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Samples returned from the asteroid Ryugu are similar to Ivuna-type carbonaceous meteorites

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Carbonaceous meteorites are thought to be fragments of C-type (carbonaceous) asteroids. Samples of the C-type asteroid (162173) Ryugu were retrieved by the Hayabusa2 spacecraft. We measure the mineralogy, bulk chemical and isotopic compositions of Ryugu samples. They are mainly composed of materials similar to carbonaceous chondrite meteorites, particularly the CI (Ivuna-type) group. The samples consist predominantly of minerals formed in aqueous fluid on a parent planetesimal. The primary minerals were altered by fluids at a temperature of 37 ± 10°C, $5.2^{+0.7}_{-0.8}$ (Stat.) $^{+1.6}_{-2.1}$ (Syst.) million years after formation of the first solids in the Solar System. After aqueous alteration, the Ryugu samples were likely never heated above ~100°C. The samples have a chemical composition that more closely resembles the Sun's photosphere than other natural samples do.

Meteorites are fragments of asteroids, but identifications of the specific parent asteroid are rarely available. Samples of asteroid (25143) Itokawa returned by the Hayabusa mission showed that S-type (stony, in a remote sensing classification) asteroids are composed of materials consistent with ordinary chondrite meteorites (*1*, *2*). The Hayabusa2 (*3*)

spacecraft was launched on 2014 December 3 to collect samples of the near-Earth asteroid (162173) Ryugu, which is of Cb-type (a sub-class of C-type (carbonaceous) asteroid in the remote sensing classification). A mission goal was to determine the relationship between C-type asteroids and the carbonaceous chondrite meteorites. Observations of Ryugu from Hayabusa2 after rendezvous showed that: (i) Ryugu is darker than every meteorite group (*4*, *5*); (ii) Ryugu contains ubiquitous phyllosilicate minerals (*4*, *6*); (iii) Ryugu's surface experienced heating above 300°C (*6*); and (iv) Ryugu materials are probably more porous than carbonaceous chondrites (*7*, *8*). These results indicated that carbonaceous chondrites are plausible analogs of Ryugu, but do not completely match the spacecraft observations. Laboratory analysis of the samples of Ryugu returned by Hayabusa2 is r equired to explain these results.

During 2019, the Hayabusa2 spacecraft made two landings on Ryugu to collect materials (*9*), then delivered the collected samples to Earth on 2020 December 6. The returned samples are rock fragments ranging in size up to ~10 mm, with a total mass of 5.4 g. Their colors, shapes, and morphologies are consistent with those observed on the surface by Hayabusa2, indicating that the returned samples are representative of Ryugu's surface (*10*, *11*). The samples were recovered in a non-destructive manner and examined under contamination-controlled conditions at the JAXA Extraterrestrial Sample Curation Center, before delivery to initial analysis teams in June 2021 (*10*). Our team was allocated ~125 mg of samples, containing both powder and particles from the first and the second touchdown sites (*12*). We used ~95 mg for this paper.

Petrology and mineralogy

We prepared polished sections of particle samples retrieved from the first touchdown site (particle designation A0058) and from the second touchdown site (C0002) (*12*). The petrography, mineralogy and chemical composition of the minerals were determined using electron microscopy (*12*).

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The Ryugu samples are mixtures of mechanical fragments - composed of fine-grained materials of phyllosilicate minerals, predominantly serpentine and saponite - and coarser grains dominated by carbonates, magnetite, and sulfides (Fig. 1, A, B, and D). No Ca-Al-rich inclusions (CAIs) or chondrules, characteristic constituents of most chondrite meteorites, were evident in the allocated samples. The serpentine to saponite molar ratio is approximately 3:2, based on the chemical compositions of the phyllosilicate minerals (Fig. 1C). The coarser-grained minerals in the polished sections are dolomite ($CaMg(CO_3)_2$), breunnerite [$(Mg, Fe, Mn)CO_3$], pyrrhotite ($Fe_{1-x}S$; where x = 0 to 0.17), and magnetite (Fe_3O_4) (Fig. 1B). These are distributed throughout the sections (Fig. 1D), and in small veins (Fig. 1A). Calcite ($CaCO_3$), pentlandite [$(Fe,Ni)_9S_8$], cubanite ($CuFe_2S_3$), ilmenite ($FeTiO_3$), apatite [$(Ca_5(PO_4)_3(OH,F,Cl)$], and Mg-Na-phosphate are present as accessory minerals. Anhydrous silicates, such as olivine and pyroxene, are common in chondrites, but are very rare in our Ryugu samples, occurring only as discrete grains smaller than ~10 μm across. No metal grains were identified. Overall, the petrology and mineralogy of the Ryugu samples most closely resembles the CI (Ivuna-like) group of chondrite meteorites, which have experienced extensive aqueous alteration (*13*). However, sulfates and ferrihydrite, which are commonly observed in CI chondrites, were not identified in the Ryugu samples we studied.

