

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

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

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

The technical developments and sample handling protocols used before, during and after the return of samples by the Hayabusa2 mission are the best and most recent examples of advanced curation techniques for volatile-rich elements collected during space missions [8,9]. Therefore, they represent a reference starting point for improving the current curation protocols and developing new solutions. Ryugu samples are thus providing perfect opportunity to assess the quality of the current techniques of curation of volatile-rich extraterrestrial samples. In this presentation we will show how Hayabusa2 samples have the potential to provide key information on the state-of-the-art of curation techniques and possible improvements.

Gas samples from Ryugu allocated by the JAXA curation center will be delivered to IPGP in fall 2023. Noble gases (Ne, Ar, Kr and Xe) elemental and isotopic composition will be immediately measured in order to : i) evaluate if the different samples prepared by the curation team have the same composition (NT1 vs NT2 sample) ; ii) compare with published data (*e.g.*, [9]) for NT1 sample and evaluate if the composition of the gas has evolved since the preliminary investigations. Samples will then be stored in distinct conditions (closed and exposed to room pressure and temperature for one sample, closed and attached to a turbo molecular pumping station for another sample, closed and exposed to moderate vacuum for another sample). New measurements will then be conducted after 6-9 months to assess which storage conditions is the most appropriate. Results will be shared and discussed with the JAXA curation team the international community concerned on this aspect of the curation of extraterrestrial samples.

Bottle (sample)	Pipette	Measurement/ Storage	Scientific investigations
NT1	new pipette #, container X NT1P#X	immediate measurement and storage at room PT conditions (6-9 months) before second measurement	<ul style="list-style-type: none"> evolution of the gas since Okazaki et al. (2022) study mid-duration (months) storage of gas in shipped containers
NT2	new pipette #, container X NT2P#X	immediate measurement and storage at room PT conditions before second measurement	<ul style="list-style-type: none"> differences between NT1/NT2 (sample preparation)
	new pipette #, container Y NT2P#Y	container attached 6-9 months to a high vacuum line (10^{-10} torr)	<ul style="list-style-type: none"> optimization of the mid-duration storage (vacuum, moderate vacuum, room PT)
NT5 (blk)	new pipette #, container Z NT2P#Z	container attached 6-9 months to a moderate vacuum chamber (90% of the pressure inside the cylinder)	<ul style="list-style-type: none"> optimization of the mid-duration storage (vacuum, moderate vacuum, room PT)
	new pipette #, container X NT5P#X	immediate measurement and measurement after 6-9 months of storage in vacuum conditions	<ul style="list-style-type: none"> monitoring of the blank level to decipher the origin of terrestrial contamination

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

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

References

- [1] Avicé G. & Marty B. 2020. Space Science Reviews 216:36. [2] McCubbin et al. 2019. Space Science Reviews 215:48. [3] Parai et al. 2022. Apollo 17 – ANGSA Workshop, LPI Contrib. N°2704:2028. [4] Yokoyama et al. 2022. Science 379:eabn7850. [5] Paquet et al. 2023. EPSL 611:118126. [6] Piani et al. 2023. Astrophysical Journal Letters 946:L43. [7] Okazaki et al. 2017. Space Science Reviews 208:107-124. [8] Miura et al. 2022. Earth Planets Space 74:76. [9] Okazaki et al. 2023. Science 379:eabo0431.