0^\circ$  (Figure 2a). Raman analysis of the olivine reveals high intensity Raman bands at 819 and 851  $\text{cm}^{-1}$ , with a Raman band calculated  $\text{Fo}$  number of 70 (Figure 3a). In addition, the  $(\text{Na,K,Ca})(\text{AlSi})_4\text{O}_8$  phase next to olivine yields a typical EBSD pattern of amorphous material (Figure 2b). Raman analysis of the plagioclase reveals a broad band of amorphous material with an intense Raman band of crystalline phase albite/oligoclase. Both EBSD and the Raman results suggest that plagioclase was partially transformed to maskelynite (feldspathic glass). Intense Raman bands at 678, 659, 334 and 1006  $\text{cm}^{-1}$  of orthopyroxene were obtained from RB-CV-0083. A cluster of forsterite ( $\text{Fo}_{68.7}$ ), augite and plagioclase ( $\text{Na}_{0.81}\text{Ca}_{0.12}\text{K}_{0.06}(\text{Al,Si})_4\text{O}_8$ ) present at the rim of the particle. A microcrystal (~5  $\mu\text{m}$  diameter) of rounded, unzoned forsterite ( $\text{Fo}_{69.5}$ ) with a nano-lath of albite/oligoclase (~1.0  $\mu\text{m} \times 500 \text{ nm}$ ) occurs in dust particle RB-CV-0083. The  $\text{Mg}/(\text{Mg}+\text{Fe}+\text{Ca})$  ratio in pyroxene based on Raman band recalculation (678 and 334  $\text{cm}^{-1}$ ) is 0.7 ( $\text{En}_{70}$ ) (Figure 3b), which is in good agreement with the EDS results ( $\text{W}_{0.3}\text{En}_{7.3}\text{Fs}_{2.4}$ ). The olivine and orthopyroxene compositions are consistent with those of an LL4-6 chondrite. The presence of maskelynite suggests that the particles experienced shock metamorphism. The compositional homogeneity of olivine and the development of plagioclase indicate that the petrologic type of Itokawa dust particles is derived from a highly equilibrated chondrite. Our study confirms that the analyzed Itokawa dust particles are from a shocked equilibrated LL4-6 chondrite that now forms part of the asteroid's regolith. The source of the dust particles remains conjectural in that they could be from fragmented projectiles that impacted Itokawa, or from excavated material from within Itokawa, which itself is probably an assemblage of multiple asteroid components. The presence of maskelynite strongly suggests that the asteroid experienced shock impact during its evolution.

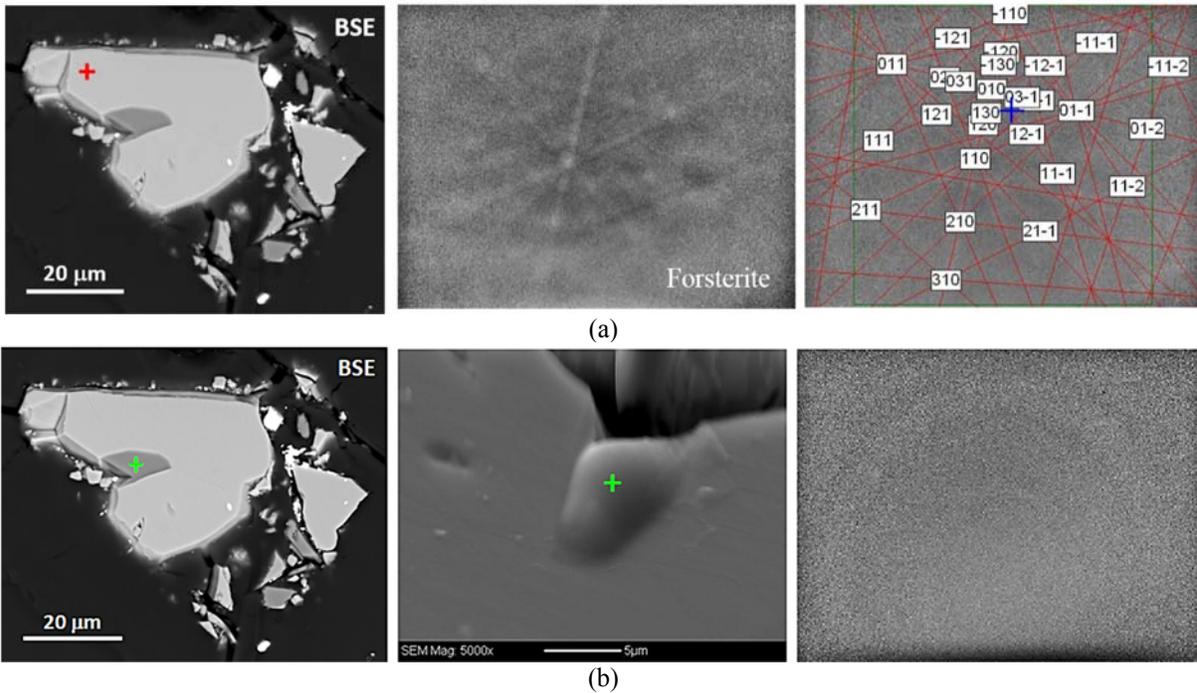


Figure 2. (a) The EBSD pattern of the (Mg,Fe)SiO<sub>4</sub> phase in RA-QD02-0011-02 matches well with the pattern of the orthorhombic crystal structure of forsterite (*Pbmm*) with unit cell dimensions  $a = 4.76 \text{ \AA}$ ,  $b = 10.21 \text{ \AA}$ ,  $c = 5.98 \text{ \AA}$ ,  $\alpha = 90.0^\circ$ ,  $\beta = 90.0^\circ$ ,  $\gamma = 90.0^\circ$ . (b) Electron backscattered diffraction patterns (EBSD) of (Na,K,Ca)AlSi<sub>3</sub>O<sub>8</sub> phases shows an amorphous EBSD diffraction pattern in the absence of Kikuchi bands.

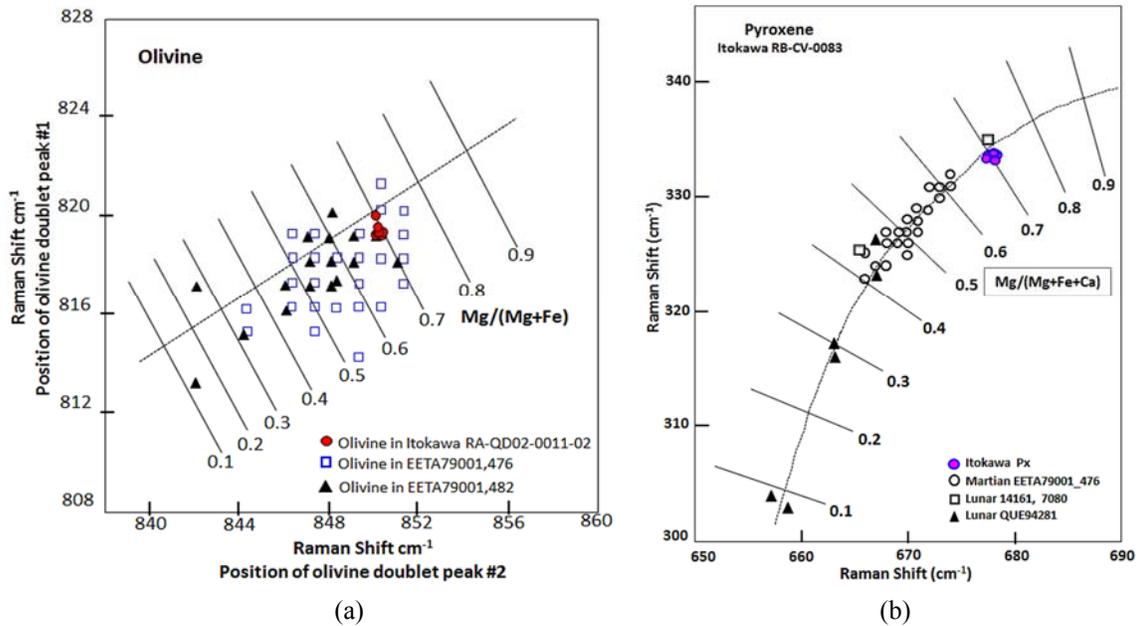


Figure 3. (a) The Raman peak positions at 851 and 819-820  $\text{cm}^{-1}$  of olivine in Itokawa sample RA-QD02-0011-02 (red dots) are plotted on a diagram of peak positions of its characteristic Raman modes of olivine [5]. The data points fall along the calibration line suggesting the Mg/(Mg+Fe) value for the Itokawa olivine  $\sim 0.7$  (Fo<sub>65-70</sub>). (b) The data for a pair of peak positions of characteristic Raman modes (678 and 334  $\text{cm}^{-1}$ ) for orthopyroxene from RB-CV-0083 are plotted on the curve (pink dots), which corresponds to Mg/(Mg+Fe+Ca) molar fraction in pyroxene values of 0.7 (En<sub>70</sub>) [6].

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## Electrical properties of Itokawa grains returned by Hayabusa

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Although a wealth of data exists on the properties of lunar regolith samples returned by Apollo missions e.g. [1,2] as well as investigations on terrestrial minerals, no such experimental data have yet been collected on asteroids material. In this study we present the measured secondary electron emission characteristics from areas of samples RA-QD02-0126-02 and RA-QD02-0136-14 [3] under electronic irradiation within the range 200eV to 5keV. Such measurements are related to surface structure, orientation and mineralogy, and compared to reference measurements including single grains and powders of reference materials of high purity, as well as terrestrial minerals and planetary analogs (see example Figure 1). In addition we observe the build-up of local electric field patterns arising from surface electrostatic charging in relation with grains morphology. Consequences on our understanding of regolith properties and electrostatic effects on planetary regolith will be discussed.

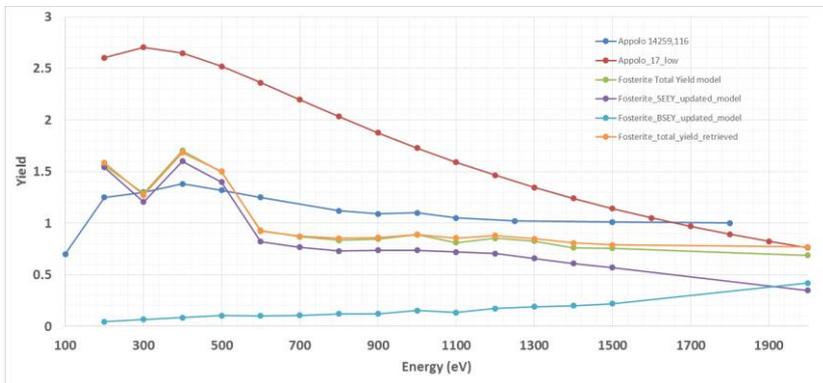


Figure 1: Secondary emission yields measured from Fosterite grains

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# Particle track densities in olivine of the heated Jbilet Winselwan CM2 chondrite: Constraints on regolith heating?

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Sample-return missions underway to the near-Earth objects 101955 Bennu (OSIRIS-REx) and 162173 Ryugu (Hayabusa 2) are expected to return surface regolith from two primitive C-group asteroids for laboratory study. Spectroscopically the C-group asteroids share similarities with CI and CM chondrites and are likely parent bodies of these meteorite groups. Material returned from the Moon and S-type asteroid 25143 Itokawa has shown that phenomena related to space weathering are well-recorded on the surface of silicate grains [1]. The degree (or maturity) of space weathering can potentially provide insights into the evolution of regoliths and, therefore, shed light on the dynamical evolution of near-Earth asteroids and their orbits [2,3,4]. Olivine is a good candidate for comparative taxonomy of space weathering due to its wide-spread occurrence in lunar and asteroidal samples and its experimentally extensively studied properties. If C-group asteroids are indeed related to CI and CM chondrites, olivine is expected to be a significant mineral in their regoliths. However, aqueous and thermal alteration processes recorded in CI and CM chondrites potentially leave morphological and chemical signatures on mineral surfaces, onto which space weathering would be superposed. This motivated us to investigate olivine grains of the Jbilet Winselwan (JW) meteorite, a moderately heated (tentatively <500 °C) CM2 chondrite [5]. In particular, we try to understand how olivine grains and the phyllosilicate mineralogy of JW can be used to constrain the heating event, which may have taken place in a number of different settings, e.g., deep in the CM2 parent body, in the regolith of a rubble-pile asteroid, or during the meteoroid stage of JW's travel towards the Earth.

**Material and Methods:** A 37.6 gram fragment of JW was sliced using a diamond wire saw and interior slices were used to produce two polished petrographic sections (~20×30 mm<sup>2</sup>) and cuboidal subsamples (~10×7×7 mm<sup>3</sup>). The cuboids were subjected to 100 to 150 cycles of freeze-thaw disaggregation in high-purity water. After drying, olivine crystals were separated by hand-picking and mounted onto SEM stubs or epoxy-embedded and polished. The grain mounts and polished petrographic sections were studied by field-emission SEM. The polished grain mounts were etched in WN solution in order to reveal damage tracks produced by ionizing, high-energy particles [6].

**Results and Discussion:** SEM imaging of the JW petrographic sections indicates subtle textural heterogeneities, most evident by variations in the abundance of serpentine/tochilinite-like aggregates. There is no obvious brecciation as seen in other CM2 chondrites [7] and specimens of JW [8]. Many components (dominantly chondrules) are surrounded by fine-grained rims, and the general texture resembles a primary accretionary rock [7]. The freeze-thaw disaggregated material is a black, non-cohesive powder (~80% <100 μm, ~50% <50 μm).

Euhedral to subhedral olivine crystals are optically prominent objects in the powder. The hand-picked olivine grains have median sizes of ~240 μm and a size range of 100 to 600 μm. Comparison with the petrographic sections suggests that the larger grains often occur as single grains within the meteorite. The smaller ones are most probably derived from porphyritic chondrules. The surface morphologies show a large diversity and can be subdivided into 'as-grown' crystal surfaces and fractured surfaces. Pristine surfaces are smooth and featureless, fresh fracture surfaces are typically characterized by step-like hackle marks. Altered surfaces have developed significant roughness through dissolution and the formation of secondary mineral scales. Such features superposed on surfaces with hackle marks suggest that fracturing had occasionally occurred before aqueous alteration.

We have studied a total of 81 olivine grains from three interior cuboids of JW for particle tracks, and etching has revealed tracks in 65 of them. In all cases the track densities are <5×10<sup>4</sup> tracks/cm<sup>2</sup> (Fig. 1), and the median is ~9400 tracks/cm<sup>2</sup> (~6500 tracks/cm<sup>2</sup>, if upper limit track densities for track-free grains are considered). The maximum track densities found in two grains are approximately consistent with the background track densities due to galactic cosmic rays (GCR) in typical CM2 chondrites [7]. However, the median values are much lower than typical GCR background track densities. The absence of brecciation and track-rich grains (>10<sup>6</sup> tracks/cm<sup>2</sup>, from irradiation by solar flare ions) indicates that the material of our JW specimen was never exposed in the upper few millimeters of a regolith. This is corroborated by the absence of solar wind noble gases in other samples of JW [9]. However, JW's unusually long Neon exposure age of 6.6±1.7 Ma [9] and the very low GCR track count suggests that GCR tracks may have been partially annealed by the, so far unidentified, heating event.