Bulk chemical and isotopic compositions

Bulk chemical compositions were determined using ~25 mg small grain aggregate samples from each site: particles A0106 and A0107 from the first touchdown site and C0108 from the second touchdown site (*12*). Elemental abundances were determined using X-ray fluorescence (XRF) analysis and inductively coupled plasma mass spectrometry (ICP-MS). After chemical analysis, the same samples, ICP-MS analysis, and thermal ionization mass spectrometry (TIMS) were used to determine isotopic compositions of titanium and chromium.

We found no systematic differences in chemical composition between the samples from the first and second touchdown sites (Fig. 2). We did find variations in bulk composition within each of those samples, which are most likely due to heterogeneity at small scales (*12*). The masses of the samples analyzed were less than 30 mg; coarser-grained water-precipitated minerals might not be uniformly distributed at that scale (a cross-section of ~10 mg block is shown in Fig. 1D). Spatial heterogeneity in the mineral distributions is observed for carbonates (dolomite) and sulfides (pyrrhotite), which both precipitate from aqueous solution, probably during aqueous alteration on Ryugu's parent planetesimal (Fig. 1). We find different concentrations of rare earth elements (REEs) between samples from the first touchdown site and the second touchdown site (*12*), with both being higher than the REE abundance in CI chondrites (Fig. 2). These variable enrichments could be due to depletion of H_2O, relative to CI chondrites (see below), and the heterogeneous distribution of REE-rich Ca-phosphate grains (*14*, *15*). Heterogeneity at similar scales has been observed in CI chondrites (*16*, *17*) and in the ungrouped carbonaceous chondrite Tagish Lake (*18*).

We do not observe systematic depletions of elemental abundances, relative to CI chondrites, as a function of the 50% condensation temperatures of each element (their volatility) (Fig. 2). This is unlike other groups of carbonaceous chondrites, which show various degrees of depletion with volatility (*19*). The high abundance of moderately and highly volatile elements in the Ryugu samples indicates that Ryugu is composed of materials related to the CI chondrite group. However, the elemental abundances of hydrogen and oxygen are highly depleted in the Ryugu samples, compared to CI chondrites, which we interpret as due to removal of H_2O.

Previous studies have found a dichotomy in the isotopic compositions of titanium and chromium between non-carbonaceous (NC)-like and carbonaceous (CC)-like isotope ratios (*20*–*23*). The bulk titanium and chromium isotopic ratios we measure for the Ryugu samples are similar to the CB (Bencubbin-like) and CI chondrite values (*12*), which are both CCs (Fig. 3). CB chondrites are metal rich (*24*), unlike the Ryugu samples, so are unlikely to be directly related.

Oxygen isotopic composition

Bulk oxygen isotopic compositions of the Ryugu samples from the first (~4 mg of aggregate sample A0107) and the second (~1 mg of fragment from particle sample C0002) touchdown sites were determined using laser-fluorination isotope-ratio mass-spectrometry (LF-IRMS) (*12*). Oxygen isotopic compositions of secondary minerals from the first touchdown site were determined by secondary ion mass spectrometry (SIMS) using the polished section used for petrology and mineralogy (*12*).

Oxygen isotopes measured in the bulk Ryugu samples overlap with those of the bulk samples of the Orgueil CI chondrite (Fig. 4). We interpret the variation in $\delta^{18}O$ (defined as the permille deviation from the $^{18}O/^{16}O$ ratio of standard mean ocean water) as due to the heterogeneous distributions of the constituent minerals, which may have very different isotopic compositions, including phyllosilicates, carbonates, and magnetite. Two ~2-mg Ryugu samples from the first touchdown site have consistent $\Delta^{17}O$ values (defined as the permille deviation from the terrestrial fractionation line) (*12*) with an average $\Delta^{17}O = 0.68 \pm 0.05‰$ [uncertainty of 2 standard deviations (SD)]. These are higher $\Delta^{17}O$ values than three samples of Orgueil analyzed in the

