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

T. Yada[1], K. Sakamoto[1], M. Yoshitake[1], K. Kumagai[1], Y. Nakano[1], T. Matsumoto[1], N. Kawasaki[1], M. Nishimura[2], S. Matsui[1], T. Okada[1], M. Abe[1], H. Yurimoto[1,3], and M. Fujimoto[1, 4]

[1]*Inst. Space Astronaut. Sci., Japan Aerosp. Explor. Agency, 3-1-1 Yoshinodai, Chuo, Sagamihara, Kanagawa 252-5210, Japan.*

[2]*Marine Works Japan Ltd., 3-54-1 Oppamahigashi, Yokosuka, Kanagawa 237-0063, Japan.*

[3]*Dept. Earth Sci., Sch. Science, Hokkaido Univ., Kita 8, Nishi 5, Kita-ku, Sapporo, Hokkaido 060-0808, Japan.*

[4]*Earth-Life Sci. Inst., Tokyo Inst. Technol., 2-12-1-1E-1 Ookayama, Meguro, Tokyo 152-8550, Japan.*

**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 $N_2$ condtion and analyzed in low vacuum condtion. 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

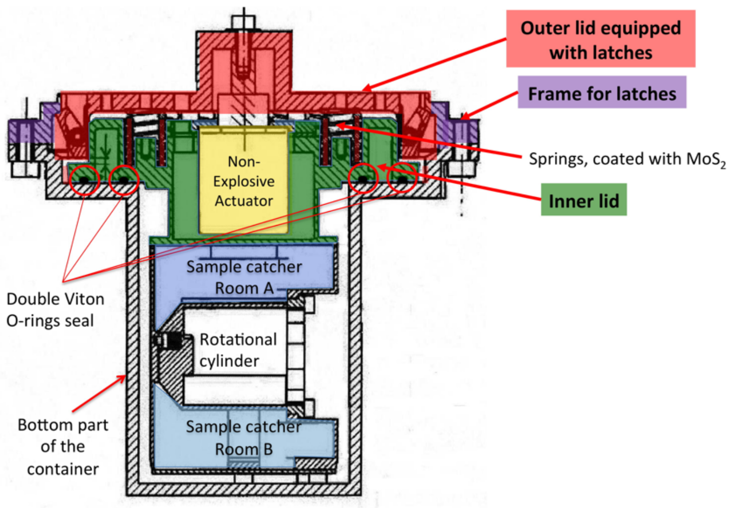


Fig. 1. A cross section of a sample container of Hayabusa. Blown-up samples entering its sampler horn go into a rotational cylinder at first and then captured in either Room A or B of the sample catcher.

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].

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

M. Abe[1,2], T. Yada[1], T. Okada[1,3], K. Sakamoto[1], M. Yoshitake[1], Y. Nakano[1], T. Matsumoto[1], N. Kawasaki[1], K. Kumagai[1], S. Matsui[1], M. Nishimura[4], and H. Yurimoto[5,1]
[1]*Institute of Space and Astronautical Science,*
[2]*SOKENDAI,*
[3]*University of Tokyo,*
[4]*Marine Works Japan LTD,*
[5]*Hokkaido University*.

**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 $N_2$ 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 cambers 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 retuned samples of Hayabusa2 until the return of the Hayabusa2 spacecraft to the Earth.

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

Y. Nakano[1], T. Yada[1], M. Abe[1], T. Okada[1] and S. Watanabe[2]
[1]Japan Aerospace Exploration Agency (JAXA) and [2]Nagoya University

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

Shogo Tachibana[1]
[1]*Department of Natural History Sciences, Hokkaido University*

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

Francis M. McCubbin and Ryan A. Zeigler

*NASA Johnson Space Center, 2101 NASA Parkway, mailcode XI2, Houston TX 77058 USA*

**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

Ryan A. Zeigler, Judith H. Allton, Cindy A. Evans, Marc D. Fries, Francis M. McCubbin, Keiko Nakamura-Messenger, Lisa Pace, Kevin Righter, Michael Zolensky

*Astromaterials Research and Exploration Division, NASA JSC, Mailcode XI, 2101 NASA Parkway, Houston, TX 77058*

**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 $N_2$ system, and annual measurements of inorganic or organic contamination in processing cabinets. Additionally, each delivery of liquid $N_2$ 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

Kevin Righter[1], Keiko Nakamura-Messenger[2] and OSIRIS-REx Curation Working Group
[1]*NASA Johnson Space Center, Mailcode XI2, 2101 NASA Parkway, Houston, TX 77058*
[2] *NASA Johnson Space Center, Mailcode XI3, 2101 NASA Parkway, Houston, TX 77058*