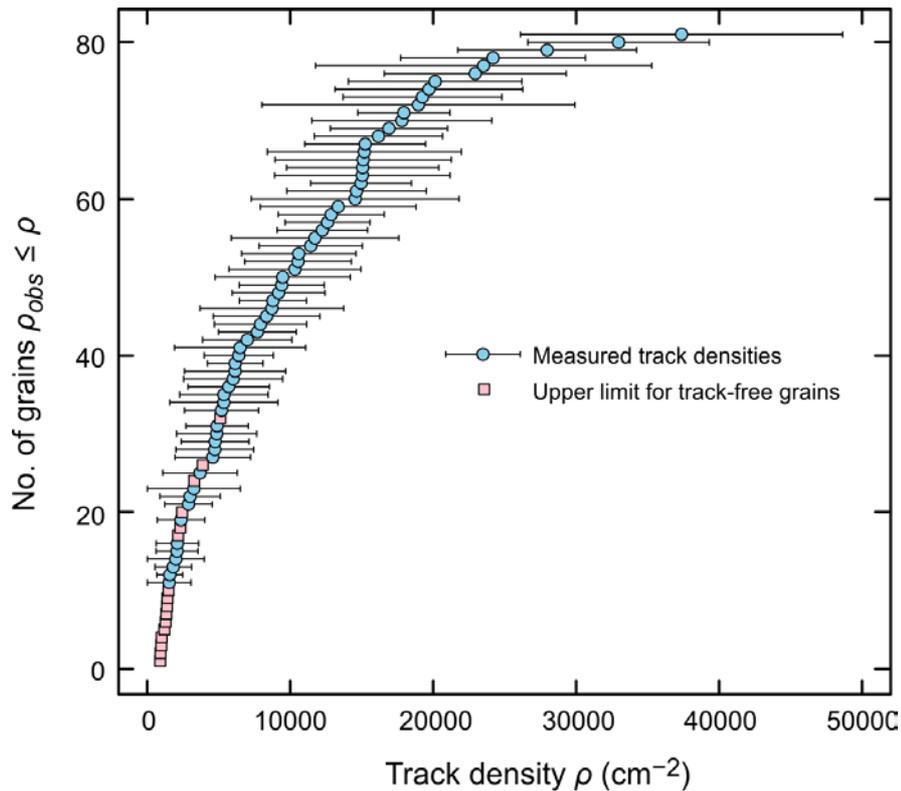


Figure 1. Cumulative plot of the particle track densities in Jbilet Winselwan olivines.

If JW was heated deep within its parent body, then GCR tracks and GCR-produced neon should have been acquired consistently during the meteoroid stage, unless the meteoroid that delivered JW to Earth was very large, and our specimen was deeply shielded within. The freshness of most JW specimens and the total known mass of JW meteorites of less than 10 kg (e.g., compared to >100 kg of Murchison) rule this possibility somewhat unlikely. Alternatively, JW may have been heated during a regolith residence or its meteoroid stage, e.g., by solar irradiation at low perihelion distances. If indeed solar heating can be made responsible for the mineralogical changes observed in JW (and possibly other heated CM and CM-like chondrites [10]), the implications for our understanding of space weathering phenomena in returned samples would be large, as heating and annealing may alter the exposure record of space-weathered grains (e.g., [3]).

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# Carbon isotopic ratios of calcite grains in the LAP 031166 CM chondrite: Implications for possible link between CM and cometary ices.

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**Introduction:** Carbonate minerals are ubiquitous in CM chondrites, which formed by aqueous alteration in the CM chondrite parent body. Previous studies have shown that C isotopic ratios of CM carbonates are highly variable at whole-rock scales as well as among individual grains in single meteorites [e.g., 1-3]. Despite extensive studies on C isotopic ratios of CM carbonates, the reason for variability in  $\delta^{13}\text{C}$  variation and the origin of the carbonate C remain poorly understood.

Here we report C isotopic ratios of calcite ( $\text{CaCO}_3$ ) in the LAP 031166 CM chondrite (CM 2.1), and discuss the origin of the carbonate C and a possible link between ices in CMs and in comets. The O isotopic ratios of calcite in this meteorite were reported by Lindgren et al. [4].

**Experimental:** Carbon-isotope analysis was performed with the NanoSIMS 50 installed at Atmosphere and Ocean Research Institute, the University of Tokyo, on the calcite grains whose O isotopic ratios were measured previously. Negative secondary ions of  $^{12}\text{C}^-$ ,  $^{13}\text{C}^-$ ,  $^{18}\text{O}^-$ ,  $^{12}\text{C}^{14}\text{N}^-$ , and  $^{28}\text{Si}^-$  produced by rastering a  $\text{Cs}^+$  primary ion beam (20-30 pA,  $\sim 1\ \mu\text{m}$  in diameter) over  $6\ \mu\text{m}^2$  sized areas were detected simultaneously with five electron multipliers.

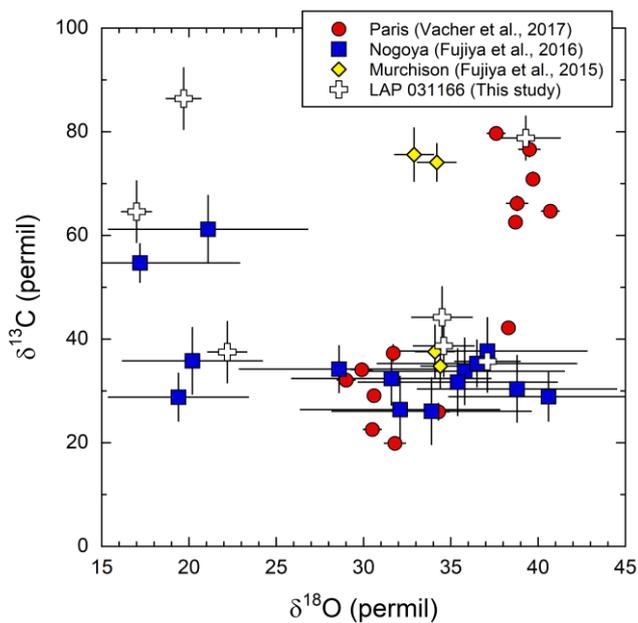
**Results and discussion:** The  $\delta^{13}\text{C}_{\text{PDB}}$  and  $\delta^{18}\text{O}_{\text{SMOW}}$  values of the calcite grains in LAP 031166 are shown in Fig. 1, together with literature data of Ca-carbonate (calcite and aragonite) in the Murchison, Nogoya, and Paris CM chondrites [3,5,6]. The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of the CM carbonates are highly variable, ranging from  $\sim 20$  to  $80\text{‰}$  and from  $\sim 15$  to  $40\text{‰}$ , respectively, and they do not correlate with each other.

Alexander et al. [1] have suggested that the range in  $\delta^{13}\text{C}$  can be explained by variable formation temperatures (0-130 °C) of CM carbonates which are isotopically equilibrated with gaseous C species dominated by CO (or  $\text{CH}_4$ ). However, this model implies that the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of the CM carbonates would correlate, which is clearly not the case as demonstrated by this work (Fig. 1). Instead, the observed  $\delta^{13}\text{C}$  range must be produced under nearly constant temperatures.

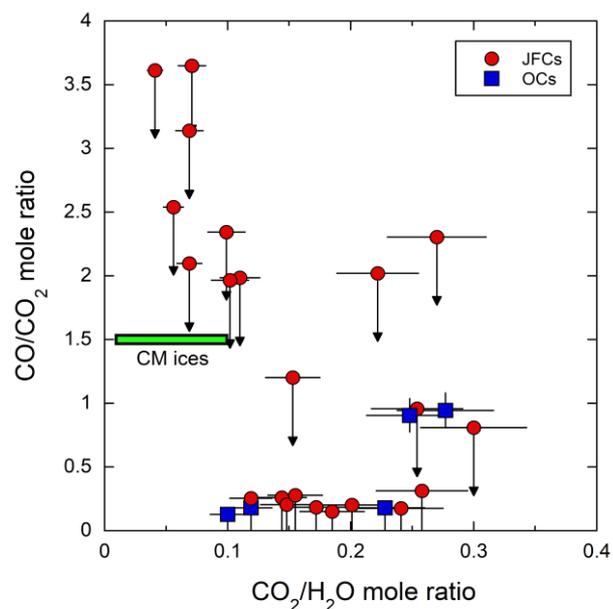
Here we propose a modified version of the model outlined by Alexander et al. [1], where we consider mixing of  $\text{CO}_2$  and CO gases with higher and lower  $\delta^{13}\text{C}$  values, respectively. Because the equilibrium  $\text{CO}/\text{CO}_2$  ratios are  $\ll 1$  for  $f_{\text{O}_2}$  higher than the iron-magnetite buffer, CO should be converted to  $\text{CO}_2$  and the  $\text{CO}/\text{CO}_2$  ratios of gas phases would have decreased with time. As the  $\text{CO}/\text{CO}_2$  ratios decreased,  $\text{CO}_2$  as well as carbonates acquired lower  $\delta^{13}\text{C}$  values. Given  $1000\ln\alpha(\text{calcite}-\text{CO}_2)$  of  $\sim 10$ -14 at 0-30 °C [7], where  $\alpha$  is a C isotopic fractionation factor, the CM carbonates with the highest  $\delta^{13}\text{C}$  values of  $\sim 80\text{‰}$  were equilibrated with  $\text{CO}_2$  with  $\delta^{13}\text{C} \sim 70\text{‰}$ . The  $\delta^{13}\text{C}$  value of the trapped CO in Murchison is  $\sim 30\text{‰}$  [8]. The lowest  $\delta^{13}\text{C}$  values of the CM carbonates are  $\sim 20$ -30‰, which is common for all the CM chondrites analyzed (Fig. 1). Therefore, the gaseous C species which coexisted with the CM carbonates with the lowest  $\delta^{13}\text{C}$  values of  $\sim 20$ -30‰ would have been dominated by  $\text{CO}_2$ , i.e., most of CO was converted to  $\text{CO}_2$ . If correct, the  $\delta^{13}\text{C}$  value of the bulk gaseous C species ( $\text{CO}_2 + \text{CO}$ ) would be  $\sim 10\text{‰}$ . Using the above numbers, mass balance calculation suggests that a  $\text{CO}/\text{CO}_2$  mole ratio of the gaseous C species which coexisted with the CM carbonates with the highest  $\delta^{13}\text{C}$  value of  $\sim 80\text{‰}$  would be  $\sim 1.5$ , which may reflect the  $\text{CO}/\text{CO}_2$  ratio of ice accreted onto the CM parent body. The carbonate  $\text{C}/\text{H}_2\text{O}$  mole ratios of most CMs range from  $\sim 0.01$  to  $0.1$  [1]. These carbonate  $\text{C}/\text{H}_2\text{O}$  ratios may set lower limits on the  $\text{CO}_2/\text{H}_2\text{O}$  ratio of the CM ices because of possible  $\text{CO}_2$  loss. Thus,  $\text{CO}_2$  accounts for at least 1 % of the CM ices.

The inferred  $\text{CO}/\text{CO}_2$  and  $\text{CO}_2/\text{H}_2\text{O}$  mole ratios of the CM ices are shown in Fig. 2, together with those of cometary ices [9]. Unfortunately, only upper limits on the  $\text{CO}/\text{CO}_2$  ratios are obtained for most of the observed comets. Nevertheless, the  $\text{CO}/\text{CO}_2$  ratios of these comets seem lower than unity, and thus, lower than those of the CM ices. Although the possible similarity between ices in CMs and in some comets cannot be ruled out, these observations suggest that ices in the two classes of bodies had a different origin, which is consistent with contrasts in the D/H ratios of water between CMs and comets [10].

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**Fig. 1.**  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of Ca-carbonates in CM chondrites. Errors are  $2\sigma$ .



**Fig. 2.**  $\text{CO}/\text{CO}_2$  and  $\text{CO}_2/\text{H}_2\text{O}$  mole ratios of the inferred CM ices and comets. Data with arrows represent upper limits. JFCs: Jupiter-family comets, OCs: Oort cloud comets. Only comets which were observed within 2.5 AU from the Sun are shown, where  $\text{H}_2\text{O}$  effectively sublimates from the nucleus of the comet.

# Volatile Contents in Vesicles in IDP Grains Analyzed with Scanning Transmission Electron Microscopy

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Chondritic porous interplanetary dust particles (IDPs) are believed to come from comets and incorporate a wide variety of primitive early solar system and interstellar materials. Alteration is thought to be from nebular processes, such as solar wind exposure, and atmospheric entry heating. The compositional and structural changes associated with these processes can be analyzed using (scanning) transmission electron microscopy (S/TEM) with energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS). Vesicles formed in the space weathered rims of grains are thought to be filled with hydrogen or helium from the solar wind, although heating may be required for the formation of the vesicles. Solar wind hydrogen has been identified in vesicles in the space weathered rim of a pyroxene grain [1], while helium was suggested as the likely source of bubbles formed in a pyrrhotite grain [2].

Stratospheric IDPs from collection plate U2012, flown on NASA Ames Research Center U2 aircraft in March 1993, were washed and embedded in epoxy, then microtomed and placed on grids for STEM analysis. The samples were baked at 140°C for six hours to drive off adsorbed water before insertion in the UHV system. Electron energy loss spectroscopy (EELS) and energy dispersive x-ray spectroscopy (EDS) data were collected with the NION UltraSTEM200-X at the U.S. Naval Research Laboratory, equipped with a Gatan Enfium ER EEL spectrometer and a Bruker SSD-EDS detector. The STEM was operated at 60 kV or 200 kV, with a ~0.1 nm probe. Spectra were collected as spectrum images (SI), with a spectrum collected for each pixel, allowing for mapping of variations in thickness and composition.

