#### Phosphorus, Calcium, and Sulfur in Two Ryugu Samples

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The Japanese Aerospace Exploration Agency (JAXA) Hayabusa2 spacecraft delivered the first samples of a primitive, carbonaceous asteroid to Earth. One of the objectives of the mission was to use the samples to characterize the formation and evolution of asteroid Ryugu or its parent body. The elemental compositions of some minerals, particularly apatite and, to a lesser extent, carbonate, are reflective of the composition of the fluid from which they were deposited. Because apatite,  $Ca_{10}(PO_4)_6(OH,F,Cl)_2$ , can host F, OH, or Cl in the anion position, its composition is a sensitive probe of the halogen and water content of the hydrothermal fluid from which it was deposited. However, the apatite structure is capable of tolerating relatively large structural distortions, allowing for diverse element substitutions, making other minor and trace elements in apatite a sensitive probe of fluid composition. Carbonate can also be deposited in hydrothermal processing, and some trace element crystals, so zoning from the interior to the rim in larger carbonates can indicate changes in the fluid composition during the formation. Sulfur, which condenses from the cooling Solar Nebula as schreibersite, an Fe-sulfide, interacts with an oxidizing fluid to alter to Fe-sulfate. In crystals where this alteration is incomplete the sulfide/sulfate ratio can indicate the degree of oxidation by the fluid. We are employing two synchrotron-based instruments to characterize the P, Ca, and S in hydrous meteorites and Ryugu samples to characterize the hydrothermal event(s) that occurred on the Ryugu parent body.

**Samples and Instruments:** We were loaned five samples of asteroid Ryugu from the Hayabusa2 collection to perform mineral identification, XRF mapping, and P, Ca and S X-ray Absorption Spectroscopy (XAS). The X-ray Fluorescence Microprobe (XFM) Beamline 4-BM of the National Synchrotron Light Source II at Brookhaven National Laboratory is a versatile XRF microscope for the characterization of elemental abundances and chemical speciation in heterogeneous materials, characterizing the K-, or L-lines of the heavier elements. XFM is an imaging beamline designed for spatially-resolved XAS spectroscopy in the 4-20 keV energy range, with a user-tunable spot size from 2 to 10  $\mu$ m. The Tender Energy Spectroscopy (TES) Beamline 8-BM of the NSLS-II at Brookhaven National Laboratory, has a user-tunable spot size, varying from 10 x 25  $\mu$ m, with a flux of up to 10<sup>11</sup> photons/s, down to 1 x 2  $\mu$ m, with a flux of up to 10<sup>9</sup> photons/s. A helium sample environment permits XRF element mapping down to 1 eV, for abundance mapping of elements as light as Na. The tunable monochrometer (2 to 5 keV) is optimized for K-edge XAS of elements from P to Ca.

Thus far, we have performed XRF maps of the polished surfaces of two of the five Ryugu samples using a 6 µm step size, at two energies; 7 keV, to provide maximum sensitivity for the low-Z elements while avoiding Fe K-edge fluorescence, in order to locate P-, S-, and Ca-bearing phases, particularly hydrothermal alteration products; and 13 keV, accessing heavier elements. The TES microprobe was then used to perform P, Ca, and S micro-XAS on targeted element hot-spots.

**Results and Discussion:** The initial XFM mapping (Figures 1 and 2) identified several likely effects of hydrothermal processing on the Ryugu parent body, some of which were characterized further by XAS using the TES instrument. The element distributions and associations were very similar to those we previously reported for several CM meteorites [1].

Figure 1: (left) Three color (P, S, Ca) map of Ryugu sample A0055-1, showing multiple Ca-rich grains (blue) including one a >0.5 µm in size, many S hot-spots (green), a few Ca and P bearing grains (purple), and several small P hot spots more easily visible in the enlarged image. Figure 2: (right) Three color (P, S, Si) map of Ryugu sample A0026-02.



Figure 3: (left) P-XAS of three P hot-spots in A0055-1 that exhibit apatite spectra. Figure 4: (right) Ca-XAS of the large Ca hot-spot in A0055-1. The arrows indicate Ca-XANES features that distinguish dolomite (a bilayered carbonate) from calcite or magnesite (monolayered carbonates).



*Apatite:* Small P hot-spots were found in both A0026-02 and A0055-1. This P appeared in three distinct element associations (Figure 1): spots with both P and Ca (appearing pink), most likely apatite grains, small P hot-spots without Ca (red in the enlarged insert in Figure 1), which will be further analyzed by XAS, and spots with both S and P (yellowish green), potentially the high-P sulfides found in CM meteorites by Nazarov [2]. Three of the most intense P hot-spots in A0055-01 each have P-XAS spectra consistent with apatite (Figure 3), which is believed to be a hydrothermal alteration product in CM chondrites. These will be studied further to investigate their compositions.

*Carbonate*: Both samples contained Ca-bearing minerals, most likely carbonates >5 mm in size. One large carbonate, >0.5 mm in size, in A0055-1 was selected for further study. This large carbonate was identified as a dolomite by XAS (Figure 4). The dolomite area of interest contains a significant amount of Mn. Mn-XAS indicated the Mn is in the 2+ oxidation state, consistent with Mn in a bilayered carbonate. Element mapping of this large carbonate will be performed to search for zooning. *Sulfur:* Sulfur hot-spots were identified in both samples. All four S hot-spots analyzed thus far in A0026-02 show XAS spectra consistent with pyrrhotite, with no detectable sulfate, consistent with models of Solar Nebular condensation which indicate that S condenses from the cooling gas as an iron-sulfide, resulting in the subsequent incorporation of this iron-sulfide into the Ryugu parent body. However, three of the largest S hot-spots in A0055-1 show mixed sulfide and sulfate in the same grain. This suggests the sulfides in A0055-1 experienced significant hydrothermal alteration to produce sulfate. This observation is

rins suggests the sumdes in A0055-1 experienced significant hydrothermal attenuion to produce sumate. This observation is consistent with the alteration of sulfide to sulfate to sulfate reported in six CM chondrites, where O-isotopic analysis indicated the alteration of sulfide to sulfate occurred on the asteroidal parent body (Airieau et al., GCA, 2005). We also identified an Fe-rich grain in A0055-1 that has an XAS spectrum consistent with magnetite, another mineral believed to be produced by interaction of Fe-metal with an oxidizing fluid. The presence of oxidized S in A0055-1 but only sulfide in A0026-02 may suggest different alteration histories for these two samples collected from the same site.

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### Paleomagnetic Evidence for Formation of Ryugu in the Distal Solar System

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Paleomagnetic studies of meteorites have demonstrated that the solar nebula generated a magnetic field that likely played an important role in accretion during the early solar system [1]. The nebular field reached intensities of  $54 \pm 21 \,\mu\text{T}$  at heliocentric distances of 1-3 AU [2] and 101 ± 48  $\mu\text{T}$  at 3-7 AU [3], and likely decayed by ~3-4 million years (Ma) after the formation of calcium aluminum-rich inclusions (CAIs) [4-7]. However, with the possible exception of Tagish Lake and Wisconsin Range (WIS) 91600, these studies have been restricted to meteorites that formed at distances <7 AU [8, 9]. Tagish Lake is of particular interest as its arrival to Earth from the asteroid belt implies that its parent body had been inwardly scattered, perhaps due to the formation and migration of the giant planets [9, 10].

The returned samples from asteroid (162173) Ryugu by the Hayabusa2 mission currently provide the best opportunity to study the nebular field in the distal solar system as the parent body may have experienced aqueous alteration at distances up to ~20 AU [11]. These particles are also highquality targets for paleomagnetic investigations as they are: 1) in pristine condition since careful sample handling limits the possibility of magnetic and terrestrial contamination, which can lead to the creation of ferromagnetic minerals that mask the primary record of the particles, and 2) contain single-vortex framboidal magnetite which can retain magnetic records over the age of the solar system [12]. If the magnetite shows evidence of magnetization produced by an ancient field, the source of the field could have been the nebular field or a dynamo on the parent body. The latter case is of particular interest since this would imply that the parent body was partially differentiated with a carbonaceous chondritic crust [13]. Our current understanding of the lifetime of the nebula suggests that if the natural remanent magnetization (NRM) was acquired < 4 Ma, the source of the field was the nebula



Figure 1: Orthographic projection of endpoints of NRM vectors on the northeast (N-E) and up-east (Z-E) planes during alternating field demagnetization of particle A0397. The LC component is shown in red, the MC component in blue, and the HC range in black. No components are observed >24 mT.

while a younger age would be indicative of a parent body dynamo. Initial Mn-Cr dating on carbonates that are thought to have formed at the same time as the magnetite yielded an age of 3.1 - 6.8 Ma after the formation of CAIs [14], but more recent dating on carbonates using the same dating system and improved calibrations suggests alteration occurred < 1.8 Ma after CAI formation [15].

An initial paleomagnetic study of two Ryugu particles concluded that the particles formed in a >  $-40 - 400 \mu$ T nebular field [14, 16]. However, this magnetization may be post-sampling contamination because: 1) magnetite can have coercivities up to 300 mT, but the NRMs of previously studied samples were unblocked to only 30 mT; 2) the previously studied samples had been analyzed with an electron microprobe which may have imparted a weak isothermal remanent magnetization (IRM); and 3) initial analysis of MasMag magnetometer data suggested that a boulder on Ryugu did not possess a measurable magnetization (< 3 × 10<sup>-6</sup>Am<sup>2</sup> kg<sup>-1</sup> at the m-scale) [17], yet the moment per unit mass of the reported samples is well above this limit (2.14 × 10<sup>-5</sup> Am<sup>2</sup> kg<sup>-1</sup>).