same laboratory session, which have $\Delta^{17}O$ = 0.42 to 0.53‰. Another Ryugu sample from the second touchdown site analyzed in a different laboratory has a lower value of $\Delta^{17}O$ = 0.44 ± 0.05‰, which is consistent with values for Orgueil analyzed with the same equipment ($\Delta^{17}O$ = 0.39 to 0.57‰). We therefore ascribe the differences between the Ryugu samples as due to heterogeneity on small scales or different sampling sites on Ryugu, not systematic differences between the laboratories. The average $\Delta^{17}O$ value of the three Ryugu samples, 0.61 ± 0.28 (2SD), is slightly higher than the average for the Orgueil samples of 0.48 ± 0.15 (2SD, five samples), a single measurement of the CI chondrite Ivuna which was 0.41 ± 0.05‰, and prior measurements of CI chondrites [0.39 to 0.47‰ (*25*)]. The difference may reflect either original heterogeneity between small samples, or result from contamination of the meteorite samples by terrestrial water incorporated by the phyllosilicates, sulfates, iron oxides and iron hydroxides. The discrepancy in the $\Delta^{17}O$ values between Ryugu and Orgueil (~0.15‰ offset) persists despite heating both groups of samples to ~116°C for 2–4 hours to remove adsorbed water, indicating that any terrestrial contamination in the Orgueil samples is part of the structure of the minerals, not adsorbed to surfaces.

Dolomite grains in the Ryugu samples are enriched in ^{18}O, relative to the whole rock values, but have $\Delta^{17}O$ values consistent with the whole rock (Fig. 4). The constituent minerals are generally consistent with mass-dependent fractionation. The oxygen isotope ratios of dolomite in Ryugu overlap with those of dolomite from Ivuna (Fig. 4). Ryugu magnetite is depleted in ^{18}O, relative to the whole rock value, with all but one measurement being consistent with mass fractionation. The oxygen isotope ratios of Ryugu magnetite grains are consistent with those of Ivuna (*26*, *27*). The distributions of $^{18}O/^{16}O$ ratios and the consistency of $\Delta^{17}O$ values indicate isotopic equilibrium during growth of the minerals produced during aqueous alteration.

In one polished section, dolomite and magnetite grains are located within ~100 μm of each another (fig. S1). The dolomite $\Delta^{17}O$ value is −0.7 ± 0.9‰ (2SD) (*12*), while the magnetite grains have consistent $\Delta^{17}O$ values, with a mean of −0.1 ± 0.4‰ [2 standard error (SE)]. Because the $\Delta^{17}O$ values of dolomite and magnetite grains are within their mutual uncertainties, they might have precipitated from the same fluid. Assuming isotopic equilibrium, we use oxygen-isotope thermometry (*28*–*31*) to estimate the temperature at which the dolomite-magnetite pair precipitated. The $\delta^{18}O$ values of the dolomite and magnetite are 29.9 ± 0.9‰ (2SD) and −3.0 ± 1.1‰ (2SD), respectively. The difference in $\delta^{18}O$ values between the dolomite and magnetite is 32.9 ± 1.4‰, corresponding to an equilibration temperature of 37 ± 10°C (fig. S2). The temperature is in the range (10 to 150°C) of previous estimates for aqueous alteration of CI chondrites (*25*, *32*–*34*). We also estimate (*12*) the oxygen isotope ratios of the water and serpentine that would have been in equilibrium with magnetite and dolomite grains, finding ($\delta^{18}O$, $\delta^{17}O$) = (1.0 ± 1.0‰, 0.3 ± 1.0‰) for the water and (18.6 ± 2.0‰, 9.2 ± 1.0‰) for serpentine (Fig. 4 and fig. S2). The value for serpentine is consistent with that of the whole rock, as we expected due to the high abundance of serpentine in the samples. These measurements indicate that oxygen-isotopes were in equilibrium, or close to it, during aqueous alteration of the Ryugu samples.

^{53}Mn-^{53}Cr dating

The precipitation of dolomite and magnetite during aqueous alteration was dated using the ^{53}Mn-^{53}Cr system (*12*), based on the decay of the short-lived radionuclide ^{53}Mn to ^{53}Cr (half-life: 3.7 Myr). The ^{53}Mn-^{53}Cr system for dolomite in the Ryugu and Ivuna samples (Fig. 5) were measured using SIMS, from the polished section used for petrology and mineralogy (*12*).