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 μm 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 μm) 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 enables 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 ($ESA^2C$) and Curation Facility – progress update

Caroline Smith[1], Sarah-Jane Gill[1], Chris Jones[1], Kamini Manick[1], Giles Miller[1], Michael Rumsey[1] and Ludovic Duvet[2]

[1]*Department of Earth Sciences, Natural History Museum, London, SW7 5BD, UK*

[2]*Human Spaceflight and Robotic Exploration Programmes Directorate, European Space Agency ECSAT, Fermi Avenue, Harwell Campus, Didcot, Oxfordshire, UK, OX11 0FD*

**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 ($ESA^2C$) 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 $ESA^2C$, 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 $ESA^2C$ 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 $ESA^2C$ - 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 $ESA^2C$ is a relevant and practical resource for technology development.

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# NASA Sample Return Missions: Recovery Operations

Pace, L. F[1], Cannon, R. E.[2]
[1]*NASA Johnson Space Center, Houston, TX USA;* [2]*Hill Air Force Base, UT, USA.*

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

Tim Haltigin [1]
[1] *Canadian Space Agency, 6767 route de l'Aéroport, St. Hubert, QC, Canada J3Y 8Y9, timothy.haltigin@canada.ca*

**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].

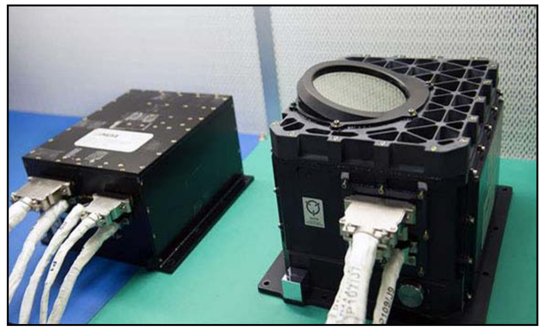

Figure 1: The OSIRIS-REx Laser Altimeter
(Image credit: NASA / Goddard / Debora McCallum)

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?

Christopher D. K. Herd[1]
[1]*Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta, T6G 2E3, Canada*

**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 $O_2$ and $H_2O$ 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 (~ -80°C) storage of specimens and the handling and processing of specimens under cold (~ -15°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

Jamie E. Elsila
[1]*NASA Goddard Space Flight Center, Greenbelt, MD USA*

**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

Z. Martins[1], P. Modica[2,3], C. Meinert[4], B. Zanda[5], L.L.S. d'Hendecourt[2,6]

[1]ESE, Imperial College London, SW7 2AZ, UK; [2]CNRS, Université Paris XI, Institut d'Astrophysique Spatiale, ''Astrochimie et Origines'', 91405 Orsay Cedex, France; [3]Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E), CNRS/Université d'Orléans, 45071 Orléans, France; [4]Université Côte d'Azur, Institut de Chimie de Nice, UMR 7272 CNRS, 06108 Nice, France ; [5]Muséum d'Histoire Naturelle, CNRS, 75005, Paris, France; [6]Equipe ASTRO, Laboratoire de Physique des Interactions Ioniques et Moléculaires, UMR CNRS 7345, Centre de Saint Jérôme - case 252, Université d'Aix-Marseille, 13397 Marseille, France.

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 synthetized 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 synthetized 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 β-alanine/glycine ($0.15 \pm 0.02$), which is the smallest β-alanine/glycine ratio observed in CM chondrites [6]. The relative abundance of β-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 β-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.

**References**

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

Yoshihiro Furukawa[1], Yoshito Chikaraishi[2], Chiaki Abe[1], Naohiko Ohkouchi[3], and Tomoki Nakamura[1]
[1]*Department of Earth Science, Tohoku University*
[2]*Institute of Low Temperature Science, Hokkaido University*
[3]*Japan Agency for Marine-Earth Science and Technology*

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.

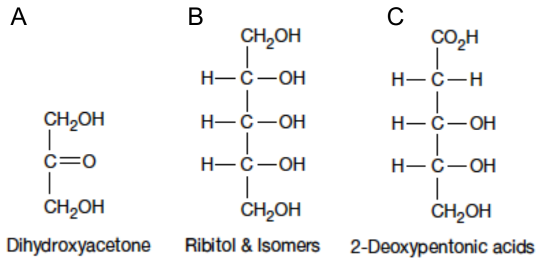


Fig. 1: Structures of sugar, sugar acids and sugar alcohols detected in meteorites. A) dihydroxyacetone, B) ribonic acid, and C) 2-Deoxypentantonic acid. Cooper *et al.*, 2001.

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.

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