To address the origin and nature of NRM in Ryugu, we conducted an additional paleomagnetic analysis on three previously unstudied Ryugu particles: A0397, C0085b, and C0006. These samples have not been previously studied using a microprobe or instrument with a strong magnet prior to our paleomagnetic analysis.

Alternating field (AF) demagnetization of the NRM in A0397 to 400 mT in steps of 0.5-1 mT revealed two non-origin trending components (Fig. 1), a low coercivity (LC) component that unblocked between 0 and 10.5 mT and a medium coercivity (MCs) component that unblocked between 11 and 23.5 mT. Above >24 mT is a high coercivity (HC) range in which no NRM components are observed. AF demagnetization of C0085b to 400 mT revealed three NRM components: an LC component that unblocked between 0 and 12.5 mT, and two MC components that unblocked between 13 and 19 mT and 19.5 and 23.5 mT, respectively. The second MC component was origin-



Figure 2: Predicted midplane nebular field assuming accretion around a solar mass star and that the nebular field and disk rotation are aligned. Accretion rates are given at the right-hand side for each curve. Colored lines represent constraints on heliocentric distance at which aqueous alteration occurred based on upper paleointensity limits from particles C0085b and A0397.

trending. As before, above >24 mT is a HC range containing no stable NRM. AF demagnetization of C0006 to 80 mT conducted in 5-10 mT steps revealed a non-origin trending LC component that unblocked between 0 and 20 mT with no apparent components in the HC range above 20 mT.

Paleointensities estimated via the anhysteretic remanent magnetization (100  $\mu$ T bias field and 260 mT AC field) method for the LC components are 125.8 ± 28.9 (95% confidence interval, as for all below), 694.6 ± 145.5 and 44.8 ± 69.5  $\mu$ T for A0397, C0085b, and C006 respectively. The MC paleointensity for A0397 is 45.6 ± 31.6  $\mu$ T, while the two MC paleointensities for C0085b are 36.0 ± 44.4 and 62.3 ± 134.7. Importantly, the HC paleointensities are all also consistent with null paleofields: 26.4 ± 30.6  $\mu$ T for C0085b, 7.4 ± 9.2  $\mu$ T for A0397, and 8.8 ± 16.4  $\mu$ T for C0006. This indicates that there are magnetic recorders with coercivities >24 mT in the particles that are capable of recording an ancient field but instead formed in the presence of a null or weak field.

Experiments conducted to determine the susceptibility of A0397 to viscous (VRM) remagnetization from prolonged exposure to an Earth-strength field indicate that the total moment gained over 4.5 years (initial sampling to NRM demagnetization) could account for 98% of the combined LC and MC components. We therefore suggest that the source of the LC and MC components in our samples are overprints, most likely a VRM from sitting in Earth's field and the field produced by spacecraft engines (10s of  $\mu$ T [16]) since sampling. The non-origin trending nature of the two A0397 components further indicate that they are not primary. We suggest that the previously reported strong paleointensities are due to a weak IRM from the electron microprobe as ratio of NRM to saturating IRM is >10% and the components are not origin trending as well.

Our results have profound implications for the history of the Ryugu parent body. Taking the alteration age to be < 1.8 Ma after CAI-formation, our most stringent upper paleointensity limit of 7.4  $\mu$ T indicates that alteration occurred at heliocentric distances >15 AU for typical accretion rates during the main lifetime of the nebula of 10<sup>-8</sup> M<sub>☉</sub> yr<sup>-1</sup> (and >5 AU for the lower range of accretion rates during the main lifetime of the nebula) (Fig. 2). Given Ryugu's current location (~1 AU), the parent body may have been scattered inward prior to catastrophic disruption, but after experiencing aqueous alteration, due to influence from the giant planets in a similar manner to that proposed for the parent body of Tagish Lake. Our results therefore provide further evidence that the formation and migration of the giant planets led to a major reconstructing of the organization of the solar system.

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## Experimental Constraints on the Concentration of Dirac Magnetic Monopoles in Primordial Material returned from Asteroid Ryugu by JAXA's Hayabusa2 Mission

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In 1931, Dirac postulated the existence of elementary particles with quantized magnetic charge as an explanation for the observed quantization of electric charge. If found, Dirac magnetic monopoles (DMMs) would require a re-evaluation of electromagnetism and all related theories. However, DMMs have not yet been empirically discovered. Their predicted magnetic charge, multiples of  $2\Phi_0$  (where  $\Phi_0$  is the magnetic flux quantum: ~2.07 fWb), would be detected easily with modern superconducting quantum interference device (SQUID) magnetometers. If cosmic DMMs were trapped on ferromagnetic grains in pre-solar materials, then a promising place to search for them would be in material sampled from primitive small bodies, preferably returned by spacecraft on low-acceleration trajectories, since intense accelerations experienced by meteorites could strip them of DMMs as they enter Earth's atmosphere. By passing material through a 2G SQUID rock magnetometer, a theoretical DMM trapped within ferromagnetic grains would return a change in measured magnetic flux ( $\Delta\Phi$ ) by multiples of 4 $\Phi_0$ , or ~8.23 fWb. We performed this experiment on three Hayabusa-2 samples returned from the asteroid Ryugu: samples collected from the sites TD1 (A0397) and TD2 (C0006 and C0085), with a combined mass of 18.7 mg. We measured  $\Delta\Phi$  as -0.3 ± 0.2 fWb for A0397, 0.3 ± 0.5 fWb for C0006, and 0.4 ± 1.1 fWb for C0085. Although our numbers were not significantly different from zero and are well below the expected magnetic charge for DMMs, we only sampled 18.7 mg of the ~5g of primitive asteroidal material returned from Ryugu, which is in turn an infinitesimal fraction of the solar system. Due to their importance for all of science, we argue that all primitive materials returned from space missions should be screened routinely for DMMs as part of their initial characterization in the sample receiving laboratories.



Summarized results of 22 pass-through experiments conducted on returned Ryugu samples A0397, C0006, and C0085. Here,  $\Delta \Phi$  is expressed as a percentage of  $4\Phi 0$  – the minimum quantized change in flux expected by a Dirac magnetic monopole. Since  $\Delta \Phi$  of all samples is much lower than  $4\Phi_0$ , we have not yet detected a magnetic monopole.

## Electron holography observation of presudo-magnetites and metallic iron nanoparticles in space weathered Ryugu sample

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The traces resulting from space weathering could provide a detailed understanding of interplanetary processes. However, most meteorites are composed of materials produced in the interior of the asteroid and have not undergone space weathering on its surface. Analysis of samples gently collected from the surface of extraterrestrial bodies by spacecraft is therefore useful for studying the details of space weathering [1,2].

Here, we focused on the space weathering of magnetite in samples brought back from the C-type asteroid Ryugu by the *Hayabusa2* spacecraft. Magnetite is an important mineral to record the nebular magnetic field, but studies on its space weathering are limited. Magnetite is universally found in carbonaceous meteorites as a major product of aqueous alteration of asteroids during the early stages of solar system formation. In particular, since most of the samples recovered by the *Hayabusa2* spacecraft were collected from the surface of the asteroid, it is important to understand the degree of space weathering influence on magnetite in order to interpret the origin of remanent magnetization. We have previously studied the magnetic domain structure of framboidal magnetite in recovered samples using electron holography [3,4]. In this study, we report on our newly discovered flamboids, which does not show a typical magnetic domain structure of magnetite.

From an area with relatively abundant Fe and containing many spherical particles similar to framboidal magnetite was selected from the surface of particle A0064-FO007 and an ultrathin section was prepared by focused ion beam (FIB) machining without applying magnetic field greater than that of the Earth. The ultrathin section contained about a dozen framboidal magnetite particles with sizes ranging from 500-900 nm (Fig. 1A). The magnetic domain structures of these particles were observed by electron holography (HF-3300EH; Hitachi High-Tech Corp., Tokyo), and it was found that the magnetic domains of each particle had a concentric magnetic structure typical of submicrometer-sized magnetite particles (Fig. 1B) [5-8].

Ultrathin sections taken from neighboring locations of the same particles also contained flamboidal particles of 400-800 nm in diameter, similar to Fig. 1A (Fig. 1C). The scanning transmission electron microscopy–energy-dispersive X-ray spectrometry analysis of this particle confirmed that it was iron oxide, consistent with magnetite, but electron holography showed no magnetic domain structure. This suggests that the particle is a nonmagnetic mineral and not magnetic. We analyzed the bonding state of iron and oxygen using electron energy loss spectroscopy and found that this nonmagnetic particle exhibited characteristics of both magnetite and wüstite in terms of the bonding state of iron and oxygen. We named such particles that exhibit both features of magnetite and wüstite, and do not show a magnetic domain structure "pseudo-magnetite".

Around the pseudo-magnetite particles, there was a decrease in signal intensity of various light elements in the region of about 2 µm below the surface. In addition, the elemental mapping of iron shows many small iron particles that may have

been released or diffused from the pseudo-magnetite (Fig. 1E). More than 100 metallic iron particles of 30-400 nm were easily counted in an alteration region 2  $\mu$ m deep, 10  $\mu$ m long, and 0.1  $\mu$ m thick from the surface. Assuming that this reduction is due to a micrometeoroid impact and that a 10- $\mu$ m diameter region is altered to a depth of 2  $\mu$ m in a single impact, the total number of iron particles produced would be ~10<sup>4</sup>, which could acquire remanent magnetization during an event involving the formation of iron nanoparticles by a micrometeoroid impact. Therefore, the iron particle precipitation associated with a micrometeoroid impact could play an important role as the remanence acquisition event.