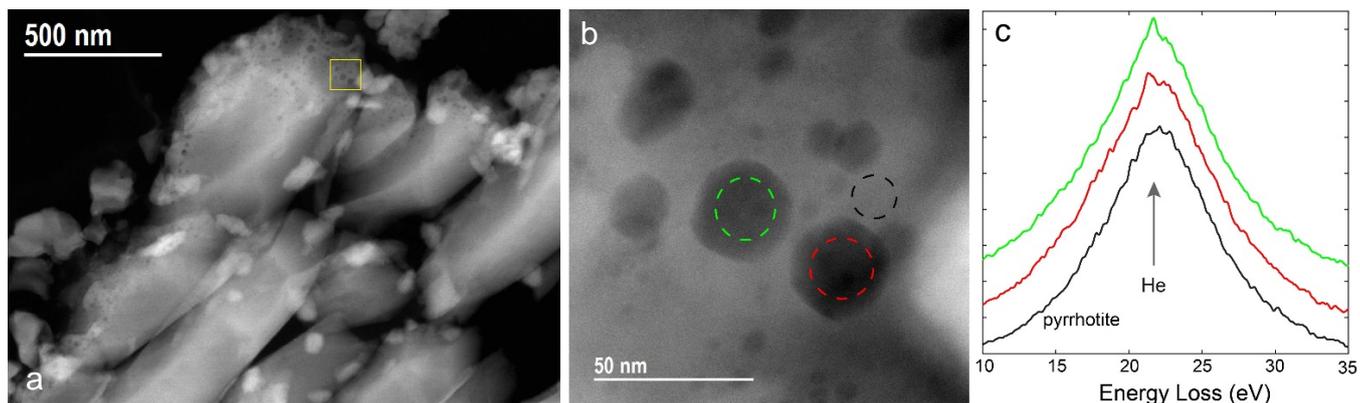
Sample U2012A-2J contains a pyrrhotite grain with a nominally continuous space weathered rim full of subhedral to euhedral vesicles. The voids range in size from a few nanometers to ~30 nm. Brownlee et al. [2] suggested that these voids formed due to helium implantation, but were unable to confirm the presence of helium in specific voids. High resolution EELS mapping of several of the voids reveals a small peak at ~22 eV associated with individual voids, indicating they are filled with helium from the solar wind (Figure 1).

A vesicular grain observed in sample U2012A-3C is much more enigmatic (Figure 2). The core of the grain is iron sulfide and it is surrounded by a highly vesicular oxygen-rich shell. EDS data show the rim material contains significant O, Fe and S, along with several at% Mg and trace (~0.5 at%) Si. EELS data from the vesicles show small peaks at 8.5 eV and ~13 eV, both associated with hydrogen [1]. Additionally, the carbon K-edge in spectra from the same vesicles shows a distinct peak at 287.4 eV due to the presence of C-H bonds. Attribution of this peak to a specific compound is ambiguous due to the ubiquity of these types of bonds in natural materials as well as laboratory sources. The peak is associated only with this particle and clearly tied to the individual vesicles, suggesting it is indigenous. A sharp peak at the same energy is seen in hexamethyl disiloxane [3], a compound related to the silicone oil in which the IDPs were collected, and hexane [4], used to wash the IDPs, both possible sources of contamination. However, the vesicles are not correlated with significant Si, as expected for silicone oil, and evidence of contamination is not seen elsewhere on the sample. Isotope measurements of the grain are planned in order to clarify the possible sources of the rim material and hydrocarbons.

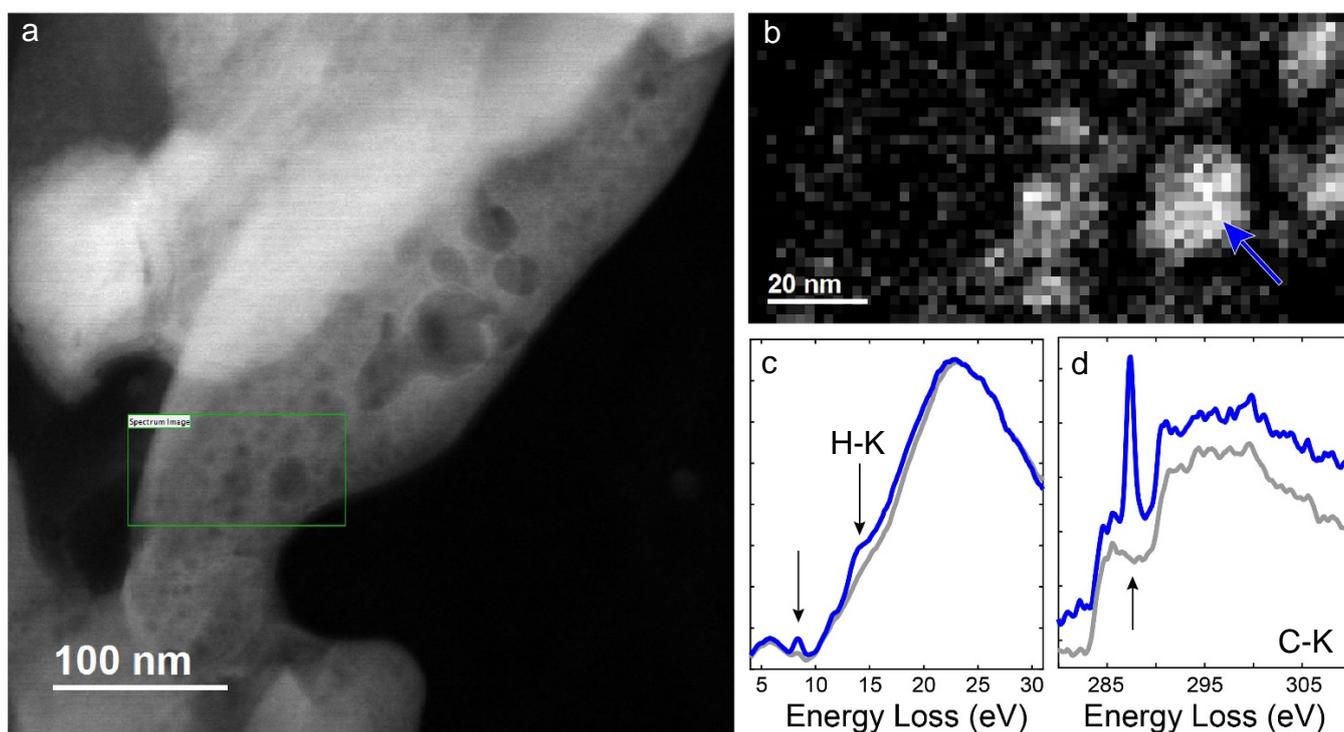
The helium- and hydrogen-filled bubbles have very different morphologies, and it is unlikely the hydrogen filled vesicles formed solely due to the influence of the solar wind. The cores of both grains are predominantly iron sulfide. However, while the helium vesicles are euhedral and in material that otherwise very closely resembles vesicle-free portions of the grain, the hydrogen vesicles are in a highly porous rim that is rich in oxygen relative to the core of the grain and also has other minor and trace elements (e.g., Mg, Si) not present in the core. Solar wind helium-filled vesicles in lunar ilmenite are not euhedral [5], indicating that both host mineral composition and heating could play a role in vesicle formation and shape.

With the ability to identify and map the volatile contents of very small vesicles in IDPs and other extraterrestrial materials, we can better understand the timing of alteration and source of volatiles, whether from atmospheric heating and decomposition of

pyllosilicates, implantation by the solar wind, or contamination during collection and laboratory preparation procedures. This technique is applicable to samples collected from many airless bodies including Itokawa, Bennu, and Ryugu.



**Figure 1.** (a) HAADF image of pyrrhotite from U2012A-2J showing vesicle-rich rim around particle. (b) Higher magnification image of several euhedral vesicles. (c) EELS data from two vesicles indicated in (b) showing small peaks at  $\sim 22$  eV indicating helium is present in the vesicles. A spectrum from a portion of the pyrrhotite not in a vesicle is shown for comparison (black).



**Figure 2.** (a) HAADF image of particle in U2012A-3C with a vesicular rim. (b) Window map of 8.5 eV peak from region outlined by green box in (a). (c) Low loss spectra from the bright vesicle highlighted in (b) (blue) and surrounding material (gray) showing peaks at  $\sim 8.5$  eV and  $\sim 13$  eV, indicating the presence of hydrogen in the vesicles. (d) Carbon K-edge spectrum showing a large peak at 287.4 eV spatially associated with H-filled vesicles. The peak is indicative of C-H bonds. Amorphous carbon spectrum from the grid substrate (gray) is shown for comparison.

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# Simulating Space Weathering of a Carbonaceous Chondrite via Pulsed Laser Irradiation

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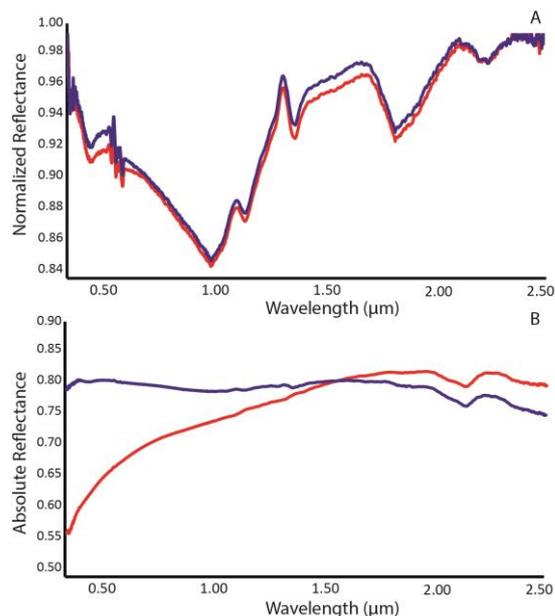
**Introduction:** Grains on the surfaces of airless bodies are continually exposed to irradiation from solar wind ions and micrometeorite impact events. These processes, collectively known as space weathering, alter the microstructure, chemical composition, and spectral properties of surface soils [1-2]. While much work has been done to understand space weathering of lunar and ordinary-chondritic materials e.g., [3-5], the effects of these processes on hydrated carbonaceous chondrites is not yet well-understood. Analysis of the space weathering of carbonaceous materials will be critical for interpreting remote sensing reflectance data and for understanding the nature of samples returned by missions targeting primitive, organic-rich airless bodies, e.g., Hayabusa2 and OSIRIS-REx.

Prior to sample return, we can simulate space weathering processes in the laboratory. Micrometeorite impacts can be simulated through pulsed-laser irradiation, and recent experiments have shown the spectral properties of carbonaceous materials are altered by such simulated weathering events e.g., [6-8]. However, the resulting type of alteration i.e., reddening vs. bluing of the reflectance spectrum, is not consistent across all experiments. Further, the microstructural and crystal chemical effects of many of these experiments have not been well characterized, making it difficult to attribute spectral changes to specific mineralogical or chemical changes in the samples. Here we report results of pulsed laser irradiation experiments on chips of the Murchison CM2 carbonaceous chondrite to simulate micrometeorite impact processing.

**Samples and Methods:** We performed three separate pulsed laser experiments by scanning a Nd-YAG laser (wavelength of 1064 nm, average energy per pulse of 48 mJ, similar to [9]) (1) once, (2) twice, and (3) five times over the surface of the sample, in order to simulate various degrees of surface exposure. Glass slides were placed above the samples enabling the collection of the recondensed vapor plume produced by the irradiation, similar to [10]. We obtained reflectance spectra (0.3-2.5  $\mu\text{m}$ ) from unirradiated and 1x-irradiated samples, as well as of the vapor deposit of the 1x-irradiated sample. We have analyzed the morphological and chemical effects of the 1x-irradiated samples using the JEOL 7600F field emission scanning electron microscope (SEM) with x-ray detector system at JSC. From this sample, we have prepared electron transparent thin sections from the vapor deposit, the meteorite matrix, and several individual mineral phases using the FEI Quanta 3D focused ion beam (FIB) instrument. These sections were analyzed using the JEOL 2500SE scanning transmission electron microscope (STEM) equipped with a Thermo thin window energy-dispersive X-ray (EDX) spectrometer. We expect to make similar spectral measurements and prepare sections for STEM analysis for the 2x and 5x-irradiated sections.

**Reflectance Measurements:** The 1x-irradiated sample is darker (1-2%) than the unirradiated material (Fig. 1a) and the vapor deposit on the glass slide shows strong reddening through the VIS-NIR wavelengths (Fig. 1b).

**Chemical and Structural Analysis: Vapor Deposit:** The vapor deposit is microstructurally and chemically complex, composed of several individual layers ranging between 30-350 nm in thickness. The first layer is a uniform (~50 nm) amorphous layer containing embedded nanoparticles. Quantitative EDX maps indicate the composition of this layer is enriched in Fe, and includes S, Si, and O. Overlying this initial deposit in several locations are thicker (up to 250 nm) deposits composed of Mg, Si, Fe, and Ca (in localized regions). There are vesicles and nanoparticles distributed throughout this layer. The outermost layer is thin (30-50 nm) and EDX maps indicate it is enriched in volatile species including Fe and S, and includes embedded nanoparticles. The



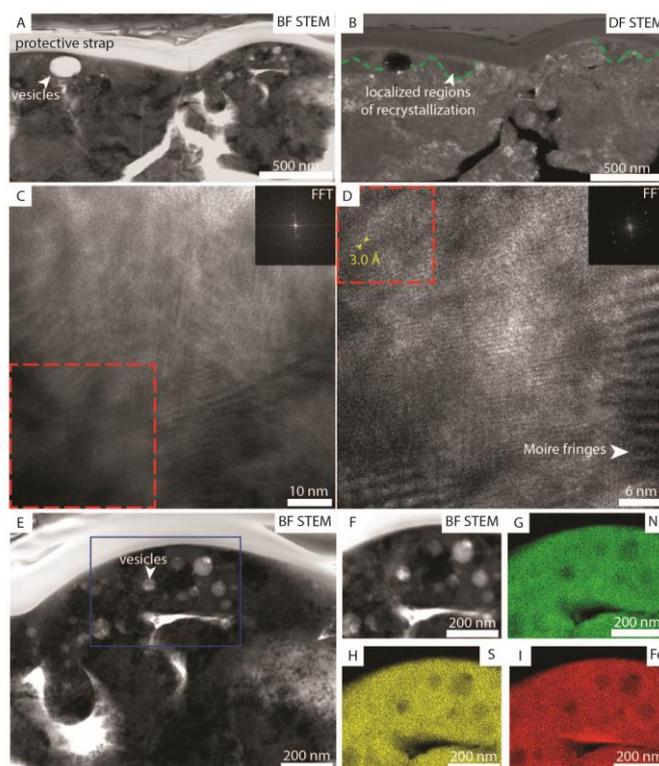
**Figure 1:** Reflectance spectra of the A) Surface of the irradiated Murchison meteorite (red) compared to the raw sample (blue), and B) The glass slide with the deposit on it (red) compared to the plain glass slide (blue).

nanoparticles distributed throughout the individual layers range in size from 2–30 nm in diameter and selected area electron diffraction (SAED) indicates at least three individual phases are present in the nanoparticle-bearing deposits including troilite (FeS), pentlandite ((FeNi)<sub>9</sub>S<sub>8</sub>), and magnetite (Fe<sub>3</sub>O<sub>4</sub>).

