MMX samples curation in Europe

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

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

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

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

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

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

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



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

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

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Pentlandite: A Compositional Indicator of Oxygen Fugacity for Chondrites

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



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

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

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

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

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

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

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

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

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

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



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

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Oxygen isotope analyses of magnetite in Ryugu

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

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

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



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

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

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



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

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Magnetite and non-magnetite framboids in Ryugu sample

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

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

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

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

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



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



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

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

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

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

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

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

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



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

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Neutron Capture ³⁶Cl in Ryugu Samples

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Hayabusa2 arrived at the C-type asteroid 162173 Ryugu in Jun. 2018, and successfully collected surface samples from two sampling sites, returning ~5.4 g of samples to Earth on Dec. 6, 2020. The surface samples stored in Chamber A were collected by the 1st touchdown (TD) on Ryugu's surface on Feb. 21, 2019. A crater (diameter of ~14 m) on Ryugu's surface was made using a collision device - denoted "Small Carry-on Impactor (SCI)" - on Apr. 5, 2019 [1]. The samples in Chamber C were collected proximal to this artificial crater and are possibly ejecta from the north side of the crater by the 2nd TD on Jul. 11, 2019 [2].

Our studies are based on the measurement of those nuclides produced in asteroidal surface materials by cosmic rays - both solar (SCR) and galactic cosmic rays (GCR). Cosmic-ray-produced (cosmogenic) nuclides are used to determine the duration and nature of the exposure of materials to energetic particles. Our goals are to understand both the fundamental processes on the asteroidal surface and the evolutionary history of its surface materials. With this information we hope to better understand asteroid-meteoroid evolutionary dynamics. For Hayabusa2 samples, there are several specific questions we aim to address: (1) are the Chamber C samples, collected during the 2nd TD ejecta deposits from the artificial crater, (2) if so, what is the original depth of each recovered sample in the Ryugu regolith, and (3) what is the surface exposure time, mixing rate, and erosion/escape rate of Ryugu's surface? To answer these questions, we were allocated and received 2 particles from Chamber A (A0105-19 and -20) and 6 particles from Chamber C (C0106-09, -10, -11, -12, C0002-V01, and -V02) for measurements of cosmogenic radionuclides and noble gases. Each sample is several hundred µm in size.

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

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

Assuming a chemical compositions for each particle the same as the bulk analysis of Ryugu [9], the thermal neutron produced ³⁶Cl in Ryugu is maximum at slightly below 100 g/cm² or between depth of C0106-10 and -11. The depth of maximum production for the low-energy neutron capture reaction on Ryugu is shifted toward surface compared to that of the Moon (~150

g/cm²). This occurs because Ryugu contains high H (0.94 %) and C (4.6 %) [9] which are effective moderators of neutrons. Since we don't have exact Cl concentration in each particle, it is hard to compare observed ³⁶Cl concentration to model calculation such as MCNP code system at present. Although we are planning measurements of thermal neutron capture ⁴¹Ca ($t_{1/2} = 0.10$ Myr) in Ryugu, it requires larger sample size than this work because low thermal neutron capture cross section on ⁴⁰Ca compared to that of ³⁵Cl (0.43 b vs. 43.6 b) and lower AMS sensitivity of ⁴¹Ca measurements.

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

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

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

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

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

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

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

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



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

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

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



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

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

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

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

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Research Complex

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



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

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



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

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

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

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

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

normalized to Orgueil and CI chondrite

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

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

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

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

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

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

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

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

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

GEMS-like material from asteroid Ryugu regolith

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

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

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

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



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

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



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

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

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

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

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

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

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Molybdenum and Osmium isotopic compositions of Ryugu sample

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

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

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



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

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

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



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

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

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Ryugu's volatiles investigated using stepped combustion and EGA methods

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

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

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



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



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

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

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

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

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



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

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

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

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

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

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

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

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

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

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

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

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Chemical heterogeneity of insoluble organic matter in Ryugu grains

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

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

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

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

Table 1

Samples investigated.



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

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

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

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

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

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



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

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

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

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



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

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

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

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

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

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

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



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

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

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

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

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

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

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

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

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

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

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



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