Micrometeoroid impacts are thought to have occurred frequently within protoplanetary disks. However, the traces left behind by these impacts are found only on the topmost surfaces of asteroids, so previous studies using meteorites have had limited opportunities to study these traces. Even if a meteorite fell to Earth leaving behind pseudo-magnetite and iron particles, these particles would be oxidized by weathering on the ground afterward. In addition to the samples obtained by the *Hayabusa2* spacecraft, the samples brought back from the asteroid Bennu by OSIRIS-REx will also have a chance to be analyzed. In this process, it is necessary to avoid changes in remanent magnetization due to oxidation of pseudo-magnetite and metallic iron nanoparticles. Although pseudomagnetite may represent only a small percentage of total magnetite, its presence should be considered when analyzing extraterrestrial samples recovered from an asteroid surface. In our presentation, the event and timing of the micrometeorite impact and other suspect magnetite particles will be discussed.



**Figure 1. Framboids with and without magnetic domain structures characteristic to magnetite. A** and **B**. Bright field TEM and the corresponding magnetic-flux-distribution images, respectively, of framboidal magnetite particles in a thin section prepared from the A0064–FO007 sample of asteroid Ryugu. **C**. Bright field TEM image of pseudo-magnetite particles in a thin section prepared from neighboring region of A. **D**. Magnetic-flux-distribution image, corresponding to the box d in C, observed by electron holography. **E**. Elemental mapping of iron corresponding to the box e in C.

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#### **Characterization Of Early Solar System Aqueous Fluids In Ryugu Samples**

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**Introduction**: The most direct and convincing evidence for the presence of water and organic molecules on protoplanetary bodies is provided by fluid inclusions trapped in secondary minerals. Our previous research has demonstrated that early solar system fluids have survived as fluid inclusions in a few astromaterials that escaped significant shock, terrestrial alteration, and invasive sample handling [1-3]. We hypothesize that the bulk molecular and isotopic composition of individual fluid inclusions can be measured to provide ground truth for exploring and thermochemical modeling of the compositional and isotopic evolution of fluids in protoplanetary bodies including asteroids, comets and icy moons.

This presentation is an update on our efforts to make measurements of elemental, molecular and isotopic compositions of individual aqueous fluid inclusions in Ryugu samples.

**Facilities**: For the following XRCT and TOF-SIMS analysis, samples were prepared using the FEI Quanta 3D 600 Dual-beam Focused Ion Beam in the ARES -NASA-JSC Electron Beam Instrument Facility. For the X-ray Computed Tomography (XRCT) scans we used the Zeiss 620 XRM instrument at the University of Texas High-Resolution X-ray Computed Tomography Facility. For the Time of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS) measurements we used the University of Texas Materials Institute's TOF-SIMS 5 and TOF-SIMS 6 instruments (ION-TOF GmbH) equipped with a pulsed Bi<sup>+</sup> analysis ion beam (30 keV ion energy) and a  $O_2^+$  sputtering ion beam (1 kV ion energy). The TOF-SIMS instruments are capable of cooling the samples to -160 and -180C, respectively, and without this capability our measurements would be impossible.

**Aqueous Fluids**: Studies of aqueous alteration in primitive meteorites, based solely on secondary mineral associations, have hinted that this process did not occur under a single set of conditions [4]. The temperatures of alteration that have been suggested are highly variable, from below 0 to ~250°C. The fluid compositions must have likewise varied, though this critical aspect is very poorly understood. Our previous molecular, O and H isotopic measurements of fluids in halite in the Monahans and Zag meteorites [2,5] have shown considerable variation in fluid composition even within individual crystals. For example, we suspect that early solar system aqueous fluids could alternate between being S-rich and S-poor, based on the alternating pyrrhotite-magnetite alteration assemblage observed in the Tagish Lake and Sutter's Mill chondrites [6]. We know from our previous studies of aqueous fluid inclusions in extraterrestrial halite and calcite in the Sutter's Mill C2 chondrite that the mineralizing fluids also contained a significant concentration of mineralizing cations such as Fe, Mg, Ca, and volatiles such as CO<sub>2</sub> and S-bearing compounds in variable abundances (though the abundances are not yet determined) [2,7]. We observed CN<sup>-</sup>, a molecular fragment of a larger nitrogenous compound, in the aqueous fluid inclusions in a Ryugu pyrrhotite crystal [1-3]. Nakamura et al. [3] reported that the earliest formed phyllosilicates in Ryugu were rich in Na, indicating significant compositional changes in the mineralizing fluid.

**Ryugu Fluid Inclusion Measurements**: Our recent successful, coordinated, XRCT and TOF-SIMS analyses of individual fluid inclusions in a Ryugu pyrrhotite crystal demonstrated that they consist of water, CO<sub>2</sub>, sulfur species, and organic material, with H<sup>-</sup>, C<sup>-</sup>, O<sup>-</sup>, S<sup>-</sup> and OH<sup>-</sup> as the main fragments detected at these locations [1,3]. In addition, various amounts of F<sup>-</sup>, Cl<sup>-</sup> and Ni<sup>-</sup> were found, together with Na<sup>+</sup>, Mg<sup>+</sup>, Al<sup>+</sup>, Cr<sup>+</sup>, K<sup>+</sup> and Ca<sup>+</sup>. Larger organic fragments such as C<sub>2</sub><sup>-</sup>, C<sub>2</sub>H<sup>-</sup>, C<sub>3</sub><sup>-</sup>, CO<sup>-</sup> and CN<sup>-</sup> were also detected, indicating the presence in these inclusions of more complex organic molecules containing H, C, N and O. We can expect to see these and additional molecular fragments in other Ryugu fluid inclusions. TOF-SIMS breaks apart molecules - it does not make new ones. Therefore, all these identified species are fragments of once larger molecules which we can identify to some degree.

Measurement of the stable isotopic compositions of aqueous fluid inclusions in Ryugu samples will enable a comparison with our measurements of a few fluid inclusions in carbonaceous chondrites (e.g. [7]), and fluids calculated to have reacted with other primitive samples (CI chondrites, OCs, HEDs, ureilites) which have  $\delta D$  ranging from ~0-3000‰. Actual direct measurements of preserved trapped fluids would thus inform us about fluid changes during aqueous alteration in a large suite of primitive bodies. Russell et al. [8] has suggested that CI materials form

two groups with distinct water/rock ratios, temperature ranges, and hydrogen isotope compositions. Are these truly distinct groups or do these just represent endmembers of a poorly sampled complete range (as also suggested by Russell et al., [8])? Our planned analyses of individual fluid inclusion oxygen and hydrogen isotope compositions in Ryugu samples will settle this issue as we will either observe narrow compositions or a compositional continuum.

Polished Ryugu sample C00025 contains large sulfides, magnesite, magnetite and dolomite crystals (Fig 1). We have already FIBed several foils from this sample and subjected one of the FIB foils to TOF-SIMS measurements. We detected no filled fluid inclusions, however we were limited to analyzing inclusions larger than about 3  $\mu$ m using the M5 TOF-SIMS instrument, and it appears the inclusions were far smaller (Fig.1). We plan to repeat the measurements of this sample using the newly-installed M6 TOF-SIMS, which has greatly expanded capabilities. We made XRCT scans of two additional Ryugu grains (A0175 and C0043) (Fig 2). From these preliminary measurements we know that A0175 contains numerous pyrrhotite, carbonate, and, probably, apatite crystals with fluid inclusion candidates measuring at least 3-5  $\mu$ m in diameter, which will permit our planned TOF-SIMS measurements.

The TOF-SIMS analytical data are counts under the peaks for each species. An example of the data is shown in Figure 3, which shows counts for OH- (indicative of H<sub>2</sub>O) and C- (here indicative of CO<sub>2</sub>). This sample was a synthetic fluid inclusion standard (quartz) prepared by Bob Bodnar where the inclusions contained a 1:1 mixture of H<sub>2</sub>O and CO<sub>2</sub>. As you can see from the included table, despite the fact that the sensitivity of the technique for CO<sub>2</sub> was much lower than for H<sub>2</sub>O, 4/5 of the inclusions showed consistent counts for these species, meaning that with continued calibration we can produce quantitative composition measurements for some species. We note that the signals for CO<sub>2</sub> we observed in the Ryugu pyrrhotite crystal were more pronounced than those we obtained using the 50:50 standard, suggesting a very high abundance of CO<sub>2</sub> in the Ryugu mineralizing fluid. In fact, solid CO<sub>2</sub> sublimed rapidly in a vacuum at our measurement temperature, making quantification very difficult.

In the coming year we will begin isotopic measurements of standards in synthetic fluid inclusions and Ryugu pyrrhotites and carbonates we have already identified, as well as increasing our stock of pre-analyzed Ryugu crystals.





(Left) Fig. 2. XRCT "slices" of Ryugu sample A0175. Fluid inclusion candidates are arrowed. (a-e) Pyrrhotite crystals. (f-g) Probable carbonates. (h) Possible apatite crystal.

(Right) Fig. 3. Results of TOF-SIMS measurements of synthetic fluid inclusion standard (quartz), with inclusions that contain a 1:1 mixture of  $H_2O$  and  $CO_2$ . Inclusions are numbered to match the table (e.g. ROI1=1). Counts = cts.