**Matrix:** The SEM images show the irradiated fine-grained matrix material has a distinctive ‘frothy’ texture, exhibiting sub- $\mu\text{m}$  voids uniformly distributed across the surface. TEM analyses of the surface of the irradiated matrix provide evidence of melting including amorphous spherules and droplets. These melt products are up to 500 nm in thickness, are often vesiculated, and contain embedded nanoparticles. Quantitative EDX maps indicate the elemental composition of the melt layers includes Fe, Mg, Si, and S, although volatile species such as Fe and S are depleted in the melt layer relative to the underlying matrix. The matrix phases maintain crystallinity up to the boundary with the melt layer, with only localized regions of amorphization. The nanoparticles range in size from 5-50 nm and EDX maps indicate they are dominated by Fe-Ni-Sulfides.

**Olivine:** Bright-field STEM images of an olivine grain indicates there is an amorphous melt layer of uniform thickness (~15 nm) on the surface of the grain. EDX maps indicate this layer has an elemental composition that includes Ca, Al, Mg, Si, and Fe, with more refractory species like Ca and Al in higher concentrations than in the underlying grain. Superimposed on this refractory deposit is a thicker, irregular (up to 70 nm) amorphous layer with high concentrations of embedded nanoparticles ranging in size from 2-30 nm.

**Fe-Ni-Sulfide:** The surface of the Fe-Ni-Sulfide grain exhibits melt textures including droplet-like features. Dark-field STEM and correlated HRTEM images of the melted region indicate localized areas near the surface of have recrystallized. Vesicles are present within 500 nm of the surface and range in size from 5-100 nm. Quantitative EDX maps indicate there is no significant difference in the composition of the sulfide grain at the melted and recrystallized surface when compared to the interior region of the sample (Fig. 2).



**Figure 2:** Analysis of the irradiated sulfide grain reveals A) melt features and vesicles in BF STEM, and B) areas of recrystallization in DF STEM, outlined by the dashed green lines. HRTEM images in C) and D) show zones of amorphization and short range order, highlighted by FFTs of regions bounded by the red dashed boxed. Measurements of the lattice fringes indicate spacings are consistent with pentlandite. Round vesicles are shown in E). The region outlined by the blue box in E) is shown in F). The chemical composition of this region is shown by EDX maps of G) Ni, H) S, and I) Fe, indicating the composition is consistent between the irradiated area and the underlying material.

**Implications for Space Weathering of Primitive Bodies:** The observed elemental fractionation between melt and vapor deposits influences the mineralogy of the nanoparticle population produced during space weathering events. The diversity of nanoparticle phases identified here indicates that the space weathering of carbonaceous materials is more complex than their lunar and ordinary chondrite-style counterparts. In addition, volatile species (including water) may play a significant role in the formation of space weathering features in carbonaceous surface materials. The prevalence of Fe-Ni-Sulfide and presence of Fe-Oxide nanoparticles may contribute to the unpredictable spectral behavior of some experimentally-produced samples. As such, an improved understanding of the optical characteristics of nanophase Fe-Ni-Sulfides is necessary to predict their effect on the spectral properties of airless body surfaces.

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## Development on non-destructive muonic X-ray analysis: Application to Earth and Planetary Science

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The muon is a lepton with a mass of  $105.7 \text{ MeV}/c^2$ , approximately 200 times heavier than the electron. So far, electron-induced characteristic X-ray analysis has been widely used to determine chemical compositions of materials in Earth and Planetary Science. In recent years, analysis of characteristic X-rays from muonic atoms, in which a muon is captured, has attracted attention because both a muon beam and a muon-induced characteristic X-ray have high transmission abilities, of which energies are about 200 times higher (e.g., muonic carbon-K $\alpha$  is 75keV, whereas electron-induced carbon-K $\alpha$  is 0.3 keV). It is known that muonic X-ray analysis has great advantages in several ways; (1) non-destructive elemental analysis from light to heavy elements, (2) depth profile analysis, (3) isotopic measurement for heavy elements and (4) investigation of chemical condition (redox-state). Such a non-destructive muonic X-ray analysis has a great potential to characterize precious extraterrestrial samples returned by spacecrafts such as Hayabusa2 and OSIRIS-REx in 2020's.

Following our successful detection of muonic X-ray spectra from carbonaceous chondrites, Murchison and Allende with intense pulsed Muon beam at J-PARC [1], we have developed on muonic X-ray analysis at the MuSIC (MuSIC; MUon Science Innovative Channel at Osaka University, [2, 3]), and obtained the fundamental data for quantitative analysis of planetary materials [4]. Using one of the world-leading intense direct current muon beam source, we successfully detected characteristic muonic X-rays of Mg, Si, Fe, O, S and C from Jbilet Winselwan CM chondrite, of which carbon content is about 2 wt%, and the obtained elemental abundance pattern was consistent with that of CM chondrites. We also checked Muon irradiation damage of pellets of mixed organic chemical reagents (alanine, glucose, paraformaldehyde, phenanthrene, and stearic acid) after 3–12 hour exposure to check the irradiation damage, and confirmed that they do not show any systematic changes with either the exposure time or the depth, and are not different from those of non-exposed samples within the variation of initial reagent mixtures. We also performed the muonic X-ray analysis of terrestrial PbS (Galena) for Pb isotopes measurement and iron meteorite to check the feasibility of chemical condition (redox-state) measurement. At the symposium, we will report on our recent progress of muonic X-ray analysis and discuss on a future prospect for applications for earth and planetary science.

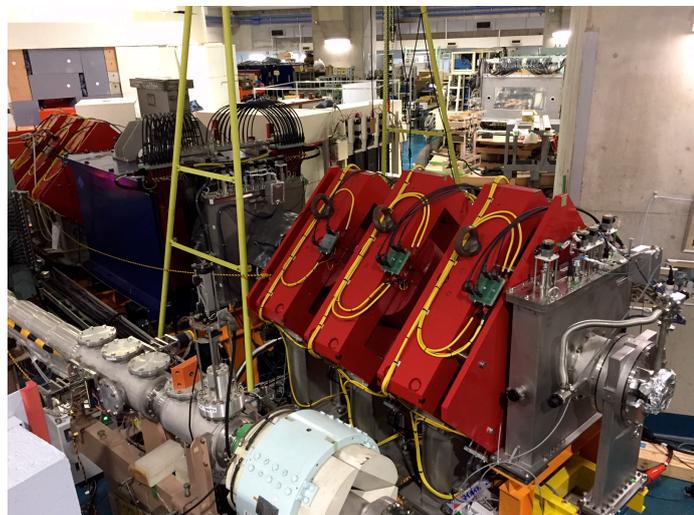


Figure 1: Direct-current Muon beam line at MuSIC, Osaka University.

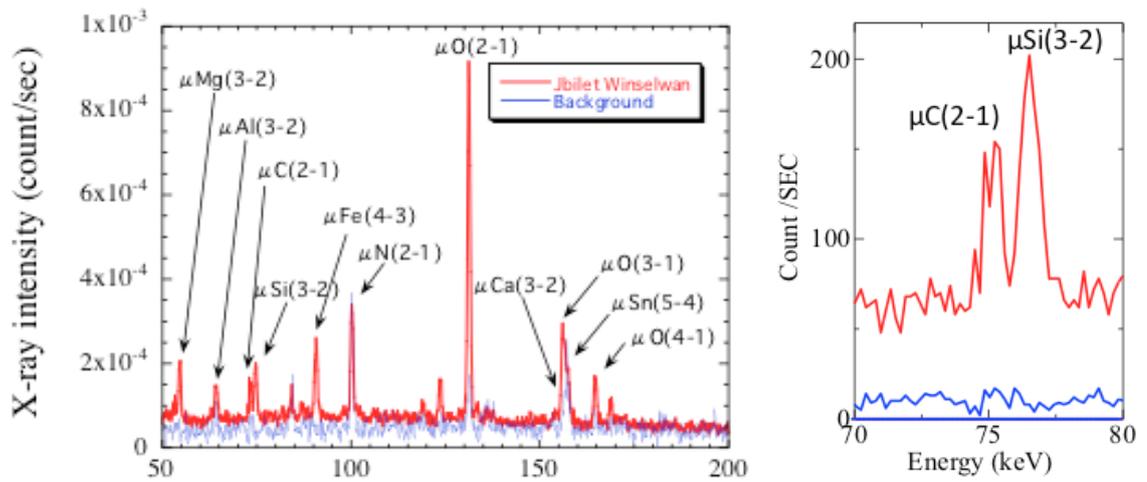


Figure 2: Muonic X-ray spectra of Jbilet Winselwan CM2 chondrite.

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# Using X-ray Microfocus Spectroscopy to determine Cometary and Asteroidal Parent-Body Processes

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Since the *Stardust* and *Hayabusa* missions, we have investigated a selection of these returned cometary and asteroidal samples using Beamline I-18 at the *Diamond Light Source* synchrotron in UK, measuring Fe-K X-ray Absorption Spectroscopy (XAS) and transmission X-ray Diffraction (XRD). Such techniques are essential to determine the origin and evolution of fine grained planetary materials, and in particular we have identified evidence for water-rock reaction on the Wild2 parent body.

## I-18 X-ray microfocus spectroscopy

Beamline I-18 has an energy range 2.0-20.7 keV and a spot size reduced to  $\sim 2.5 \mu\text{m}$ . X-ray Fluorescence (XRF) can provide chemical compositions, with XRF maps providing the opportunity to accurately locate features of interest at the micron-scale. Fe-K XAS measurements typically range 6900-7500 eV at variable energy resolutions 1.0-10 eV, with higher resolution steps of 0.1 eV focused over the XAS near-edge (XANES) region 7090-7150 eV necessary to accurately determine minor shifts and variations in the  $1s \rightarrow 3d$  transition pre-edge peak structure and absorption edge. The  $1s \rightarrow 3d$  centroid position is estimated from the intensity-weighted average energy position over the pre-edge peaks, and the absorption edge position is the energy at which intensity is 0.5 of the normalized spectra. Comparisons are made to reference materials, in particular the ferric content of silicates are estimated by comparing pre-edge centroids with the ferrous-ferric energy shift in standards [1]. Combined with XRF mapping, producing XANES maps can reveal any variations in the ferric content. Additionally, in-situ measurements of transmission-XRD are acquired at 13 keV, with observable  $2\theta$  ranging  $5.5^\circ$ - $38.4^\circ$ , corresponding to  $d$ -spacings 9-1.5 Å.

## Identifying magnetite in Comet Wild 2 samples

Initial investigations of Comet Wild 2 samples returned by *Stardust* identified mostly high temperature ferromagnesian silicates [2], but additional constituents have included CAI's and chondrule-like fragments, suggesting links between carbonaceous chondrites and the Wild 2 material [3].

Hicks et al. (2017) [4] investigated the terminal grains of eight *Stardust* aerogel tracks, which include terminal grains identified as near pure magnetite  $\text{Fe}_3\text{O}_4$ . *Stardust* track C2045,4,178,0,0 (#178) featured a magnetite terminal grain measuring  $10 \mu\text{m}$  in diameter, and a  $5 \mu\text{m}$  magnetite terminal grain in track C2065,4,187,0,0 (#187), both visibly identified via XAS structure (Figure 1). In particular, absorption edge positions at 7121.5 and 7121.0 eV, and  $1s \rightarrow 3d$  centroid positions estimated at 7113.1 and 7113.5 eV, closely resemble that of a magnetite powder standard with edge and centroid positions at 7120.8 eV and 7113.2 eV respectively. A small positive shift of up to  $\sim 0.5$  eV in the Wild 2 grains, compared to the magnetite standard, could be due to a minor  $\text{Ni}^{2+}$  content identified with XRF, which replaces some  $\text{Fe}^{2+}$ , resulting in a higher  $\text{Fe}^{3+}/\Sigma\text{Fe}$  content, thus a positive shift in the energy of the Fe-K XAS spectra.

In-situ transmission XRD analyses also identified magnetite with  $2\theta$  peaks at  $d$ -spacings 1.48 Å, 1.61 Å, 1.71 Å, 2.10 Å, 2.42 Å, 2.53 Å, and 2.96 Å for the cometary #178 (Tg1a and Tg2) and #187 (Tg1), closely matching the  $2\theta$  peaks a magnetite reference material. However, with unit cell dimensions ranging 8.355-8.370 Å for the cometary grains being slightly lower than that of a pure magnetite at 8.387 Å, this shift also suggests a Ni-bearing magnetite. Raman analyses performed at University of Kent also confirmed a Ni-bearing magnetite. Material in other *Stardust* tracks, identified via XAS analyses on I-18 at *Diamond*, include olivine (#177, #178, #187), pyroxene (#189, #190), Fe,Ni-metal (#170, #176), and Fe,Ni-sulfide (#187, #188) [4].

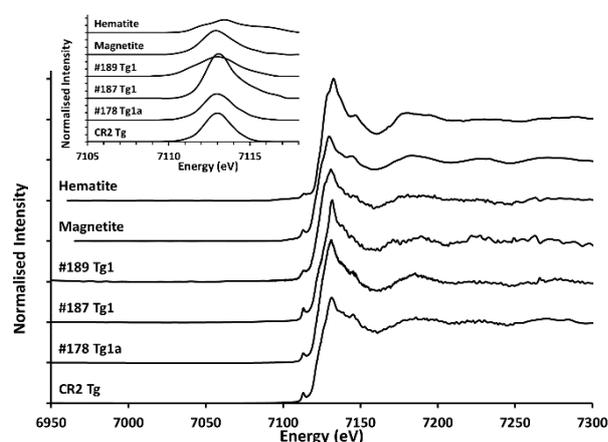


Figure 1. The Fe-K XAS and pre-edge centroid (inset) of terminal grains in tracks #178 (Tg1a), #187 (Tg1), and #189 (Tg1), and an analogue CR2 terminal grain (Tg) shot into aerogel, compared to powdered magnetite and hematite standard reference material.

Magnetite grains are prominent in carbonaceous chondrites, if they have been oxidised and aqueously altered [5], thus the presence of magnetite in the Wild 2 mineral assemblage suggests further affinities to carbonaceous chondrites, probably resulting from hydrothermal alteration of the co-existing FeNi and ferromagnesian silicates in the cometary parent-body. Exploring this hypothesis further, powdered NWA 10256 CR2 chondrite material was shot into aerogel at 6.1 kms<sup>-1</sup>, using a light gas gun [6], simulating the conditions of the *Stardust* collection. Fe-K XAS identified CR2 magnetite terminal grains (Figure 1) establishing the likelihood of preserving magnetite during capture in silica aerogel.

### Itokawa ferromagnesian silicates and LL5 chondrite

Initial analyses of the Itokawa asteroid particles returned by *Hayabusa* had already found mineralogical, petrological, and oxygen isotopic affinities to LL5-6 chondrites [7,8,9]. We used Fe-K XAS to investigate the relative abundance of Fe<sup>3+</sup> and Fe<sup>2+</sup> ions in the ferromagnesian silicates of the Itokawa grains, comparing them to the Tuxtuac LL5 chondrite meteorite.