The slopes of linear models fitted to the data indicate initial $^{53}Mn/^{55}Mn$ ratios of (2.55 ± 0.35) $\times10^{-6}$ (2SD) for Ryugu and (3.14 ± 0.28) $\times10^{-6}$ (2SD) for Ivuna (*12*). Both initial values are consistent with those of CI dolomites obtained in previous studies (*35*, *36*). We compare the initial $^{53}Mn/^{55}Mn$ ratio to that of the D'Orbigny meteorite (*37*), an angrite which has been precisely dated and can be related to the ages of the oldest CAIs, from CV (Vigarano-type) chondrites (*38*–*40*). We find that dolomite precipitation in the Ryugu sample occurred at $5.2^{+0.7}_{-0.8}$ million years after the oldest CAI formation, which is conventionally used to represent the formation of the Solar System. However, there is additional systematic uncertainty in this dolomite precipitation date because the initial Solar System ratio of $^{53}Mn/^{55}Mn$ is not precisely constrained. If we adopt different initial $^{53}Mn/^{55}Mn$ ratios than found for D'Orbigny, the dolomite precipitation date changes to 4.8 million years [using the value in (*41*)] or 6.8 million years [for the value in (*42*)] after CAI formation. There may be additional systematic uncertainty in the ^{53}Mn-^{53}Cr age due to inherent analytical limitations of the measurement technique (*12*). We conclude the Ryugu precipitation date is in the range 3.1 to 6.8 million years after CAI formation.

H_2O and CO_2 sources

Gas release curves were measured for Ryugu samples from the first touchdown site (particle samples of A0040 and A0094) and Ivuna. Gas release was measured by increasing heating temperatures using thermogravimetric analysis coupled with mass spectrometry (TG-MS) and combination analyses of pyrolysis and combustion (EMIA-Step) (*12*). The

mass decrease of the samples during heating (mass loss) was measured simaltaneously.

The mass loss curve and differential mass loss (DTG) curve (*12*) for our Ryugu and Ivuna samples are shown in Fig. 6 [see also (*12*)]. The results for Ivuna are similar to previous studies (*43*). For Ryugu, we find a total mass loss of 15.38 ± 0.50 wt.%, which is ~30% smaller than that of Ivuna (data S6). The species responsible for the mass loss are mainly H_2O and CO_2, for both Ivuna and Ryugu (Fig. 6). SO_2 might also contribute substantially, but we were unable to quantify it due to lack of an appropriate standard (*12*).

The total weight fractions of H_2O and CO_2 gases released from the Ryugu sample measured using TG-MS are larger (20.78 ± 1.40 wt.%) than the total mass loss (15.38 ± 0.50 wt.%) measured using TG alone (*12*). We interpret this as indicating that carbonates were not the only sources of CO_2 during the TG-MS measurement, with organic carbon being oxidized to CO_2 by residual O_2 in the He gas flow used for the experiment, producing a spurious excess of CO_2 in the mass spectrometry. Because decomposition of carbonates occurs within a small temperature range (*43*), we assign the sharp CO_2 peaks at 600–800°C (Fig. 6) as due to carbonates. We observed two carbonate peaks for the Ryugu samples, which the petrographic results above showed contain three types of carbonate (dolomite, breunnerite, and calcite). We were unable to attribute specific peaks to specific carbonates. The double peaks might arise from sealed pore spaces, because we analyzed intact chips, not powders.

The remaining broad continuum in Fig. 6 is probably due to oxidation of organic carbon, by the indigenous oxygen contained in organics in the sample or by residual O_2 in the He gas flow. Therefore, we assign the CO_2 peak to carbonates and the reminder to organics (Fig. 6). The organic carbon contents are lower limits, because the TG-MS leaves some organic carbon in the sample. The organic carbon and total carbon concentrations we found using TG-MS were lower than those measured using EMIA-Step (*12*) (data S6). We estimate that 74 ± 3% of Ryugu organic carbon was released in TG-MS, as the broad organic carbon continuum, and 93 ± 4% for Ivuna. The profiles of the broad organic carbon continuum are different for both samples, indicating differing organic components in Ryugu and Ivuna.

Many peaks are apparent in the H_2O release curves (Fig. 6). We identify adsorbed H_2O from sulfates released at ~250°C, and a larger amount of H_2O from phyllosilicates at ~600°C. Because the phyllosilicates consist of serpentine and saponite (Fig. 1C), serpentine contains structural OH sites in the crystal structure, while saponite contains interlayer H_2O in addition to structural OH sites. The petrologic and mineralogic observations suggest that the sulfate contribution is negligible for Ryugu, but not for Ivuna. The SO_2 and H_2O peak releases coincide in Ivuna (at both 250°C and 450°C), but not Ryugu. We conclude that phyllosilicates are the dominant source of H_2O released from the Ryugu sample.