## Three-dimensional description and characterization of lithologies in Ryugu sample

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Ryugu is a rubble-pile asteroid. Similarly to CI chondrites, the samples returned by Hayabusa2 mission showed the presence of adjoining fragments of different lithologies [1, 2]. These fragments are different in mineralogy, petrology, physical structure (size, porosity) and testify the heterogeneity of Ryugu's asteroid, its complex geological history and evolution [3]. So far, several lithologies have been observed and described partly in polished sections [1, 2, 3]. In this work we used micro-computed tomography ( $\mu$ -XCT) to observe, analyze and investigate lithologies in 3D. We analyzed their properties (internal structure, shape, size, composition, porosity) and their assemblages with each other in a Ryugu millimeter-sized sample with the objective to better understand Ryugu's heterogeneity and its complexity in term of formation and evolution.

We studied the 3D lithologies of the mm-sized  $(1.45\times2.85\times2.1 \text{ mm})$  sample A0159 from Chamber A. Data were obtained at PSYCHÉ beam-line of Synchrotron SOLEIL (France) using a monochromatic X-ray beam operating at 25 keV. Our analysis was conducted on 3D reconstructed images (CT-images, or "slices") with a voxel volume of 1.295  $\mu$ m<sup>3</sup> and based on the linear attenuation coefficient (LAC). As a first method of data processing, we used pixel segmentation, which classifies each voxel into 5 major domains by its LAC value. The domains are, sorted by increasing LAC, 1-porosity, voids, fractures, 2-matrix, 3-carbonates, 4-sulfides and oxides. Some LAC values were difficult to associate with a specific domain so we classified them as 5-uncharacterized. This method allows us to obtain the proportion of each component within each slice and then in the entire sampl5, but also the 3D reconstruction of each component.

Contrary to the first method, the local histogram segmentation considers areas of 49×49 voxels. For each area, the calculated histogram of the proportion of pixels for a given LAC value gives access to i) the number of pixels for each of the 5 previously cited domain and ii) the LAC histogram data distribution. Then, each area was locally described in regard to composition and physical properties giving rise to lithologies. This method allowed us to obtain a 3D reconstruction of each lithology in the sample. Tomviz software was used for 3D representation and visualization.

Our preliminary results from the pixel segmentation method showed that, on average, A0159 is made of  $42.0\pm7.0$  % of matrix component,  $1.2\pm0.5$  % of sulfides and oxides,  $4.7\pm2.8$  % of porosity, voids and/or fractures and  $27.5\pm4.7$  % of uncharacterized material (undefined components, or technique artifacts). Finally, carbonate components represents 24.1±2.5 % of the sample, a much higher value than previous studies [4]. The 3D reconstruction of carbonates shows a mm-sized vein going through A0159 (fig. 1), indicating important fluid circulation. The vein is about 1100×900×100 µm and it is the largest vein observed so far in a Ryugu sample. Its presence explains the high proportion of carbonate material in A0159. We detected two highly fractured plans along both sides of the vein. The vein ends up with coarse and elongated to rounded carbonate grains with inter-grains voids. In other studies, a complex and elongated structure of size >100 µm was observed in sample C0041 and found to have a wide range of (Mg-Fe)-carbonate composition between siderite-magnesite (or breunnerite) [5, 6]. In sample C0009, [3] found elongated Ca-carbonates forming a chain that they proposed to be a potential remnant of a vein. The detection of a mm-sized vein in A0159 suggests that Ryugu's parent-body has probably undergone notable water flow through, at least, a mm-sized fracture and that carbonate precipitated as a vein.



Figure 1: 3D reconstruction of the Ryugu sample A0159 (in grey) combined with the distribution of carbonates (in yellow).

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The preliminary results of the second method allowed us to detect several different lithologies. A study is ongoing to determine the exact number of lithologies. These lithologies are mostly composed of matrix with various size and proportion of carbonates, sulfides, oxides, and porosity. One peculiar lithology is made of a compact matrix component, few carbonates, uncharacterized material, sulfides and oxides. This lithology could match the "massive domain" seen by [1] in A0035 or the "fine-grained dark lithology" in C0009 by [3]. The compact lithology is surrounded by long (up to 800 µm) and large fractures (up to 20 µm) and, similarly to [1], some fractures also cross the lithology. Another lithology is rich in rounded and elongated grains of carbonates about 50 µm in size and is located at the end of the vein. This lithology has many small fractures (up to 100 µm long and 10 µm large) which seem to be preferably located around the grains such as in A0037 [3]. However, crossing and surrounding fractures are not present in each lithology. The second method is still ongoing and it is not clear yet whether the carbonate vein crosses a single lithology. However, our preliminary results confirm that Ryugu is a breccia with adjoining fragments of various size (from 100 to 500 µm), composition and physical properties. The analysis of the fractures (distribution, size and shape) strongly indicates a heterogeneity in the mechanical properties of lithologies. All these observations testify the complexity of Ryugu and/or parent-body formation and evolution and its geological past.

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# Size distribution and elemental compositions of anhydrous minerals in the Ryugu samples C0224 and C0260: Implications for radial transport mechanism and source regions of anhydrous minerals

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**Introduction:** Samples returned from C-type asteroid Ryugu by the Hayabusa2 spacecraft are mineralogically and chemically similar to CI chondrites [1-4]. It was suggested from the initial analysis of the Ryugu samples that the Ryugu original parent body formed beyond the H<sub>2</sub>O and CO<sub>2</sub> snow lines (> 3 - 4 au) in the solar nebula at 1.8 - 2.9 Myr after CAI formation [1]. Nakashima et al. [5] reported elemental compositions and oxygen isotope ratios of chondrule-like objects and Ca-Al-rich inclusions (CAIs) in the Ryugu samples. The objects (<  $30 \mu$ m) are as small as those from comet Wild2, suggesting radial transport favoring smaller objects from the inner solar nebula (solar neighborhood and chondrule formation regions) to the formation location of the Ryugu original parent body, which is farther from the Sun and scarce in chondrules [5]. Besides chondrule-like objects and CAIs, anhydrous minerals such as olivine, pyroxene, spinel, and hibonite occur in the Ryugu samples and are much more abundant [1]. In the present study, we measured size distribution of anhydrous minerals in the newly allocated Ryugu samples (C0224 and C0260) using FE-SEM and FE-EPMA to test the hypothesis of radial transport favoring smaller objects [5] and elemental compositions to elucidate the source regions of individual anhydrous minerals.

**Results:** Synchrotron radiation X-ray computed tomography at SPring-8 showed that C0224 has a homogeneous lithology except for the presence of large carbonate crystals of few hundred  $\mu$ m in size and C0260 contains clasts with different lithologies. Three hundred ten anhydrous minerals including chondrule-like objects were found in eight polished sections from C0260 (C0260-01, 02, and 03) and C0224 (C0224-01, 02, 03, 04, and 05), and most of them were from C0260. Polished sections of C0224 were repolished multiple times but only 6 grains were observed. Most anhydrous minerals occur along with calcite, Ca phosphate, and Na-Mg phosphate in FeO-rich phyllosilicate regions, which is characteristic for lithology II clasts (less-altered clasts; [6]). Anhydrous minerals have angular shapes, so that diameters are calculated from surface areas of anhydrous minerals using ImageJ assuming they have spherical shapes. The largest one is 24  $\mu$ m and smallest one is 0.5  $\mu$ m. As shown in Fig. 1a, the peak of size distribution of anhydrous minerals including chondrule-like objects occurs at 2 – 3  $\mu$ m. It should be noted that we counted anhydrous minerals detected by FE-SEM mapping, and therefore there is counting loss of tiny minerals (<< 1  $\mu$ m). Olivine is most abundant followed by spinel, pyroxene, and hibonite. Mg#'s of olivine are from 89.5 to 99.4, which is consistent with the initial analysis [1]. Low-iron manganese-enriched (LIME) olivine with MnO/FeO ratio (wt%) exceeding 1 [7] is observed. Pyroxene and hibonite grains are too small to obtain precise compositions. Spinel contains variable amounts of Cr<sub>2</sub>O<sub>3</sub> (0.21 – 4.0 wt%).

Six chondrule-like objects are observed (Fig. 1b). They have rounded shapes and mainly consist of FeO-poor olivine with Mg# from 92.0 to 99.2 along with diopside, rounded (oxidized) Fe-Ni metal, and altered phase. The chondrule-like objects are similar to those found in the initial analysis [1,5].

**Discussion:** Most anhydrous minerals occur in less-altered clasts in the Ryugu samples [1, this study]. The clasts have protected anhydrous minerals from aqueous alteration and brecciation for ~ 4.6 Gyr, so that sizes of the anhydrous minerals reflect those during accretion onto the Ryugu original parent body. Our new data (Fig. 1a) show that anhydrous minerals in the Ryugu samples (< 24  $\mu$ m) are smaller than chondrules in chondrites (~ 500  $\mu$ m; [8]) and isolated olivine in chondrites (> 20  $\mu$ m; [9]), suggesting radial transport favoring smaller objects to the formation location of the Ryugu original parent body. There are two possible mechanisms for radial transport: a combination of advection and turbulent diffusion [10] and photophoresis [11]. Both mechanisms can transport grains smaller than 30  $\mu$ m. While the Ryugu original parent body formed at ~ 2 Myr after the CAI formation [1], photophoresis transports 10  $\mu$ m grains beyond 10 au later than ~ 5 Myr after the CAI formation [11]. Considering the time window, a combination of advection and turbulent diffusion that transports  $\leq 20 \ \mu$ m grains beyond 25 au within 1 Myr [10] would be more likely for Ryugu. It will be more plausible by size distributions of anhydrous minerals in other Ryugu samples and CI chondrites.