Noguchi et al. (2014) [10] investigated four samples from the first *Hayabusa* touch-down location: RB-QD04-0008; RB-QD04-0011; RB-QD04-0015; and RBQD04-0024. These samples, each embedded in epoxy resin, featured olivine with trace amounts of opaque minerals (0011 and 0015), olivine and high-Ca pyroxene (0008), and low-Ca pyroxene with plagioclase and small (<2 µm) opaque minerals (0024).

Fe-K XAS for the olivines (Figure 2) estimated absorption edges and 1s→3d centroids at 7119.5-7119.8 eV and 7112.5-7112.6 eV respectively, indistinguishable from those estimated for the Tuxtuac olivine and in terrestrial olivine. Edges and centroids for the low-Ca Itokawa pyroxene (7119.7 eV and 7112.6 eV), and the high-Ca Itokawa pyroxene (7119.4 eV and 7112.6 eV), are also indistinguishable from Tuxtuac and from Fe<sup>2+</sup> in terrestrial augite. EXAFS analyses of the high-Ca Itokawa pyroxene suggested a disordered structure which may be partial equilibration or shock. A Ni-bearing phase associated with that high-Ca Itokawa pyroxene (0008) was also measured for Ni-K XAS, finding similarities to taenite in the LL5 Tuxtuac.

The Fe-K XAS analyses suggested a negligible abundance of Fe<sup>3+</sup> ions in Itokawa and the LL5 ferromagnesian silicates, consistent with the initial analyses [7,8,9]. However, the EPMA analyses of the four Itokawa grains, that followed the Fe-K XAS analysis, suggested a wide range of thermal metamorphism corresponding to petrologic chondrite types LL4 to LL6.

### Future XAS investigations of Planetary Sample Returns

As we continue to investigate planetary materials further, and as missions such as *Hayabusa 2* and *OSIRIS-REx* return samples to Earth, more advanced techniques will be essential to analyse micron-sized material, furthering our understanding of planetary formation. Offering similar techniques to I-18, but with higher spatial resolution down to ~50 nm, the new I-14 hard X-ray nanoprobe beamline at *Diamond* offers nanoscale microscopy with an energy range 5-23 keV, capable of XAS, XANES mapping, and XRD. Additionally, the I-08 Scanning X-ray Microscope (SXM) beamline performs XRF and XANES, but in the soft X-ray energy range 0.25-4.4 keV, including Si-K XANES, with a spatial resolution down to ~200 nm.

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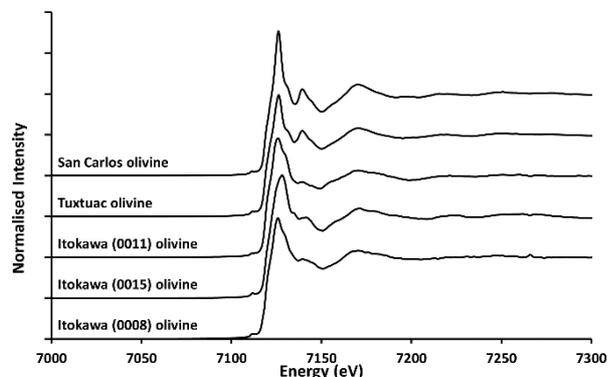


Figure 2. The Fe-K XAS for olivine in three Itokawa particles, the Tuxtuac LL5 chondrite, and a terrestrial olivine (San Carlos).

# The Astromaterials X-Ray Computed Tomography Laboratory at Johnson Space Center

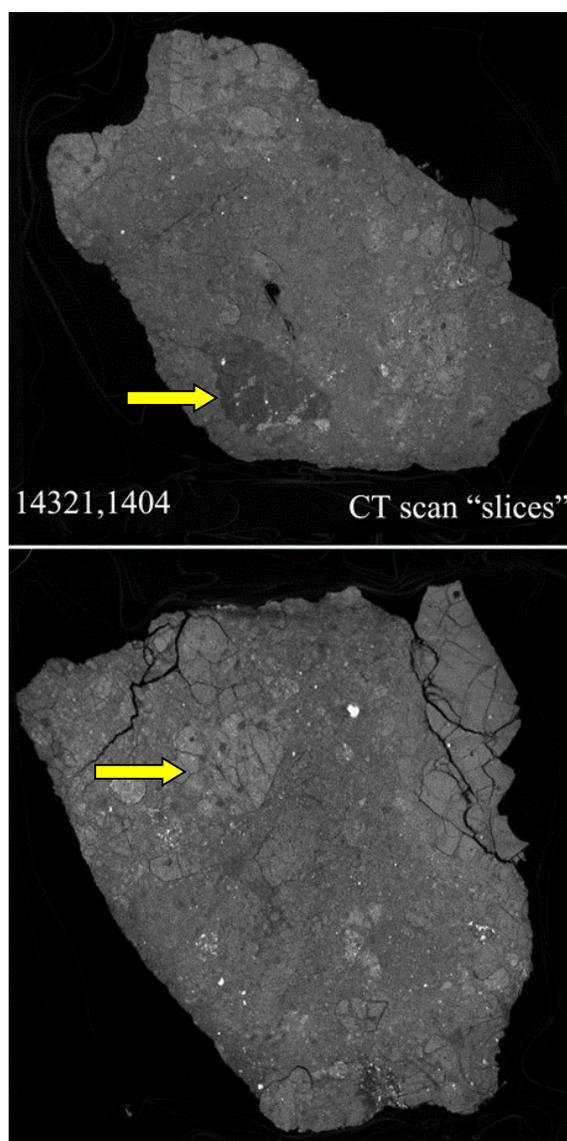
Ryan A. Zeigler, Poorna Srinivasan, Lindsay P. Keller, Francis McCubbin, and Daniel M. Coleff

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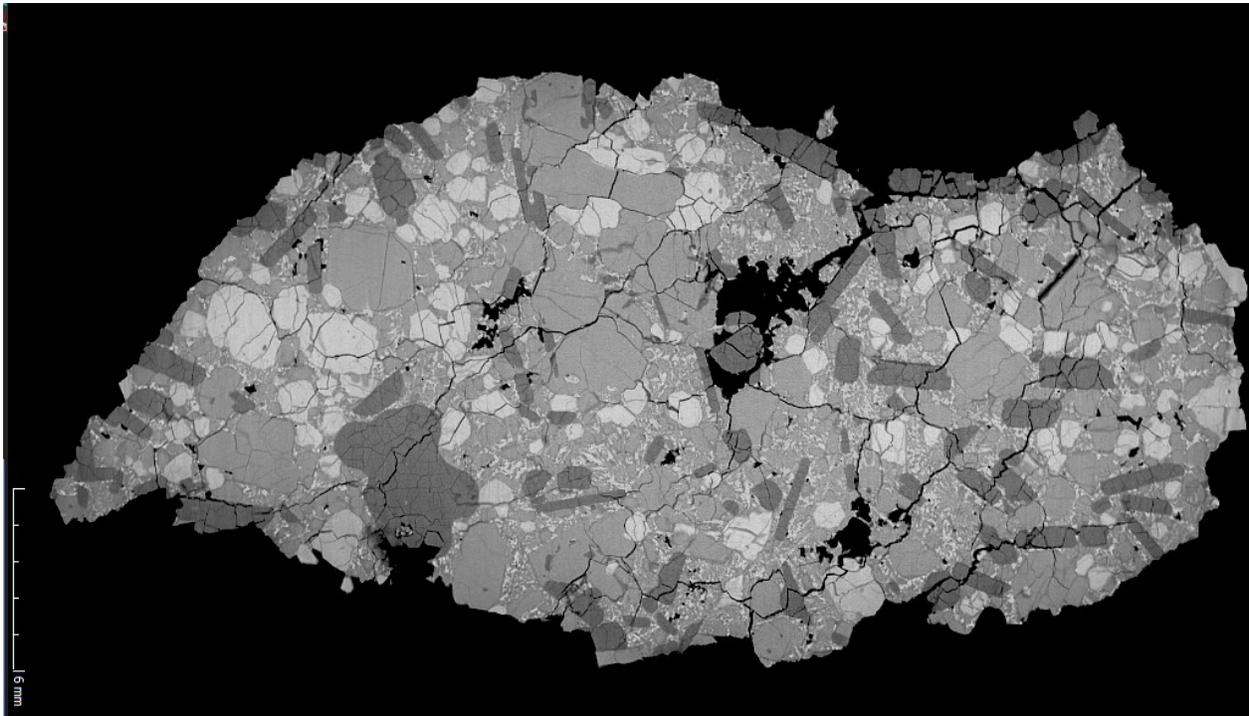
**Overview:** The Astromaterials Acquisition and Curation Office at NASA's Johnson Space Center (hereafter JSC curation) is the past, present, and future home of all of NASA's astromaterials sample collections. JSC curation currently houses all or part of nine different sample collections. Our primary goals are to maintain the long-term integrity of the samples and ensure that the samples are distributed for scientific study in a fair, timely, and responsible manner, thus maximizing the return on each sample. Part of the curation process is planning for the future, thus we also perform fundamental research in advanced curation initiatives. Advanced Curation is tasked with developing procedures, technology, and data sets necessary for curating new types of sample collections, or getting new results from existing sample collections [1]. As part of these advanced curation efforts we are augmenting our analytical facilities. A micro X-ray computed tomography (micro-XCT) laboratory dedicated to the study of astromaterials came online within the JSC Curation office this summer, and we plan to add additional facilities that will enable non-destructive (or minimally-destructive) analyses of astromaterials in the near future (micro-XRF, confocal imaging Raman Spectroscopy). These facilities will be available to: (1) develop sample handling and storage techniques for future sample return missions, (2) be utilized by PET for future sample return missions, (3) be used for retroactive PET-style analyses of our existing collections, and (4) for periodic assessments of the existing sample collections. Here we describe the new micro-XCT system, as well as some of the ongoing or anticipated applications of the instrument.

**Instrument:** We have installed a Nikon XTH 320 micro-XCT system in JSC curation. It has four interchangeable X-ray sources: 180 kV nano focus transmission source, 225 kV reflection source with multi-metal target (Mo, W, Ag, Cu), a 225 kV rotating target (W) reflection source, and a 320 kV reflection source. The system also has a 16-bit, 400 mm<sup>2</sup> (2000 x 2000 pixel) CCD detector, as well as a heavy-duty stage that will accommodate large (up to 30 cm) and heavy (up to 100 kg) samples. The multiple sources, high-resolution detector, and large stage allow us the flexibility to analyze a wide range of sample sizes. The 180 kV transmission source will allow for high resolution (submicron) scans on small samples (less than ~5 mm), whereas the 225 kV and 320 kV sources will allow scans of larger samples at resolutions on the order of 10s or 100s of microns per voxel depending on the sample size. The maximum size high-density rock sample that can be scanned has yet to be determined, but test scans on basalt samples >15 cm in diameter have been successful.

**Discussion:** High-intensity XCT scanners have been used to study astromaterials (and other geologic samples) for over 15 years [2-3], and the practice is becoming ever more prevalent. They have a wide range of scientific uses, including (but certainly not limited to) measuring porosity, determining the modal abundance and 3D distribution of phases inside samples, and identification of fabrics or strain patterns in samples. In addition to their use for research, XCT scans have increasingly been utilized as a part of the astromaterials curation process, beginning with meteorites [4-5], and more recently with the Apollo samples [6]. Their utility in



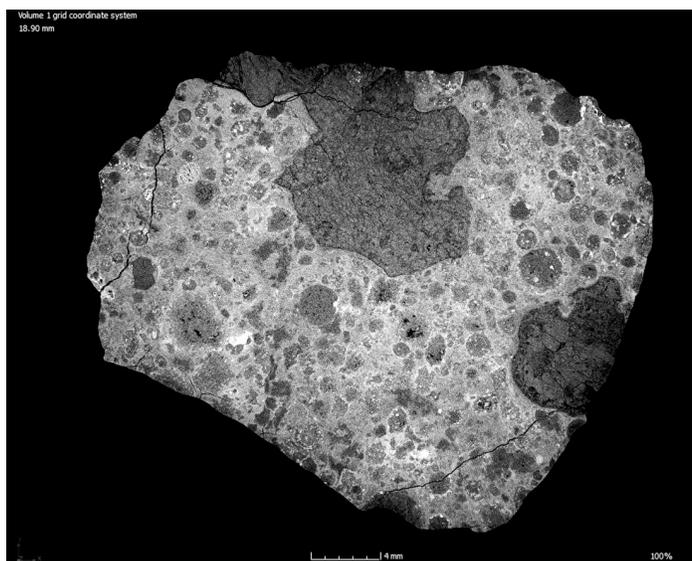
**Figure 1:** Slices of the micro-CT scan of sample 14321,1404. Brightness of the phases are proportional to x-ray attenuation (a measure of composition and density of the phase). Yellow arrows highlight interesting feldspathic (top) and mafic (bottom) clasts. Sample is ~ 6 cm in diameter.



**Figure 2:** Single 2D slice of the micro-CT scan of ungrouped achondrite NWA 11119 showing the igneous textures and major mineralogical phases within the sample. Sample is ~ 3 cm long.

curations lies in their ability to non-destructively map out the phases and voids within a sample. As an example, we have scanned several large Apollo polymict breccias, and we were able to identify and tentatively classify the lithologies in these clasts. The samples can then be subdivided, either through sawing or careful chipping, and those “new” clasts made available to scientists. In addition to the myriad curatorial uses, we have begun to use the XCT system as an integral part of coordinated analyses of astromaterials. Two examples of this are the mapping of textures within ungrouped achondrite NWA 11119 (Figure 2), as well as a newly acquired unclassified carbonaceous chondrite from Morocco (Figure 3). In each case, the XCT scans were able to characterize the major phases with the meteorites, and identify areas of interest for additional higher resolution study (e.g., by TEM). The penetrative nature of the XCT scans allows for astromaterials samples to be analyzed within sealed low-density containers, preserving the pristinity of the samples. The XCT technique is not completely non-destructive, however. A recent study by [7] has shown that XCT scans of meteorites can alter the natural radiation dose of the sample. The number of techniques where this is applicable (e.g., thermo-luminescence) is limited, however. Nevertheless, XCT scans could cause damage for other types of studies (e.g., organics), and we plan to undertake extensive studies to fully characterize the impact XCT scans have on the samples. In the meantime, the percentage of any one sample that is studied by XCT will be limited to ensure that no irreparable damage is done to an entire sample.

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**Figure 3:** Single slice of the micro-CT scan of an unclassified Moroccan carbonaceous chondrite. Large dark grey areas are large zoned CAIs. Sample is ~4 cm in diameter.