Dehydration of the interlayer H_2O of saponite is complete at 170°C (peaking at 90°C) for Ryugu and complete at 350°C (peaking at 100°C) for Ivuna. Dehydroxylation of structural OH in saponite and serpentine occurs at 300 – 800°C for Ryugu and at 350–800°C for Ivuna. The structural OH is dominant (6.54 ± 0.32 wt.% H_2O) in the Ryugu sample, with smaller amounts of interlayer H_2O (0.30 ± 0.01 wt.% H_2O). Both forms of H_2O are present at similar levels in Ivuna (data S6).

Organic/inorganic fractions for hydrogen and carbon

We performed an EMIA-Step analyses of the Ryugu and Ivuna samples (*12*). For Ivuna, this showed the total carbon concentration is 3.31 ± 0.33 wt.% (*12*), of which 90% is organic carbon (Fig. 7 and data S6). The total hydrogen in Ivuna is 1.59 ± 0.08 wt.%, of which 89% is inorganic hydrogen. All these values are consistent with previous measurements of the same meteorite (*44*). The total H_2O for Ivuna is 12.73 ± 0.63 wt.%, distributed as 6.58 ± 0.32 wt.% interlayer H_2O and 6.15 ± 0.30 wt.% as structural-OH or H_2O in the phyllosilicate minerals.

The Ryugu samples contains less H_2O than Ivuna. The total H_2O is 6.84 ± 0.34 wt.%, including 0.30 ± 0.01 wt.% interlayer H_2O and 6.54 ± 0.32 wt.% structural-OH or H_2O (data S6). The structural value is similar to Ivuna, but the interlayer water is substantially lower. The total hydrogen is 0.94 ± 0.05 wt.% for Ryugu, and the inorganic hydrogen (i.e., H_2O) comprises 81% of the total hydrogen. The amount of organic carbon in Ryugu is 3.08 ± 0.30 wt.%, indistinguishable from that in Ivuna (2.97 ± 0.29 wt.%) (Fig. 7 and data S6). This implies the inorganic/organic matter ratio is similar in the Ryugu and the Ivuna samples studied, excluding a previous proposal that Ryugu's low albedo is due to higher organic carbon contents than CI chondrites (*45*). However, the total carbon is higher in Ryugu (4.63 ± 0.23 wt.%) than in Ivuna, due to the higher abundances of carbonates in the Ryugu samples.

Formation history of Ryugu

Ryugu is thought to have formed by re-accumulation of material ejected from a parent body by an impact (*5*). The aqueous alteration of the samples must have occurred on the parent body, because aqueous fluid is not stable in the current Ryugu asteroid. The CI-like elemental abundances of Ryugu suggest that the parent body accreted all elements with 50% condensation temperatures higher than 500 K that were present at Solar System formation, along with some ice-forming elements (Fig. 2). Ryugu's parent body was probably closely related to the parent body (or bodies)

of the CI chondrites. We assume that the accreted material was mainly anhydrous dust and ice. Physical modeling of the thermal evolution of a water ice-bearing CI-like planetesimal (*35*), compared to our oxygen-isotope thermometry, suggests that the Ryugu parent body accreted 2–4 million years after the formation of the Solar System (as defined by the ages of the oldest CAIs).

Approximately one to two million years later, roughly 5 million years after Solar System formation (Fig. 5), the material that would later be incorporated into Ryugu experienced aqueous alteration. This caused precipitation of dolomite and magnetite from an aqueous solution at about 37°C. The aqueous alteration of the primary minerals was very extensive. The saponite produced by this fluid-assisted alteration in the parent body must have contained large amounts of interlayer water (~7 wt.%) in its crystal structure, when it formed under saturated water activity, as observed in Ivuna (data S6). The low abundance of interlayer water in the Ryugu samples (0.3 wt.%) indicates that much of this water later escaped to space, most likely after disruption of the parent body and formation of the rubble pile asteroid Ryugu. We cannot definitively identify the dehydration mechanism, but suggest it may have included some combination of impact heating, solar heating, space weathering, and long-term exposure of the asteroid surface to the ultra-high vacuum of space.