Olivine in type I chondrules is more enriched in  $Cr_2O_3$  and CaO than olivine in amoeboid olivine aggregates (AOAs) (Fig. 2a) [5]. <sup>16</sup>O-rich chondrule-like objects, CAIs, and <sup>16</sup>O-rich olivine in the Ryugu samples are distributed in the AOA area, while <sup>16</sup>O-poor chondrule-like object and <sup>16</sup>O-poor olivine are distributed in the type I chondrule area. The difference in the elemental compositions of olivine with different origins is explained by AOA olivine condensation from a residual gas depleted in the refractory elements followed by isolation from the gas before condensation of Cr [5]. Olivine depleted in  $Cr_2O_3$  and CaO may have formed

near the Sun, and olivine relatively enriched in the two elements may have formed in the chondrule formation regions. Thus, it is possible to deduce the source regions of isolated olivine and chondrule-like objects based on the  $Cr_2O_3$  and CaO concentrations. Many of isolated olivine grains and olivine in chondrule-like objects in C0260 and C0224 distribute in the AOA area (Fig. 2b), which is consistent with the FE-EPMA analysis of olivine in CI chondrites [12]. The AOA-like olivine may have formed near the Sun. It is considered from the high abundance of AOA-like olivine in the Ryugu samples and frequent occurrence of <sup>16</sup>O-rich olivine in Wild2 particles [13] that olivine formed near the Sun were transported to the outer regions of the early solar nebula and survived due to lack of chondrule forming event that erases <sup>16</sup>O-rich signature and original elemental compositions. On the contrary, isolated olivine in chondrites in the type I chondrule area (Fig. 2c), and <sup>16</sup>O-rich olivine is rare in chondrites [14]. It is considered that <sup>16</sup>O-rich olivine passed the chondrule formation regions and/or melted during chondrule forming events.

Nakashima et al. [5] reported that spinel in the Ryugu CAIs contain small amounts of  $Cr_2O_3$  with < 0.2 wt% and suggested that the CAIs escaped from remelting event and may be as old as the oldest CAIs. Isolated spinel in C0260 show variable  $Cr_2O_3$  concentrations up to 4.0 wt%. Therefore, spinel that acquired Cr by remelting events are also present in the Ryugu samples. Considering the time window of accretion (within ~ 2 Myr after CAI formation; [1]), remelting events may have occurred during that period.

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Fig. 1: Size distribution of anhydrous minerals including chondrulelike objects in C0224 and C0260 (a) and backscattered electron image of the chondrule-like object C0260-02-Chd2 (b). Ol, olivine; Diop, diopside.

Fig. 2: Comparison of concentrations between  $Cr_2O_3$  and CaO in olivine in chondrule-like objects, type I chondrules, AOAs, <sup>16</sup>O-rich and -poor chondrules (a), isolated olivine and olivine in chondrule-like objects in C0224 and C0260 (b), and isolated olivine in chondrites (c). The panel a is from Nakashima et al. [5]. Olivine data in the panel c are from [15-22].

## Microstructural and microchemical characteristics of dolomite in Ryugu regolith particles

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**Introduction.** Previous studies of Ryugu material have reported that the regolith particles record extensive aqueous alteration as the result of water activity in the original parent body [1,2]. The aqueous alteration finally resulted in the almost complete overprint of the primary mineralogical composition and the precipitation of secondary minerals, i.e. phyllosilicates, carbonates, phosphates, sulfides, and oxides. The isotopic <sup>18</sup>O/<sup>16</sup>O and <sup>13</sup>C/<sup>12</sup>C signatures of carbonates were recently studied in great detail to obtain information on the conditions of aqueous alteration [3]. Here, we focus on the characterization of the defect microstructures and nanoscale element distributions in dolomite of Ryugu samples to obtain further insights into the formation history and mechanisms of carbonates.

**Samples and methods.** In the context of the Hayabusa2 initial analysis phase, we have mainly studied polished sections prepared from larger particles recovered in the C chamber, i.e. C0033-01 and C0033-04, and C0055-01 [detailed in 1]. Eleven slices of carbonate-bearing regions were cut from the thin sections by focused ion beam (FIB) preparation on a scanning electron microscope (SEM). Subsequent analytical transmission electron microscopy (TEM) were performed according to the procedure described by [4].

**Results and discussion.** TEM observations reveal numerous curled dislocations as the most dominant lattice defect in almost all dolomite grains. This shape of dislocation lines indicate that dislocations are not in glide configuration and thus may have been incorporated during imperfect growth from the aqueous fluid. In the vicinity of fractures, sample C0055-01 contains also straight glissile dislocations, which were previously assigned to mild shock [5]. Deformation twins, which are generally regarded as typical for shock-metamorphosed carbonates, are however absent in C0055-01. An explanation for their absence could be that deformation twinning in dolomite requires enhanced temperatures [6], which do not prevail during low shock metamorphism [6].

Mapping of elemental distributions in scanning mode using energy-dispersive X-ray emission spectroscopy show complex and variable zoning of dolomite grains. Many grains show sharp, non-concentric, up to 1  $\mu$ m thin rims with a significant enrichment in manganese (up to 8 wt% MnO). This observation points, at least, to a second precipitation event, when the fluid became apparently enriched in manganese. A preferential mobilization of manganese might be explained by a (localized) change in the reduction potential. In addition, manganese-enriched dolomites with continuously decreasing manganese concentration from core to rim exist and monitor a gradual change in the fluid chemistry controlled by carbonate growth.

Most interesting is the observation of nanoscale modulations in the rims of dolomite. Such microstructures have also been observed in sedimentary calcian dolomites and are interpreted as growth microstructures [7]. The modulations appear as almost parallel lamellae with regular alternating light and dark contrast, resembling microstructures known for spinodal decomposition. A periodical variation of the fluid composition at the mineral-solution interface during progressing growth is a plausible explanation for this microchemical peculiarity [8].

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## Investigating the ammonium-bearing phase in Ryugu samples

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#### Introduction

The JAXA/Hayabusa2 mission collected 5.4 g of samples from two different sites (i.e., A and C) on the surface of the C-type asteroid (162173) Ryugu [1; 2]. This asteroid is characterized by a low albedo and by the presence of hydrous and carbonaceous materials [3]. The Ryugu surface spectra collected by the Hayabusa2/NIRS 3 spectrometer reveal a narrow absorption feature at 2.72 µm [4] resembling that observed on the surface of Ceres by the Dawn/VIR spectrometer [5; 6]. Laboratory analysis of returned grains confirmed that Ryugu samples contain hydrated silicates, sulfides, oxides, carbonates, and organics and have spectroscopic similarities to CI chondrites [7]. MicrOmega hyperspectral microscope observation [8] revealed the presence of a band at 3.06 µm, indicating the possible presence of NH-bearing phases in most of the returned grains [9]. This ammonium-related absorption feature was confirmed by FTIR measurements [10]. The 3.06 µm band was also observed in the spectra of Ceres by telescopic observations [11] and by the Dawn/VIR spectrometer that accurately characterized its distribution on the dwarf planet's surface [12]. Current interpretations of Ceres spectra suggest that the most likely mineralogical phases hosting ammonium are phyllosilicates [13; 14], but the presence of ammonium salts has also been inferred in specific areas of the Cerean surface [15; 16]. Hydrated silicates represent the main reservoir of water in Ryugu samples, and their presence is indicative of extensive aqueous alteration in the parent body, likely the alteration path that occurred on Ceres. Even if phyllosilicates are the most likely carriers, the specific ammonium-bearing phase determining the 3.06 µm band on Ryugu samples and the surface of Ceres is not fully constrained, nor are the processes that led to ammonium enrichment on these C-type bodies.

#### Sample selection

Our selection criterion of the samples among those available in the first allocation (2022A) was the presence of the absorption band at 3.06 µm as observed in the spectroscopic data obtained from the preliminary screening by FTIR and MicrOmega. We have considered: 1. Similarities of the 3.06 µm absorption between Ryugu samples and Ceres spectra, in terms of wavelength range and band center position; 2. The presence of surface features or morphological structures suggests some mineralogical diversity.

Through the first allocation, we obtained two samples: A0198 and C0091. The preliminary FTIR data provided by JAXA collected on particle C0091 show the presence of a remarkable absorption close to  $3.06 \ \mu\text{m}$ . On the contrary, the spectroscopic data collected on particle A0198 show a shallow absorption ascribed to the presence of ammonium and several surface features that comply with our scientific requirements. Moreover, the two assigned samples were collected at different sites which will allow us to make further considerations.

#### Objectives and research plan

With this work, we aim to contribute to the definition of the physical and mineralogical characteristics of the Ryugu asteroid to understand the initial stages of formation and evolution of C-type bodies; particular attention will be given to the identification of the ammonium-bearing phase(s) and its/their interplay with hydrated silicates. In addition, we aim to define Ryugu's path of alteration and its similarities with Ceres.