# Reproduction of GEMS-like materials in the induction thermal plasma system

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Amorphous silicates are considered to be one of the most primitive materials of the solar system and some of them came from pre-solar environments. Chondritic porous interplanetary dust particles (CP IDPs) contain abundant amorphous silicate grains of ~100 nm in size with Fe-Ni and FeS nanoparticles known as GEMS (glass with embedded metal and sulfides) [1,2]. Solar and interstellar origins of GEMS have been proposed [1, 2]. Experimental study on non-equilibrium condensation of GEMS-like materials is crucial for determination of the GEMS origin.

The ITP system (induction thermal plasma) offers rapid vaporization condition by a discharged high temperature flame (~10,000 K) and rapid cooling rate ( $10^4\sim 10^5$  K/s). Amorphous silicates with metallic iron nanoparticles inside, which are similar to the characteristics of GEMS, were experimentally reproduced using an ITP system [3]. In order to constrain the formation condition of GEMS, we systematically changed ITP operation conditions and performed evaporation and condensation experiments with a new ITP system [4].

The ITP system used in the present study was JEOL TP-40020NPS with 6 kW RF plasma torch. We carried out the vaporization and condensation experiments with a mixed Ar-He plasma flame in the system of Si-Mg-Fe-Na-Al-Ca-Ni-O with the averaged chemical composition of GEMS [1] without sulfur. The plasma generating condition was controlled by selection of a plasma forming gas injecting direction (tangential and radial flame patterns) and reactor pressure (30 and 70 kPa). The tangential flame of the thermal plasma provides more higher cooling rate than the radial flame, and higher reactor pressure enhances the vaporization degree of the starting material [4].

All run products show presence of amorphous silicate, metallic iron, and FeNi in X-ray diffraction spectra and peaks of amorphous silicate at ~10  $\mu\text{m}$  in the FTIR spectra. TEM observation shows that the run products have a variety of textures; amorphous silicate grains from <a few nm to >100 nm with or without aggregation and with or without embedded metallic iron or iron nickel nanoparticles. Among them, the most similar nanomaterial with GEMS was reproduced in a tangential flame condition at 70 kPa (Fig. 1). Although the condensation condition was not quantitatively investigated yet, the present result shows that GEMS-like nanomaterial can form in a limited parameter range of the ITP system, which indicates that the formation conditions and environments of actual GEMS might also be limited.

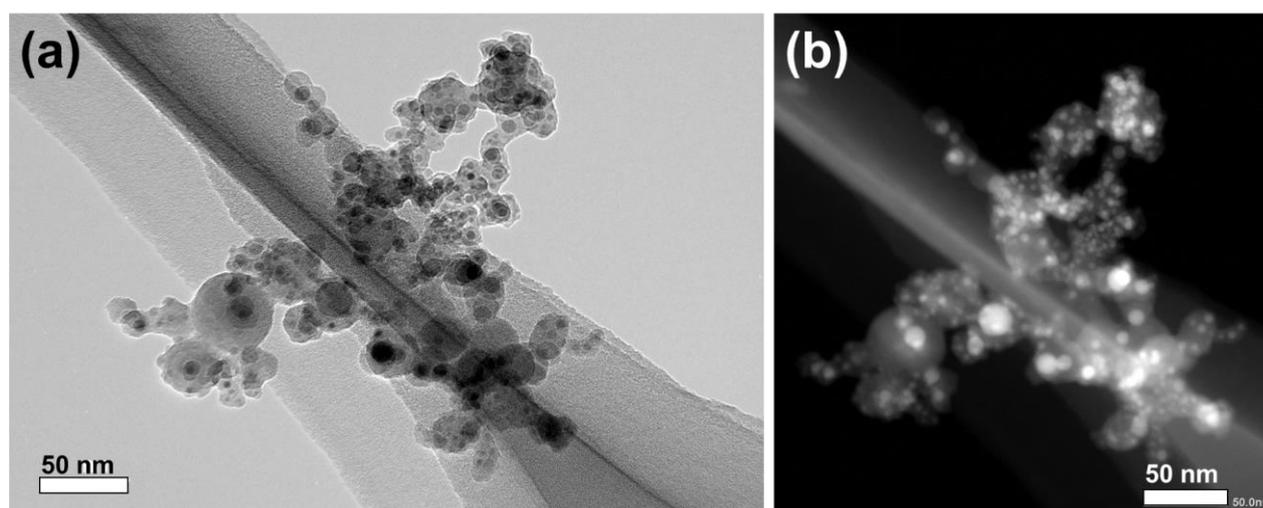


Figure 1. (a) TEM image and (b) STEM-HAADF image of metal embedded amorphous silicate grains produced in tangential plasma flame condition at 70 kPa.

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# **GRAVITATIONAL INSTABILITY ON PROPAGATION OF MHD WAVES IN ASTROPHYSICAL PLASMA**

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Abstract

We determine the general dispersion relation for the propagation of magnetohydrodynamic (MHD) waves in astrophysical plasma by considering the effect of gravitational instability and viscosity with anisotropic pressure tensor and heat-conducting plasma. Basic MHD equations have been derived and linearized by the method of perturbation to develop the general form of dispersion relation equation. Our result indicates that the transverse propagation of waves in such a plasma is affected by the inclusion of heat conduction. For wave propagation, parallel to the magnetic field direction, we find that the fairhose mode is unaffected, whereas the mode corresponding to the gravitational instability is modified in astrophysical plasma with anisotropic pressure tensor being stable in the presence of viscosity and strong magnetic field at considerable wavelength.

## Study of solar cycle variation and its impact on critical frequency of F2 layer

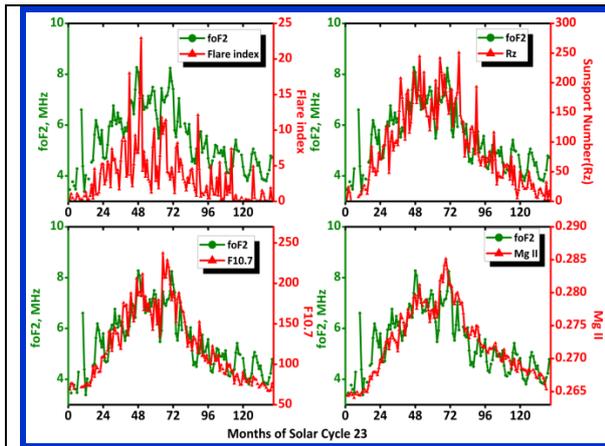
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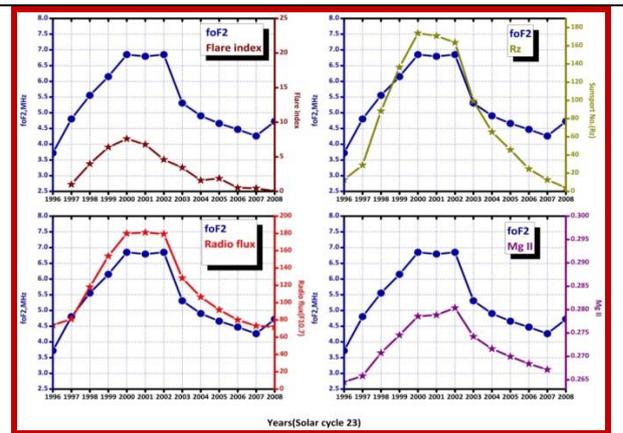
The period of approximately 11 year cycle of solar activity is characterized by the rise and fall in the numbers and surface area of sunspots. We observed a number of other solar activity indices, including the 10.7 cm radio flux, solar Mg II core to wing ratio, relative sunspot number Rz and solar flare index geomagnetic activity that vary in association with the sunspots for solar cycles 23 (1996–2008). This paper presents an analysis of the F-region variability of the ionospheric F2 layer critical frequency (foF2) at Australian mid latitude ionosonde station, Hobart (42.88° S and 147.32° E) during the period 1996 – 2008 of solar cycle 23. The diurnal, monthly, and yearly characteristics of ionospheric F-region parameter foF2 have been studied in detail. We also compared the dependence of foF2 on solar activity indices by using a correlation analysis, and showed a significant linear relationship between the foF2 values and Solar indices. The foF2 variation is strongly influenced by solar activity with about an 11-year solar cycle from the solar maximum to solar minimum.

Table 1. Correlation of foF2 with solar indices during different phases of solar cycle 23.

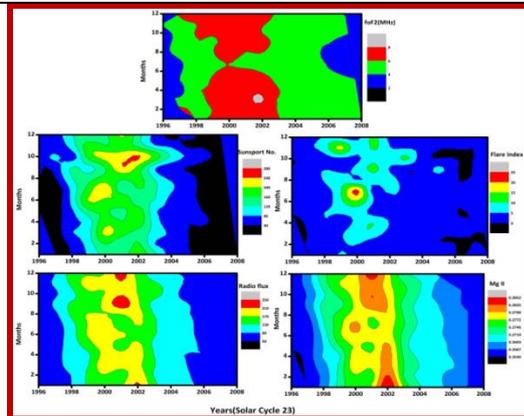
Geomagnetic Indices Vs Fof2	Correlation
Flare Index-foF2	0.85
Rz-foF2	0.92
F10.7-foF2	0.93
Mg II c/w-foF2	0.88



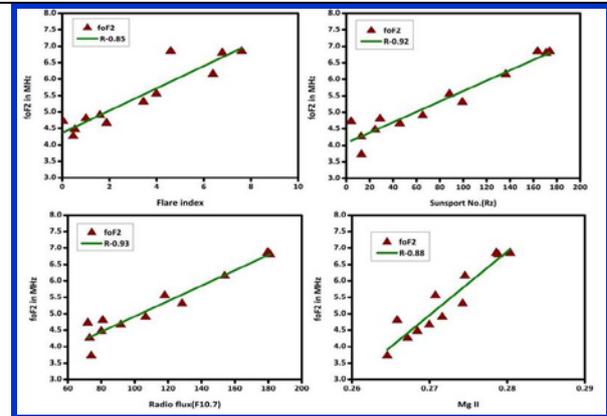
**Figure – 1:** Monthly variation of solar indices with critical frequency foF2 during Solar Cycle 23.



**Figure–2:** Annual variation of solar indices with critical frequency foF2 during Solar Cycle 23.



**Figure-3:** Behavior of critical frequency foF2 and solar indices during the solar cycle 23.



**Figure – 4:** Scatter and Correlation of foF2 with Flare index, sunspot number (Rz), Radio flux (F10.7) and Mg II core to wing ratio during the solar cycle 23.

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## Study of magnetic storm effects on the variation of TEC over low, mid and high latitude station

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The ionosphere is very important because of its influence on the passage of radio waves. Total electron content (TEC) is a key ionospheric parameter that describes the major impact of the ionosphere on the propagation of radio waves which are crucial for terrestrial and space communication. The present investigation is dedicated to study the latitudinal variation of ionosphere. The study is carried out by taking three stations one each in low, mid and high latitude regions namely IISC, Bangalore, India (13.020 N, 77.570E), GUAO, Urumqi, China (43.820N, 87.600E) and NYAL, NY-Alesund, Norway (78.920N, 11.860E) respectively. To study the changes in the ionosphere at three selected station we have considered the GPS observations. The GPS derived TEC values have been collected from the SOPAC (Scripps Orbits and Permanent Array Center) data archive of the IGS (International GPS service). We studied the behaviour of ionospheric Total Electron Content (TEC) during the geomagnetic storms. We have selected 5 intense geomagnetic storms ( $Dst \leq -100nT$ ) that were observed during the year 2012. From our analysis we observed that the effect of geomagnetic storms on VTEC is highest at low latitude, moderate at mid latitude and low at high latitude.

Table 1. Catalogue of all the five selected intense geomagnetic storm events along with Peak Dst.

Event Date	Peak Dst(Min.)
9 March 2012	-143nT
24 April 2012	-104nT
15 July 2012	-133nT
1 October 2012	-133nT
14 November 2012	-109nT

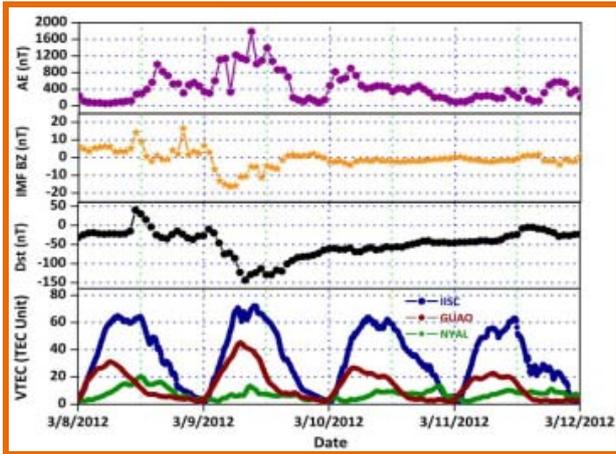


Figure 1:

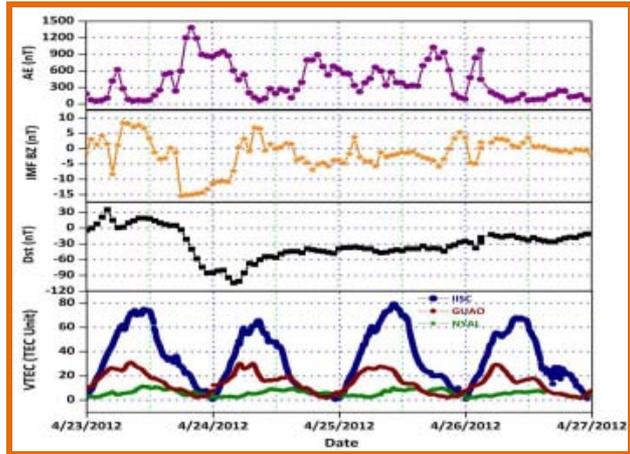


Figure 2

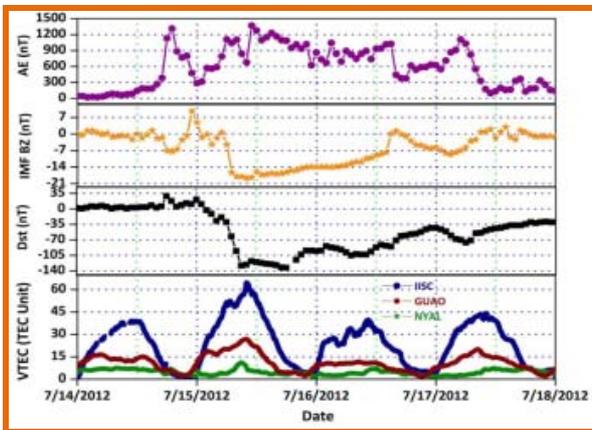


Figure 3

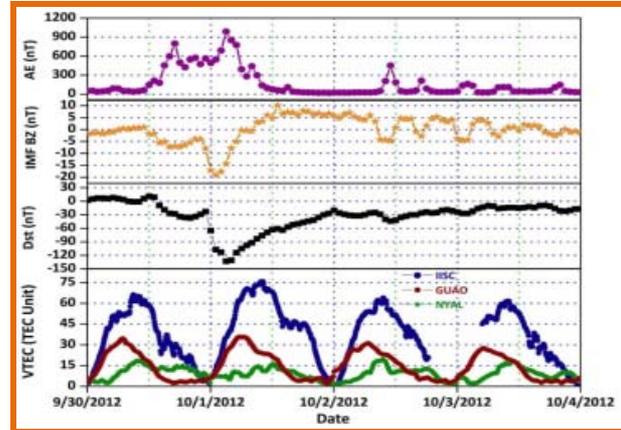


Figure 4

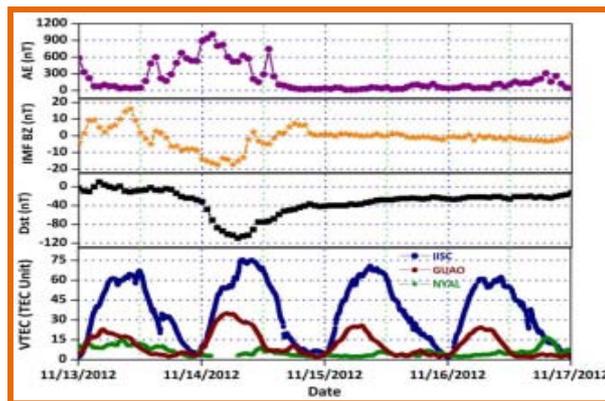


Figure 5

Figure 1, 2, 3, 4 and 5. Plot of temporal evolution of ionospheric VTEC along with Dst, IMF Bz and AE during the geomagnetic storm of 9 March, 24 April, 15 July, 1 October, and 14 November 2012.

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## **Moon-Earth: global basaltic effusions, their different ages, common chemical trends (alkalinity, iron content)**

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Global basaltic covers are very characteristic phenomena in the inner solar system. Basaltic effusions of different ages and compositions originated in asthenospheric layers of the planetary mantles. To heat and melt some parts of the mantle, a part of enormous mechanical energy of orbiting cosmic bodies was transferred to the heat energy.

“Orbits make structures” – a main point of the new wave planetology based on one important property of the Keplerian elliptical planetary orbits [2, 3]. The ellipticity implies periodical changes of accelerations and, thus, orbital forces structuring cosmic bodies. The Earth and the Moon sharing the same circumsolar orbit have similar main structural features. Among them there are terrestrial Oceans and lunar Basins. The most obvious are two tectonic triads: Pacific Ocean – Malay Archipelago – Indian Ocean on Earth and Procellarum Basin – Mare Orientale – SPA Basin on the Moon. The planetary depressions of both bodies are covered with basalts, but basaltic effusions are drastically different in age: the AR on Moon and Mz-Cz on Earth. These ages well correlate with the bodies masses. The more massive and inert Earth has heated and melted mantle much later (The Newton’s law of inertia). Energy of movement transfers to the heat energy.

The both cosmic bodies, as well as the rest of them, are tectonically dichotomous. Their subsided hemispheres, for keeping angular momentum of hemispheres equal, are filled with dense basaltic material. But times of the fillings are significantly different.

The Earth-Moon system expands with time, that is increases its angular momentum. A natural response to it is in slowing down rotation of both bodies diminishing their angular momentum (action - opposite action). Diminishing momenta are compensated by melting and uplifting to surfaces dense basaltic material. But on the Moon it happened much earlier (4.5-3 billion years ago) because of diminished inertia of the small mass satellite. At much larger and massive with large inertia Earth this process was significantly “delayed” in time.(Mz-Cz). Earth is 81 times more massive than Moon. (3-4.5 billions) :  $81 = 37-55$  million years. According to this calculation, a “peak” of the basaltic reaction of Earth, filling in by basalts the oceanic depressions is in the boundary of Mesozoic and Cenozoic [3]].

Despite of enormous age differences between lunar and terrestrial basaltic covers (billions of years!) some common chemical shift of their compositions is notable and significant. Let us compare Procellarum Basin and Pacific Ocean basalts. The oldest parts of their covers occur mainly in the West of Procellarum (KREEP) and SW of the Pacific (Ontong Java Plateau – the largest LIP of Earth). Potassium, phosphorus, rare earths, thorium enrich the older lunar KREEP basalts. The older terrestrial oceanic Ontong Java basalts (Cretaceous age-about 122 mln. y) also show “KREEP trend”. They belong to E-MORBs and have elevated values of potassium, lithium, chlorine, REE, thorium. Elevated Fe/Mg (and siderophile platinum group elements) also is in Ontong Java basalts [1]. All these chemical peculiarities distinguish them from the younger N-MORBs of other parts of the Pacific Ocean (EPR, for example). As all considered basalt melts of both bodies originate in asthenospheres, the older parts of these melts derive from relatively earlier “cool” asthenosphere. It means that only easily melted alkali and iron rich parts were involved in the process. Later on, significantly heated asthenospheres produced enormous volumes of chemically different (less alkaline and more magnesian) basalts. In this sense, rather impressive is a comparison of the lunar iron and

thorium geochemical maps stressing coincidence of their anomalies in the Procellarum KREEP terrain area (Fig. 1, 2).

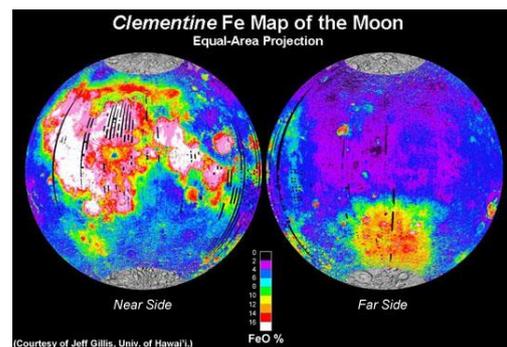
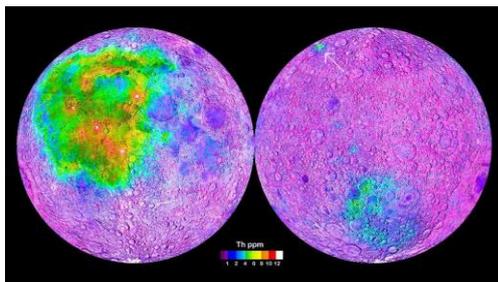
The considered time development of basaltic magmatism could be paralleled with the development of alkaline terrestrial magmatism. Its earlier older parts often are more alkaline than later Cenozoic parts. Famous large agpaitic massifs are mainly Proterozoic-Paleozoic in age. Again, early “cold” asthenosphere produces more easily melted relatively small alkaline parts than the later “hot” asthenosphere making large volumes of deeply melted more magnesian less alkaline ones.

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# On the bulk silicate composition of carbonaceous chondrites

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## Introduction:

The bulk compositions of the stony meteorites have been dominated by silicates and oxides. The one part of meteoritic minerals came through different grade of the chemical and/or physical transformations during the formation of the Solar-System. There are ancient mineral constituents, which survived the early stage of the evolution of the Solar-System and they appears original form: presolar dust grains. Primitive meteorites contain presolar dust grains: silicates, oxides, nanodiamonds, silicon carbide graphite, silicon nitride. The dominant sources of dust grains are the AGB stars and supernovae. The presolar silicate abundance is greater than the abundances of other presolar minerals [1].

Carbonaceous chondrites (CC, c-chondrites) are primitive meteorites with significant silicate and oxide amounts, some of them contain a relatively larger amount of elemental carbon (diamonds, graphite) and carbon-based compounds (silicon-carbide, different organic compounds). They are composed mostly of chondrules, inclusions and the fine-grained matrix. C-chondrites can be classified according to that their parent bodies formed in different regions of the early Solar-system. Accordingly, different CC-groups may distinguished as CI, CM, CV, CO, CR, CK, and CH type chondrites [2]. The groups are further divided into different subgroups.

Similarities and significant differences also appears in the abundances of given compounds in the different chondrites depending on the formation conditions of their parent bodies. For instance, the bulk composition of Allende matrix is Fe-rich obtained by Inoue et al. [3], the CM2 Murchison meteorite is an organic rich carbonaceous chondrite [4]. Chemical similarities appear between CM and CO chondrite chondrules [5], while considerable differences show the Murchison (CM2) and the Allende (CV3) chondrites in carbon content of the matrix.

In carbonaceous chondrites, highly forsteritic ( $Mg_2SiO_4$ ) olivine can be found for example in the chondrules, in the (Amoebid Olivine Aggregates (AOA) and in the grains and aggregates embedded in the matrix. Fayalitic olivine ( $Fe_2SiO_4$ ) is also identified in the mineral structures, but its amount is smaller than that of the forsterite. Enstatite ( $MgSiO_3$ ) and ferrosillite ( $FeSiO_3$ ) are also known in the mineral textures of chondrites.

*Bulk silicate composition of c-chondrites* The investigation for characteristics of silicates based on in detail the Kaba primitive CV3 c-chondrite [6], otherwise we studied the pure matrix material of the Allende CV3 c-chondrite with the concerning data utilized from the results of Inoue N. et al. 2004 [3]. We determined the Mg/Fe ratio in the silicates and the results have been summarized in the Table 1.

Kaba (CV3) mineral structure	Mineral sample	FeO(wt%)	MgO(wt%)	Mg/Fe
<b>Porphyritic chondrule</b>	Forsterite Fo1-1	0.30	55	Mg0.993Fe0.007
<b>Granular ol-px chondrule</b>	Forsterite Fo3-1	0.89	54.99	Mg0.98 Fe0.02
	Forsterite Fo3-2	1.02	54.70	Mg0.976Fe0.024
<b>Isolated olivine grain</b>	Forsterite Fo8-2	0.21	56.91	Mg0.995Fe0.005
<b>Comlicated aggregate</b>	Fayalite Fa9-2	68.05	0.26	Mg0.003Fe0.997

Allende (CV3)				
Pure matrix	A1	36.60	19.19	Mg0.407Fe0.593

Table 1. The FeO and the MgO abundances in different mineral structures of the Kaba meteorite (CV3) and in the bulk chemical composition of the matrix of the Allende (CV3) chondrite. The Mg/Fe ratio is calculated from the basic data that are taken from Gucsik A. et al. (2013) and from Inoue M. et al. (2004).

As seen in the Table 1, the mineral components of the Kaba meteorite is rich in highly forsteritic ( $Fo > 0.99$ ) olivines, while the bulk silicate composition of the Allende matrix enriched in iron. In fact, the mineral composition of chondritic meteorites has been dominated by silicates. The elemental abundances of chondrites approximately consistent with the cosmic abundances of elements and minerals. The high ratio of Mg, Si, and O in meteorites refers to the dominance of magnesium silicates for the case of chemical characteristics of the Galaxy as opposed to the abundances of Fe-, Ca-, Al-silicates.

**Summary:** The carbonaceous chondrites are known to have been dominated by silicates but they may contain carbonaceous mineral constituents in small amounts. The bulk composition of the planet-building materials in the most circumstellar environments is assumed to be chondritic-like.

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## NASA Curation Preparation for Ryugu Sample Returned by JAXA's Hayabusa2 Mission

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The NASA OSIRIS-REx and JAXA Hayabusa2 missions to near-Earth asteroids Bennu and Ryugu share similar mission goals of understanding the origins of primitive, organic-rich asteroids. Under an agreement between JAXA and NASA, there is an on-going and productive collaboration between science teams of Hayabusa2 [1] and OSIRIS-REx missions [2]. Under this agreement, a portion of each of the returned sample masses will be exchanged between the agencies and the scientific results of their study will be shared. NASA's portion of the returned Hayabusa2 sample, consisting of 10% of the returned mass, will be jointly separated by NASA and JAXA. The sample will be legally and physically transferred to NASA's dedicated Hayabusa2 curation facility at Johnson Space Center (JSC) no later than one year after the return of the Hayabusa2 sample to Earth (December 2020). The JSC Hayabusa2 curation cleanroom facility design has now been completed. In the same manner, JAXA will receive 0.5% of the total returned OSIRIS-REx sample (minimum required sample to return 60 g, maximum sample return capacity of 2 kg) from the rest of the specimen [2]. No later than one year after the return of the OSIRIS-REx sample to Earth (September 2023), legal, physical, and permanent custody of this sample subset will be transferred to JAXA, and the sample subset will be brought to JAXA's Extraterrestrial Sample Curation Center (ESCuC) at Institute of Space and Astronautical Science, Sagami-hara City Japan.

Both the Hayabusa2 sample to be sent to NASA and the OSIRIS-REx sample to be sent to JAXA will be unprocessed and representative of the returned bulk sample. "Unprocessed" means that the sample will be handled in a way that minimizes chemical and physical changes to the sample, including avoidance of harsh radiation and heating environments such as electron beams and Raman microscopy. The exchange samples will also be protected from organic and other forms of contamination to the greatest extent possible. "Representative" means that the separated sample has, as well as can be determined on the unprocessed sample, very similar characteristics to the bulk returned sample, including grain size, color, and other physical properties readily determined by optical observation.

The overarching objectives of NASA's Hayabusa2 curation are to preserve and protect the returned Ryugu subset samples to maximize the science return. Curation scientists at JSC together with ESCuC members and the OSIRIS-REx science team have been working to identify requirements on contamination and sample environmental controls. The Hayabusa2 curation requirements can be categorized into the following nine major responsibilities: 1) Contamination control, 2) Curation procedures for solid and gas samples from Ryugu surfaces, 3) Clean laboratory design and construction, 4) Sample characterization for catalog (non-destructive organic-nonorganic lithology identification in a glovebox), 5) Sample distribution, and 6) long term curation activity. Many of the aspects of NASA Hayabusa2 curation for the Ryugu samples are already well developed and have strong heritage at JSC. Examples of existing knowledge and application in this area include ppb level organic residue monitoring of the gaseous curation grade nitrogen, precision cleaning of ultrapure water circulating in the clean labs, particle count monitoring, and metal material control for terrestrial trace element contamination control (Apollo, Genesis samples), and sample handling of small particles (cosmic dust, Stardust cometary particles, Hayabusa1 asteroid samples), to mm-cm sized rocks (Antarctic meteorites). The Hayabusa2 sample storage and handling facility at JSC have been co-designed with the OSIRIS-REx sample curation clean facility to protect the samples from contamination, cross-contamination, temperature excursions, and moisture that could alter the sample. The construction of the facility will start in 2018 [3].