The following laboratory analyses will be used to characterize the samples:

•VIS-IR imaging spectroscopy (0.4-5  $\mu$ m) will be carried out with the SPectral IMager (SPIM) facility [17] on whole samples. Data will allow a first characterization of the mineralogic composition of their external surface, including an assessment of the presence of water, organic matter, and ammonium in addition to the minerals. Furthermore, by using the SPIM facility (i.e., the Dawn/VIR replica), we can perform a compelling comparison between the data collected on the samples with those provided by the Dawn/VIR spectrometer on Ceres;

•X-ray microscopy (XRM). This non-destructive technique has been used to obtain a high-resolution (submicron scale) 3D tomography of the samples, revealing their internal structure (including pore structure and fracturing), as well as the morphology and composition of the individual grains contained in them; XRM data will also enable the location of regions of interest (ROIs) within the samples to be analyzed by transmission electron microscopy (TEM);

•Raman µ-spectroscopy, to obtain compositional maps of the surface of the samples at the micro-metric scale;

•Focused ion beam-field emission gun-scanning electron microscopy (FIB-FEG-SEM) will be used to identify the main mineralogical phases and to extract the electron-transparent lamellae for TEM analyses;

•Transmission Electron Microscopy (TEM), electron diffraction, and energy-dispersive X-ray spectroscopy (EDS) will be used to identify cryptocrystalline mineral phases and crystal defects through high-resolution techniques.

## Results

The VIS-NIR spectra obtained with the SPIM facility on the surface of the two particles show the almost ubiquitous presence of a deep V-band centered at lengths slightly above 2.7  $\mu$ m, and absorptions near 3.4  $\mu$ m and in the range 3.7-3.9  $\mu$ m, however, limited at specific points on the surface returning an inhomogeneous surface composition at the scale of ~40  $\mu$ m (SPIM pixel size). These absorption features can be related to the presence of phyllosilicates and carbonates, respectively.

In addition, at some specific points, the band at 3.06 µm is found indicating the presence of ammonium-bearing compounds.

The Raman spectra acquired on the two particles are characterized by a high fluorescence background and by the presence of the Raman D and G-bands related to the presence of poorly ordered carbonaceous matter. The spectral parameters derived from the mathematical fitting of the acquired spectra as band positions, and band intensity ratio do not differ significantly between the two particles. Raman analysis identifies dolomite as the most common carbonate on both particles.

The interpretation of spectral data acquired by both particles is currently in progress. However, at the moment there do not appear to be notable differences in spectral terms (VIS-NIR and Raman) between the two particles coming from the two different sampling sites.

The two samples (A0198 and C0091) are characterized by a generally similar composition in terms of phase abundance and composition. Energy Dispersive X-ray spectroscopic (EDX) data obtained using the FE-SEM confirmed the presence of hydrated silicates, sulfides (Ni-rich and Fe-rich), carbonates, fosfates, and oxides (mainly magnetite). Sulfides form dominantly euhedral grains (up to 5 µm in size), whereas oxides form submicrometric framboid, platy, or columnar structures. The internal distribution of silicates, sulfides, and oxide in the interior of the two samples, as revealed by XRM data, is rather homogeneous. Notably, sample C0091 displays a slightly smaller grain size and a slightly higher porosity compared to particle A0198.

#### Conclusions

The notable similarities of the spectra of some Ryugu samples with Ceres' average spectrum [18] sparked scientific curiosity. To date, interpretation of remotely sensed data coupled with spectroscopic investigation of analogs has not enabled a full understanding of the mechanisms of ammonium enrichment and the nature of the mineral assemblage hosting ammonium on the surface of C-type objects. Furthermore, studies on meteorites have not provided morphological and compositional information on the mineral phases that preceded the alteration of their progenitor body.

Therefore, we consider that spectroscopic measurements and nanoscale mineralogical investigations that we are conducting on the samples returned from Ryugu represent a unique opportunity to definitively establish the link, if any, between ammonium and the mineralogy of this type of object.

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## Speciation of various elements using scanning transmission/fluorescnece X-ray microscopy (STXM/SFXM) and bulk XANES analysis related to aqueous environment in the Ryugu parent body

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The parent body of the C-type asteroid Ryuguu is thought to have been rich in volatile elements and abundant in liquid water, making it an important research target for the origin of water and organic matter on Earth. The water caused various alteration in the surrounding minerals, resulting in layered silicates such as smectite (saponite) and serpentinite being the main constituent minerals of the Ryugu (Nakamura et al., 2023). In this process, the organic matter of the Ryuguu parent body also underwent chemical reactions and a wide variety of organic matter was synthesised (Naraoka et al., 2023). It is particularly important to obtain information on the water environment during the aqueous alteration, as the products of chemical reactions of organic matter in water depend on the pH and redox potential (Eh) of the water. In this study, speciation of various elements including iron (Fe), magnesium (Mg), calcium (Ca), and carbon (C) was investigated using scanning transmission X-ray microscopy (STXM) and bulk X-ray absorption near-edge structure (XANES) analysis in the soft X-ray region related to the aqueous environment in the Ryugu parent body. For the elements with conentrations below the detection limit of STXM, scanning fluorescnece X-ray microscopy (SFXM), newly developed in SPring-8 and Photon Factory was applied such as nitrogen (N) and sodium (Na). The speication of these elements in saponite is particularly important, since the Fe oxidaiton state and chemical composition within the interlayer of the saponite can indiciate Eh-pH condition of the Ryugu water.

The Fe(II)/Fe(III) ratio in the octahedral structure of saponite was conducted by STXM. Based on our laboratory experiments, dithionite reduction of natural Fe-bering saponite corresponding to Eh range from -0.47 to -0.66 (V) at pH = 7 shows the Fe(II)/Fe<sub>total</sub> ratio around 0.55. The incomplete reduction by dithionite reveals that Fe(II)-bering saponite is a strong reductant. Assuming that the relationship between the Fe(II)/Fe<sub>total</sub> ratio and Eh of nontronite in Gorski et al. (2013) is similar to that of saponite, the Fe(II) /Fe<sub>total</sub> ratio greater than 0.68 measured by STXM indicates that the Eh was less than -0.45 (V).

On the other hand, because saponite has a negative charge in its layered structure, cations from the aqueous phase are adsorbed between the saponite layers during aqueous alteration. In this case, as shown by Fukushi et al. (2019), which cations are retained in the interlayer depends on the concentration of various cations in the coexisting aqueous phase and the selectivity coefficient K. Therefore, the cation composition in the water layer at the time of aqueous alteration can be estimated from the interlayer cation ratio determined by various analytical methods. In this processes, speciation of Na, K, and Ca were conducted to obtain their fractions retained in the interlayer. The comparison of the Al content in saponite enables us to estimate the Mg content in the interlayer. Contents of these cations with assumptions of dissolved silica etc. were used to construct an Eh-pH diagram of Mg. We have estimated pH range that can explain the presence of both saponite and dolomite, which are widely distributed in the altered crust in the Ryugu particles. The pH range estimated by the method was pH from 7.8 to 10. Although the range is somewhat wide, the range is consistent with the results suggested in Nakamura et al. (2022).

The cmbination of Eh around -0.45 (V) and the alkaline pH range estimated above showed that the water was highly reducing, which reveals that  $H_2$  and  $CH_4$  were present in the Ryugu water if we assume the equilibrium condition. Such an alkaline condition is suitable for the polymerisation of amino acids (Kitadai and Maruyama, 2018).

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## Investigating the organic compounds in the asteroid Ryugu

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Organic compounds in meteorites provide insights into the carbon chemistry present in the interstellar medium and solar nebula and on their alteration on the parent bodies. Further, delivery of these organic compounds could have contributed to Earth's habitability and life. However, studying these compounds in meteorites is complicated by their exposure to terrestrial organic contamination after entering the Earth's atmosphere. As such, one of the goals of the Hayabusa2 sample return mission (asteroid (162173) Ryugu) is to understand the nature, origin, and evolution of organic compounds in the early solar system but from samples free of terrestrial organic contamination. Here, we examine further samples from asteroid Ryugu that were collected during the first touchdown (Chamber A, samples A0079 and A0169; allocated in first Ryugu AO). The goals of our research are to understand diversity, origin, and formation mechanisms of the macromolecular material that dominates Ryugu organics, as well as the secondary processes involved in their modification, such as heating and aqueous alteration.

Fragments of the two Ryugu samples up to a few 10s of microns in size were pressed into Au foils for H, C, and N isotope analysis with the Carnegie NanoSIMS 50L ion microprobe. We used a ~0.4 pA, ~100-nm Cs<sup>+</sup> primary beam and acquired data for C and N isotopes, including <sup>12</sup>C<sub>2</sub>, <sup>12</sup>C<sup>13</sup>C, <sup>12</sup>C<sup>14</sup>N, and <sup>12</sup>C<sup>15</sup>N, as well as <sup>16</sup>O, <sup>32</sup>S, and secondary electrons. The prepared samples were then analyzed for <sup>1</sup>H, D, and <sup>12</sup>C and secondary electrons with a slightly more intense primary beam. C-rich regions of interest (ROIs) were defined in the C-N images and subsequently located and analyzed in the H-D images.

We have analyzed a total area of ~9,000  $\mu$ m<sup>2</sup> across the two samples. Data reduction is in progress. The majority of C-rich ROIs appear rounded in the ion images and range from ~100 to 900 nm with some to up to a few  $\mu$ m (e.g., Fig.1). Consistent with previous measurements [2-6], our data shows that the organic material is on average enriched in D and <sup>15</sup>N with most ROIs having compositions consistent within error with average values of  $\delta$ D of a few 100 ‰ and  $\delta^{15}$ N~ +50‰. However, one lath-like rectangular grain was identified in a particle within A0079 (Fig. 1), similar in shape to a grain previously reported in Chamber C [5; Fig.3], but larger. This 4.5 × 1 µm grain has an extreme isotopic composition:  $\delta$ D ≈10,000 ‰ and  $\delta^{15}$ N ≈ +800‰. In order to clarify the nature and origin of this unusual grain and other select C-rich ROIs, we are currently extracting focused ion beam (FIB) lift-out sections of D and <sup>15</sup>N hotspots. The FIB sections will be studied with transmission electron microscopy, scanning transmission electron microscopy, energy dispersive spectroscopy and electron energy loss spectroscopy at Arizona State University. Results from these investigations will be presented at the symposium.



Figure 1. (a) Secondary electron (SE) image of a Ryugu particle from chamber A (A0079) pressed into gold foil. (b) D and <sup>15</sup>N-enriched lath-like (whisker) detected in same particle.

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## Constraining Ryugu's earliest fluid composition by the analyses of phosphates

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Volatile elements and compounds like F, Cl, S, H<sub>2</sub>O and CO<sub>2</sub>, indisputably exert a strong influence on the nature and evolution of (exo)planets, of which water is arguably the most prominent for the habitability of the Earth. Most volatiles were likely brought to Earth by carbonaceous chondrite-like material, including asteroids, making the undisturbed material of Ryugu key samples to improve our understanding of the distribution of water in our solar system and the origin of water on Earth.

The water concentration in CI chondrites is distinct from that of Ryugu (13 to 20 wt% compared to 6.8 wt%, respectively; [1,2]), which might be explained (i) by loss of water from Ryugu during the disruption of the parent body, (ii) impact heating, (iii) that CI chondrites derive from parent asteroids with higher water content than Ryugu, or (iv) that CI chondrites got contaminated by water during their residence time on Earth [2-4]. Importantly, the apatite grains found in Ryugu likely originate from the aqueous alteration of Ryugu that predates the events that might have lead to the loss of some of Ryugu's water inventory (see points i and ii, [5,6]). Thus, measuring the chemical and isotopic compositions (e.g. H, O, etc) of these apatites will likely help to better constrain the initial composition of Ryugus water, prior to its disruption, which is the aim of different research projects currently ongoing.

We will present the developed method on how we measured the H-isotopic composition of the apatites in Ryugu and discuss this preliminary results in the context of the initial dD value of Ryugu's water.

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## Interpreting the thermal alteration history from organic matter in Ryugu samples

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**Introduction:** The Hayabusa2 mission visited the near-Earth Cb-type asteroid (162173) Ryugu and has returned to Earth with the surface material of Ryugu. Ryugu is an airless rubble pile asteroid exposed to space weathering [1]. Near infrared remote observations recorded an absorption feature at 2.72  $\mu$ m indicating the presence of OH–bearing hydrous components. However, the 2.72  $\mu$ m feature is weak, suggesting that Ryugu was once organic- and water-rich and subsequently dehydrated by a brief period of surficial heating. This feature has also been observed in "thermally metamorphosed carbonaceous chondrites", "CI-/CM-like", or "CY" chondrites [2, 3]. Initial examination of the returned samples did not identify any significant heating at >150 °C [4, 5]; however, amino acid analyses suggested similarities to thermally-altered meteorites on the grounds of the predominant straight-chain n- $\omega$ -amino acid abundances [6]. It remains unclear as to what caused the nonconformal interpretations of the thermal alteration history of Ryugu.

Here we investigate the alteration history of Ryugu by comparing the organic composition of fresh Ryugu samples to that of naturally and experimentally heated chondritic meteorites. This study describes a coordinated effort in analysing organic matter in Ryugu samples using micro–x-ray computed tomography (µ-CT), micro-Raman spectroscopy, focused ion beam (FIB), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), micro-X-ray diffraction (µ-XRD), scanning transmission X-ray microscopy (STXM), X-ray absorption near edge structure (XANES), and synchrotron radiation-based X-ray computed tomography (SR-CT).

**Samples and Analytical Techniques:** We studied Ryugu samples allocated during the Hayabusa2 preliminary examination (A0063-FC016, A0063-FC017, A0064-FO012, A0067-FC008, C0002-FC014, C0002-FC015, C0025-FC003, C0033-FC003, C0046-FO003) and AO1 (A0009 and C0011), plus raw fragments of naturally long-term (CIs: Orgueil, Ivuna; CMs: Murchison, Murray; CV: Allende; CRs: Grosvenor Mountains 95577; OCs: Yamato (Y)-74191, Queen Alexandra Range 93010) and short-term heated meteorites (Belgica-7904, Jbilet Winselwan, Y-793321, Y-86720, Y-982086) [7, 8]. We also analysed samples of Murchison, Murray and Orgueil experimentally heated to 300, 400, 500, 600, 700 and 900 °C for 1, 10, 50, 100, 500 and 1000 hours. Raman analyses were conducted using a Jobin-Yvon Horiba LabRAM HR Raman microprobe with a 514 nm laser for which the power was maintained at <100  $\mu$ W at the sample surface. The mineralogy of the raw Ryugu samples was characterised using low-voltage SEM-EDS (FEI Quanta 650) and  $\mu$ -XRD. We identified regions of interest (ROIs) within A0009 and C0011 by conducting  $\mu$ -CT analysis using a cabinet-based industrial Zeiss Xradia Versa 520 CT system. Targeted ROIs were picked using sterile tools, pressed into indium, and prepared into electron-transparent sections (~100 nm thick) mounted on TEM Cu grids using a FEI Quanta 3D 600 dual beam FIB-SEM, which were studied by STXM-XANES to determine the organic composition. Euhedral sulphide crystals were lifted and mounted on W-needles by the FIB-SEM, and potential fluid inclusions within them were then located by SR-CT conducted at SPring-8 BL47XU at the X-ray energy of 7 keV.

**Results and Discussion:** Increased heating of carbonaceous materials results in a transition from amorphous to graphitic carbon, and such ordering is traceable using Raman spectroscopy as a cosmothermometer [9]. Raman spectroscopic analysis of

the Ryugu samples indicates significant heterogeneity (Figure 1), evident by Raman spectral features that are comparable to the organic matter in both relatively unheated primitive chondrites and those that experienced short duration heating like Y-793321, a Stage II heated chondrite [10].

The Raman spectral features of the organic matter in most of the Ryugu samples are similar to those observed from CIs, consistent with previous studies [11]. However, localised areas within several Ryugu samples show a wider G band, comparable to organic matter processed by short duration heating. The Raman features of the organic matter in broad areas within A0009, A0064 and C0011 clearly deviate from that observed from the other Ryugu samples and Orgueil, with significantly lower D band positions and D band widths that are comparable to chondritic organics that had been heated at elevated temperatures [9], and larger G band widths that are not observed in naturally metamorphosed chondritic meteorites (Figure 1). These trends are similar to those



Figure 1. Comparison of the Raman D and G band parameters of Ryugu samples (yellow symbols), and naturally short-term heated samples (black symbols; Stage II CCs peak heating temperature ~250–500°C; Stage IV CCs >750°C).  $\Gamma$ =Full width half maximum;  $\omega$  = Peak location.

exhibited by astromaterials heated by short-term heating, like interplanetary dust particles [12] and some meteorites [13]. The Raman spectra of A0009, A0064 and C0011 are similar to those of Orgueil experimentally heated to 300 °C for 500 h.

Analysis of A0064 by SEM-EDS and  $\mu$ -XRD shows the presence of hydrated phyllosilicates, suggesting that the particle did not experience significant heating above ~300– 400 °C. Moreover, the SR-CT data validated the  $\mu$ -CT scans, and indicate that C0011 contains a sulphide grain hosting an inclusion with X-ray attenuation that is clearly distinct from air (Figure 2). Previous studies have revealed H<sub>2</sub>O and CO<sub>2</sub> within such inclusions [14], suggesting that they have not been metamorphosed after aqueous alteration. Analysing these more "evolved" particles with STXM-XANES helped



Figure 2. SR-CT images of a sulphide grain picked from C0011.

us understand the organic structure corresponding to the Raman features. C-XANES spectra of A0009 and C0011 indicate the presence of aromatic or olefinic groups (C=C) at ~285 eV and carboxylic groups (COOH) at ~288.5 eV within the matrix associated with carbonate grains (CO<sub>3</sub> absorption at 290.3 eV). While thermally stable oxygenated functional groups were observed in short term (impact induced) heated meteorites [15], the association of the organic matter with carbonates is comparable to the carboxylic-rich diffuse organic matter in CM and CI chondrites [16]. Based on our coordinated investigation, we have drawn two possible scenarios that can explain our observations: (1) some carbonaceous matter in Ryugu had experienced post aqueous alteration short duration heating (impact induced and/or solar irradiation), resulting in the presence of thermally stable oxygenated moieties like furan and phenol that were formed via dehydration and cyclisation of polyalcohols. These "evolved" materials were subsequently disrupted and redistributed by impacts, thermal fatigue, and/or mass wasting processes [17], intermixed with fresh, undisturbed and pristine Ryugu materials. Alternatively, (2) the formation of the macromolecular organic matter occurred at the final stages of aqueous alteration in low-temperature, highly oxidizing fluids, e.g., fluid with OH radicals contributing through H<sub>2</sub>O<sub>2</sub> dissociation [18], co-precipitating carboxylic enriched components in the immediate vicinity of carbonate.

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# First direct detection of large aromatic molecules on asteroid (162173) Ryugu sample C0083 and A00145: an interstellar heritage

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Although meteorite analysis has revealed various types of pre-solar grains, the presence of large polycyclic aromatic hydrocarbons (PAHs) of interstellar origin has not been firmly established. Here we present a search for these compounds in the C0083 and A00145 grains from the Ryugu asteroid. The experiment takes advantages of the ultra-sensitivity of the AROMA (Astrochemistry Research of Organics with Molecular Analyzer) setup to target these species.