As with every new extraterrestrial collection, returned primitive Ryugu samples bring special new requirements for potentially organic rich samples. Hayabusa2 mission will attempt to collect three samples from the surface of the asteroid in order to return a minimum of 100 mg of material. Prior to its third touchdown, Hayabusa2 will release an impactor to the asteroid that will create a small crater, possibly exposing more pristine materials from beneath the surface from which sample collection may be attempted. Each of the three samples may have different characteristics and they should be properly handled to preserve them. Hayabusa2 Science Team will attempt to extract the gas sample before opening the pneumatically sealed sample container. JSC will develop the gas sample curation and handling technique under our advanced curation activity [4].

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## Current status of developments by the collaboration team with ESCuC/JAXA for curation works and analysis of Hayabusa2 returned samples

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<sup>5</sup>Tokyo Metropolitan University, <sup>6</sup>Japan Aerospace Exploration Agency (JAXA).

Extraterrestrial sample curation center (ESCuC) of Japan aerospace exploration agency (JAXA) organized a special team for the development of techniques and devices for the handling, transfer and analysis of samples returned by Hayabusa2 spacecraft, from 2015 under the agreements of collaboration. The special team constitutes of members of institutes those having state-of-the-art analytical instruments and experiences of curatorial works of precious natural samples, but beyond the specialists of the extraterrestrial materials. Through the collaboration, we can introduce latest specialties and knowledges from diverse scientific and technological fields into the processes of analysis of Hayabusa2 returned samples [1,2].

So far, we finished the development sample transfer container for the inter-institute transfer, even international transfer of samples, without contamination of terrestrial materials and sample damages such as breaking and sample lost. We also evaluated the sealing performance of the container and confirmed that it has enough sealing performance against even positive pressure inside the container. The container, named as Facility to Facility Transfer Container (FFTC), is already available commercially.

Currently, the team members are working for (1) development of sample holders for the sample transfer in high cleanness environment, (2) development of devices for the atmosphere shielding environment for the sample handling, (3) development of sample holders applicable for multiple analytical methods, and (4) development of techniques for the evaluation of cleanness of those developed materials and environments. Although those devices and techniques are still under development, we already applied them for the analysis of samples in each institute, and evaluated its applicability and problem for the analysis of Hayabusa2 returned samples.

We also started development of new analytical protocols of extraterrestrial materials, which includes method of sample transfer, sample separation and data sharing, through the rehearsals of the curation works for the initial description of Hayabusa2-returned samples using extraterrestrial materials. Currently, 5 Antarctic micrometeorites provided by national institute of polar research (NIPR) were imaged by synchrotron radiation computed tomography (SR-CT) and x-ray diffraction (XRD) at SPring-8, and investigated by high resolution field emission scanning electron microscopy and energy dispersive spectroscopy (FE-SEM-EDS) system at institute for molecular sciences (IMS). Through the series of non-destructive analysis, we selected Antarctic micrometeorites those having similar characteristics of carbonaceous chondrites, and formed thin sections by focused ion beam (FIB) for the characterization of organic materials by scanning transmitted x-ray microscopy and near edge x-ray absorption fine structure analysis (STXM-NEXAFS) at IMS, high resolution analysis by transmission electron microscopy (TEM), and isotopic analysis of light elements such as hydrogen, carbon, nitrogen and oxygen by secondary ion mass spectrometry (SIMS) at Japan agency for marine-earth science and technology (JAMSTEC).

In order to make possible such large scale collaboration for the series of sample analysis between institutes, we need to evaluate sample damages and contaminations through the analysis, and develop the methods for cleaning of sample holder and protocols for suppressing sample damages, as well as sample transfer system. Sample holders are already under the examination. So we can start the evaluation of cleanness and development of method for the cleaning of them by ultrasonic cleaning and acid-alkali cleaning [3,4]. We will start the development in this year, and will report the result near future.

Thus progress of our development is going along quite smoothly. We can share the result of our development with preliminary examination team of Hayabusa2 sample analysis organized by Hayabusa2 project, and can make their start process faster.

In future work, we will develop the cutting method of samples with low-contamination processes, including sample mounting devices and handling method after the cutting. In order to include rare and trace element analysis using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in our protocol, we will also start the development of sample holders and examination of it, in parallel with the rehearsals of the initial description of Hayabusa2 returned samples.

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## Systematic detection of carbonaceous phases in chondrites – request for sophisticated techniques for Hayabusa 2 particle analyses

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The Asteroid Explorer “Hayabusa 2” is the successor of “Hayabusa” (MUSES-C), which for the first time ever returned pristine samples from an asteroid [1]. 25143 “Itokawa” is a small Near-Earth S-type asteroid consisting mainly of ordinary chondrite type material [2, and refs herein]. The mission was a major step towards further elucidating the origin and formation of our solar system. The “Hayabusa 2” mission, launched in 2014, will target another Near-Earth asteroid, namely 162173 “Ryugu” (1999 JU3) which is a C-type asteroid. To learn more about the formation and evolution of our solar system, investigating different types of asteroids, namely S-, C-, and D-type, is mandatory. C-type asteroids such as “Ryugu” are interpreted as more primordial bodies than for example “Itokawa” and are considered to contain more carbonaceous, organic or hydrated mineral phases. Spectroscopical data show that this asteroid type might be closely related to primitive carbonaceous chondrites or comets in terms of material composition [3].

Very sophisticated techniques are required for the investigation of pristine “Ryugu” particles in our laboratories (return planned end of 2020). LASER Micro Raman Spectroscopy is perfectly suited for identifying and discriminating (extra-) terrestrial mineralogy: (a) fully non-destructive (repeated experiments possible on one and the same spot under variable conditions), (b) investigations with high sensitivity and in parallel high resolution, optionally in 3 dimensions, (c) as a major advantage experiments on pristine material without any preparation or coating, and (d) mineral polytypes (eg diamonds) can be well discriminated. Variable LASER frequencies allow to optimize and fine-tune the Raman system to specific sample and experiment requirements. High resolution scanning can produce very detailed distribution maps of selected mineral phases. Micron- or even nano-sized particles such as various diamond polytypes can be detected in this way. Within our Hayabusa sample analyses project we have successfully applied LASER Micro Raman Spectroscopy on several individual Itokawa particles [2].

Generally, the carbon-phase mineralogy has not really been investigated systematically in most meteorite types [4,5]. The main focus was on ureilites and certain carbonaceous chondrites [4-7], and priority was set on graphitic components and diamonds. The presence of very rare carbonaceous phases such as graphenes, fullerenes or nanotubes which can be expected in a number of meteorite types has not been investigated to our best knowledge. Therefore we have started detailed and systematic investigations on the carbon-phase mineralogy of a larger set of various stony meteorite types. Priority is presently set on the following selected recent falls and finds [8-13]: (a) Ordinary chondrites Machtenstein H5 (find around 1956, classified 2014), Braunschweig L6 (fall 2013), Stubenberg LL6 (fall 2016), and for comparison the HED meteorite Saricicek (howardite fall 2015) as well as a large series of Almahata Sitta individuals [polymict ureilite, 12,13 and refs]. In our poster we will present first detailed results concerning the carbon phase mineralogy in these meteorites and will also focus on hypotheses concerning the possible formation processes of the meteoritic micro-nano diamonds [6,7,14,15]: (a) Chemical Vapor Deposition (CVD) and (b) shock metamorphism as optional in situ diamond producing processes, and (c) presolar diamonds of extrasolar origin (eg from supernovae explosions).

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# The evolution of water-rich asteroids: Linking the mineralogy and spectroscopy of fully hydrated CM carbonaceous chondrites

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**Introduction:** The C-complex asteroids (which include B, C, F and G-types [1]) are of interest because they are thought to be volatile-rich, and may be able to tell us about the evolution of water and organic compounds in the early Solar System. Additionally, C-complex asteroids likely made a significant contribution to the volatile budget of the terrestrial planets [2,3]. Carbonaceous chondrite meteorites are physical samples of C-complex asteroids; linking laboratory spectra of carbonaceous chondrites to remote sensing observations of asteroids can therefore give insight into the processes, which occur on primitive bodies in the Solar System.

Spectrally, many C-complex asteroids show evidence for aqueous alteration and links with CM and CI carbonaceous chondrites on their surfaces [4–7]. Most spectral links have been between the C-complex asteroids and moderately altered CM2 chondrites. Although there have been limited studies on the association of these asteroids with fully hydrated (“type 1”) chondrites, Clark et al. [8] suggested a possible relationship between more aqueously altered CM and/or CI chondrites and the surface mineralogy of the B-type, OSIRIS-REx target asteroid, Bennu.

The CM1 chondrites are among the most hydrated extra-terrestrial materials available to study; their precursor mineral assemblages have been almost entirely transformed into secondary, hydrated phases. King et al. [9] investigated CM1 and CM1/2 chondrites with the aim of establishing modal mineralogy and examining variations in the extent of aqueous alteration. In this study we collected reflectance spectra from the same powders used by King et al. [9] so that any spectral trends could be put into context of the mineralogy and degree of aqueous alteration for each meteorite sample.

**Experimental:** The suite of meteorites investigated included six CM1/2 chondrites and four CM1 chondrites. Approximately 100 mg of each sample was ground into a fine powder using an agate mortar and pestle to a particle size of <35  $\mu\text{m}$ . Infrared reflectance spectra of the powders were obtained using a Bruker VERTEX 70v Fourier Transform Infrared (FTIR) spectrometer at the University of Oxford, using a wide range MIR-FIR beam splitter and a room temperature deuterated L-alanine doped tryglycine sulfate (RT-DLaTGS) detector to measure the reflectance between 6000 - 200  $\text{cm}^{-1}$  (1.7-50  $\mu\text{m}$ ). All observations were obtained under vacuum ( $\sim 5$  hPa), at a resolution of 4  $\text{cm}^{-1}$ . In order to remove instrumental effects, spectra were calibrated by dividing each meteorite spectrum with a spectrum of a gold calibration target,

**Results & Discussion:** Initial observations of the mid-infrared spectra show samples, which are mostly composed of hydrated minerals, particularly serpentine-group phyllosilicates. Upon further investigation of individual spectral regions - the 3  $\mu\text{m}$  band, 6  $\mu\text{m}$  band, Christiansen features (CF: 7.5-9.5  $\mu\text{m}$ ), and the transparency features (TF: 10.5-14  $\mu\text{m}$ ) - different phyllosilicate compositions and abundances resulted in different, distinguishable spectral features.

The 3  $\mu\text{m}$  band centres are affected by the Fe-cronstedtite abundances in the samples, with higher abundances shifting the feature to longer wavelengths. The 6  $\mu\text{m}$  band features appear to reflect the anhydrous silicate content, with greater band depths for higher olivine contents. The CFs are identified at similar wavelength positions for all samples (8.8 - 8.9  $\mu\text{m}$ ) suggesting the meteorites have similar bulk mineralogy. The TFs were affected by the total phyllosilicate abundance, with higher abundances shifting the peaks to shorter wavelengths.

The above conclusions resulted in splitting the meteorites into two groups. Group A samples had larger 6  $\mu\text{m}$  band features, a 3  $\mu\text{m}$  band centre, and TF peak at longer wavelengths ( $\sim 2.8$   $\mu\text{m}$  and  $\sim 12.5$   $\mu\text{m}$  respectively). Group B samples had smaller 6  $\mu\text{m}$  band features, a 3  $\mu\text{m}$  band centre, and TF peak at shorter wavelengths ( $\sim 2.7$   $\mu\text{m}$  and  $\sim 11.6$   $\mu\text{m}$  respectively).

Group A samples represent the least altered CM1/2s, which have significant Fe-cronstedtite abundances of 30.8 – 36.9% and anhydrous olivine abundances of 18.2 – 19.6%. Group B samples represent the most altered CM1s, which have significant Mg-serpentine (52.4 – 71.6%) and low olivine abundances (3.6 – 8.0%). This study shows that slight variations in aqueous alteration might be discernible in current and future telescopic and space mission observations of C-complex asteroids.

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### **Current status of consortium study of silica-containing Hayabusa-returned particle.**

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**Introduction:** About 730 particles of Hayabusa-returned sample of 10 to 300  $\mu\text{m}$  size are collected by Extraterrestrial Sample Curation Center (ESCuC) in Astromaterials Science Research Group (ASRG) of JAXA, so far [1]. The preliminary examinations and international AOs revealed that Itokawa particles were equivalent to equilibrated LL chondrites [e.g. 2-10]. Some of the Hayabusa-returned particles show unique characteristics including mineralogy, composition, structure, and/or size. Therefore, consortium studies have been conducted by team of ESCuC in order to obtain maximum scientific results from such particles [11-13].

We proposed a new consortium study of particle RB-QD04-0069 containing silica [14]. This is the only particle which contains silica coexist with other silicate minerals among catalogued Hayabusa-returned samples, so far. Silica is widespread in ordinary chondrites, but its abundance is very low (usually  $< \sim 1$  vol %) [15]. Therefore, the particle RB-QD04-0069 is precious and it should be investigated as consortium study. Evidence of shock processes have been revealed from Hayabusa-returned particles by previous studies and shock and/or thermal history of the particles were discussed [2, 8-10]. Because silica has many polymorph, it should be useful indicator to constrain thermal and/or shock history of the particle [16]. In this paper, we report current status of the consortium study of particle RB-QD04-0069.

**Sample and Analytical flows:** RB-QD04-0069 is a particle with a size of 33  $\mu\text{m}$ , which was captured from the first touchdown site on Itokawa. The particle consists of olivine, high-Ca pyroxene, low-Ca pyroxene, plagioclase, and silica revealed by initial description by FE-SEM-EDS.

The XRD analysis will provide us crystallographic information of silica and other silicate minerals. Moreover, textural information of the particle will be obtained by the SR XCT imaging. After the synchrotron radiation analyses, the particle will be embedded in epoxy resin EPON-812, followed by polishing until the surface of the particle is exposed. Then, oxygen isotope compositions will be measured by SIMS in order to identify the origin of the particle. Furthermore, FE-EMP analysis and TEM observations will be carried out on the particle to obtain important constraints on formation condition of the particle, especially its shock and thermal history.

**Current status:** The particle RB-QD04-0069 was picked up from a slide glass in pure nitrogen-filled environment clean chamber in ESCuC by quartz glass probe using manipulator system last year. Then, the particle was tried to attach to the top of C fiber with epoxy resin Embed-812 using manipulator system in a clean booth at ESCuC for Synchrotron radiation (SR) XRD analysis and SR XCT imaging. However, during the procedure, the particle RB-QD04-0069 was failed to attach to C fiber and fell down on the slide glass or Al foil on heater used for the handling.

By optical microscope and SEM-EDS analysis, three candidate particles were found from Al foil on the heater. We plan to analyze these candidate particles by detailed FESEM-EDS to narrow down the candidates. Then, the surrounding region (Al foil) of the candidates will be cut by FIB at Kyoto University and attach them to C fiber using Pt depo for SR-XRD and XCT analysis to identify true particle using characteristics of silica, olivine, pyroxene, and plagioclase.

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