The AROMA setup was developed specifically for studying the carbonaceous molecular composition of meteorites and cosmic dust analogues [1]. It consists of a laser desorption ionization (LDI) source combined with a segmented linear quadrupole ion trap (LQIT), all connected to an orthogonal time-of-flight mass spectrometer (oTOF). The ion source is at a low pressure of 10<sup>-6</sup> mbar and can be operated using a two-step laser desorption ionization scheme. This L2MS analysis provides ultra-sensitivity for PAHs and fullerenes as demonstrated in our earlier study [2]. This laser technique also requires little or no sample preparation and uses very little material.

Subsamples of the two Ryugu grains have been isolated and used either as bulk or crushed in the form of powder to improve sensitivity. The data obtained are compared to previous AROMA analyses of carbonaceous chondrites (CCs) such as Murchison and Orgueil. This reveals a number of peculiarities in the distribution of PAHs in Ryugu grains. In particular we report the presence of PAHs containing as much as 50 carbon atoms, which can be considered as interstellar candidates. Moreover, we have identified aromatic compounds that incorporate nitrogen (N) and oxygen (O) heteroatoms, with carbon atoms extending up to 48. These findings impact our view on the complexification of organic matter in the cycle of matter from the interstellar matter to the Solar System. It also motivates the research for these large compounds in other CCs

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## FIB Tomography-STXM-TEM on organic material from Hayabusa-2 grain A0083.

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**Introduction** The success of the *Hayabusa-2* mission provides unique insight into prebiotic evolution from a known asteroid free from terrestrial contamination. Asteroid 16273Ryugu (Ryugu here on in) is of CI (Ivuna-type) composition, lacking any distinct chondrules and calcium aluminium inclusions, and is composed mainly of secondary minerals including phyllosilicate, carbonates, (Fe, Ni) sulphides, Fe-oxides and phosphates [1]. Organic material (OM) also pervades Ryugu, characteristic of OM found in primitive chondrite matrices. Micron to submicron organic particles (OPs) – macromolecular organic objects completely surrounded by inorganic material – make up the major mass fraction of OM [e.g. 2], consistent with insoluble organic matter (IOM). A volumetrically diffuse organic component aromatic-poorer and carboxylic-richer than OPs found within chondritic hydrated silicates [3] also occurs in Ryugu [4]. This study is on a grain from the 1st touch-and-go (TAG) site on Ryugu, characterising the distribution, functional chemical variation and mineral setting of OM *in situ*.

**Samples & Methods** Grain A0083 (Radegast here on in) is a 1.3 and 1.7 mm grain from Chamber A of the *Hayabusa-2* collector TAG site. Radegast was prepared and analyzed taking an approach of minimal damage and material loss for characterisation. Radegast was picked up with vacuum tweezers and placed on a clean Au base with an ~2 mm divot, mounted on an Al stub. An ~1.5 mm circular hole in clean Al foil was placed over the top of Radegast and fastened at the edge of the stub, exposing the grain out of the hole and securing it. This has the advantage that the grain can be turned over by lifting the foil for any further characterization whilst leaving the grain intact. Focused Ion Beam (FIB) ~100 nm lamella of Radegast were prepared for Scanning Transmission X-ray (STXM) and Transmission electron Microscopy (TEM). The TESCAN *AMBERX* and *LYRA3* at TESCAN GROUP and the Central European Institute of Engineering & Technology (CEITEC)-nano, respectively, were used to compare the effects of Xe+ plasma FIB with Ga+ FIB lamella preparation on the STXM measurements of OM in the samples. To minimize sample information losses by destruction from the traditional FIB lamella sample preparation, FIB tomography was performed from the edge of the grain during milling prior to lift-out. Grains of Ivuna were also embedded in molten S for ultramicrotome using methods in [5]. 110 nm samples were cut using a Leica UC7 at CEITEC-Muni to compare the STXM measurements between Xe-, Ga- FIB lamella and microtome samples. Scanning Transmission X-ray Microscopy (STXM) measurements were made at BL 19A at the Photon Factory, Japan. S/TEM was performed with the CEITEC-MUNI Thermofisher *Talos* F200C, and the J'Heyrovski Institute's JEOL 2100.



Figure 1. BSE images of particle A0083 (Radegast). (a) Entire image of Radegast. Insets show various phases on the top of the particle. Blue and purple are Fe-Sulphides (probably hexagonal pyrrhotite) Yellow is Fe-oxides (magnetite). Pink is a mixture of minerals. Green rectangle shows the region of tomography from the top edge of Radegast. (b) Tomography and Lamella liftout regions. Inset show the milled regions for tomography and lamella liftout made between Ga+ (*LYRA3*) and Xe+ (*AMBERX*) FIB instruments. (c) A Coarse grained organic particle (arrowed) from 1<sup>st</sup> cross section of tomography volume.

**Results & Discussion** Radegast displays CI composition similar to samples from both TAG sites, suggesting widespread alteration across the asteroid. Organic particles are mostly submicron with IOM morphology. Some coarser OPs identified in the tomography completely surround phyllosilicate, suggesting post-formation of the primary mineralogy within them (Fig. 2).



Figure 2. FIB Tomography slices of a coarse-grained organic particle in Radegast.

Organic particles and diffuse OM are consistent between FIB and microtome samples of Ivuna (diffuse OM in microtome samples have not been previously reported), implying that both Ga+ and Xe+ FIB preserve the functional chemistry of OPs and diffuse OM (Fig. 3). Carbon-XANES shows that individual OPs in closer proximity to one another are more equilibrated, suggesting that the alteration recorded in the grain was a common process evolving them. They have aromatic-rich, 3-peak spectra similar to the 'aromatic' particles in [4]. Notably, OPs in Ivuna are aromatic poorer, with lower aromatic/ketone ratios than those in Radegast and other Ryugu samples. Aromatic-rich OPs are however in higher abundance in the CR1 GRO 95577 [2] and Orgueil [3] than the type 2/3 carbonaceous chondrites. Diffuse OM (aromatic-poorer and aliphatic/carboxylic-richer OM than OPs) in Radegast is also more similar to diffuse OM found in Ivuna (Fig. 3) and GRO 95577 [2], with higher carboxyl/aromatic peak ratios than type 2/3. It is also similar by being in phyllosilicate rather than amorphous hydrated silicates found in type 2/3 chondrites. SEM and TEM (Fig. 5) shows coarse and finer domains of phyllosilicate. Diffuse OM occurs in both domains of phyllosilicate but is less concentrated in the coarse domains than the finer ones that are also intermixed mostly with Fe and Fe,Ni-rich sulphides (Fig. 3a). HRTEM shows the coarse domains as mixed layers of serpentine and smectite, consistent with previous studies [6].



**Conclusion** Organic material in Radegast evolved into aromatic-rich organic particles and aliphatic/carboxyl-rich diffuse OM by alteration on Ryugu, similar to those found in type C1 planetary materials.

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## New view on the paleomagnetic record of samples from asteroid Ryugu

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The JAXA Hayabusa 2 mission returned  $\sim 5$  g of material from the C-type asteroid Ryugu. Ryugu material contains abundant magnetite and pyrrhotite, formed during aqueous alteration on its parent body. The timing of aqueous alteration is not yet well constrained, with estimates ranging between 1.8 and 6.8 Myr after CAI formation (Yokoyama et al., 2022; McCain et al., 2023). Given these uncertainties, aqueous alteration on Ryugu's parent body may have occurred during the lifetime of the solar nebula magnetic field (i.e., up to  $\sim 5$  Myr after CAI formation; Weiss et al., 2017). Magnetite and pyrrhotite may therefore carry a chemical remanent magnetization reflecting the intensity of this field.

Rock magnetic and paleomagnetic data of Ryugu samples were recently published (Nakamura et al. 2022; Sato et al., 2022). The authors measured the NRM of two samples (0.425 mg and 1.556 mg) and demagnetized the NRM using alternating fields (AF). They identified stable remanence components in both samples up to 24 mT and 32 mT, respectively, which they interpreted as evidence that Ryugu material experienced a 41- to 390-µT solar nebula field.

We conducted a new paleomagnetic investigation of two other Ryugu samples with mass 0.8 mg and 20.8 mg. Data are very consistent among our two samples, but their mass-normalized NRM intensities are 20 to 100 times weaker than the published ones. NRM demagnetization data exhibit a poorly defined low-coercivity component up to ~8 mT, but become completely erratic at higher AF field steps. A similar demagnetization behavior is found after applying anhysteretic remanent magnetizations (ARM) acquired in bias fields up to 10  $\mu$ T. For ARM bias fields of 20  $\mu$ T and greater, we can identify a component of the magnetization in the coercivity range 10-50 mT. Although further analyses are being conducted, this favors the idea that the samples experienced magnetization. This upper limit is compatible with both (i) the nebula field intensity estimated from other meteorites with similar age of the NRM, and (ii) the absence of field.

We suspect that the samples used by Nakamura, Sato and colleagues may have been contaminated by exposure to strong magnetic fields up to  $\sim 20$  mT. We will discuss how such a contamination can be identified using measurements that are non-destructive for the NRM. This highlights the need for extreme caution to avoid magnetic contamination during handling of returned extraterrestrial material. Our data show, however, that the samples were not remagnetized *en masse* during sampling on the asteroid, in transit in the spacecraft or during curation preceding any measurements.

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