We estimate the dehydration temperature as 170°C, the temperature at which interlayer water currently in the Ryugu samples completely dehydrates. The dehydration speed of the interlayer water in our experiments is 20% of total interlayer water per minute, around the peak temperature of 90°C (data S7) (*12*). The ambient space pressure in Ryugu, which is much lower than the experimental pressure of 10^5 Pa, would accelerate this dehydration speed. Such high dehydration rates are sufficient to completely dehydrate the interlayer water for any plausible geological heating events that occurred in Ryugu. Because a small peak of interlayer water is still emitted at 90°C in our experiments, it is possible that the Ryugu samples have never been heated above ~100°C since their aqueous alteration (Fig. 6). These temperatures rule out the previously proposed thermal history of Ryugu (*6*), which was based on laboratory heating experiments of carbonaceous chondrites. The temperatures we estimate are consist with Hayabusa2 observations of the surface temperature at the present orbit of Ryugu (*7*).

Some asteroids show comet-like activity, the origin of which is uncertain and could involve several mechanisms (*46*). This activity can be subtle, as in the B-type (bluish and spectroscopically similar to C-type) asteroid Bennu, where small ejections of dust particles and rocks have been observed (*47*). Thermal fracturing, phyllosilicate dehydration, and micro-meteoroid impacts have been proposed (*47*) as explanations for the ejection of solid particles from Bennu. Our finding that saponite in Ryugu is partially dehydrated supports the possibility that volatile release from phyllosilicates can induce comet-like activity at the surface of inner Solar System carbonaceous asteroids. Possible mechanisms to lift dust and rocks from asteroid surfaces include (i) anisotropic release of water molecules from phyllosilicate-rich dust particles, imparting a net momentum to those particles, or (ii) buildup of vapor pressure in sealed pore spaces, leading to pore bursting which propels dust particles away from the surface. Phyllosilicate dehydration could also play a role in the production of interplanetary dust particles and micrometeorites. The thermal release pattern of Ivuna (Fig. 6) shows that interlayer water is lost from saponite at a temperature of ~0 to 200°C. The observed maximum current surface temperatures of ~100°C for Ryugu (*7*) and ~170°C for Bennu (*48*) would therefore be sufficient for such devolatilization to take place. If so, the devolatilization must be largely complete for surface particles on Ryugu, as no particle ejections were observed by the Hayabusa2 spacecraft.

Implications for CI chondrites and cosmochemistry

The elemental compositions of CI chondrites more closely match measurements of the solar photosphere than other types of meteorite (*49*), CIs differ from the Sun in the abundances of the noble gases, hydrogen, carbon, nitrogen, oxygen and lithium. CI chondrites experienced pervasive aqueous alteration, during water-rock interactions in the early Solar System. Less than a dozen CI chondrites are known, and they have all been on Earth for decades to centuries (the most recent fall was in 1965). It is therefore unknown how far handling and exposure to atmospheric moisture has modified their mineralogies and elemental compositions. Unlike CI chondrites, the Ryugu samples are nearly free of sulfates, ferrihydrite, and interlayer water. This could be due to either CI chondrites having originated on parent asteroids with higher water contents than Ryugu, or having been contaminated by terrestrial moisture during residence on Earth (*50*, *51*). The lower abundance of anhydrous silicates, and the small but measurable offset in $\Delta^{17}O$ between Ryugu and the Orgueil CI chondrite (Fig. 4), support the terrestrial contamination explanation. The slightly higher $\Delta^{17}O$ values of Orgueil in this study compared to earlier studies could be explained if O-isotope exchange in structural-OH water of CI chondrites occurred under room temperature conditions. The gas emission patterns measured in the TG-MS and EMIA-Step analyses of Ryugu differ from those of the Ivuna CI chondrite (Figs. 6 and 7). This suggests that the structures of the organic matter differ between Ryugu samples and Ivuna, possibly due to modifica-

tion during residence on Earth.

We conclude that the Ryugu samples are more chemically pristine that other Solar System materials analyzed in laboratories, including CI meteorites. The materials observed in CI chondrites may have been modified on Earth, so no longer reflect their states in space. Possible causes are phyllosilicate hydration, organic matter transformation and contamination, adsorption or reaction of atmospheric components, and oxidation. These modifications might have changed the albedo, porosity, and density of the CI chondrites, causing the differences between Cis and the observations of Ryugu by Hayabusa2 (*5*, *7*), and between CIs and the Ryugu samples returned to Earth (*10*).

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SUPPLEMENTARY MATERIALS

science.org/doi/10.1126/science.abn7850
Materials and Methods
Supplementary Text
Figs. S1 to S4
Data S1 to S9
References (*56–82*)

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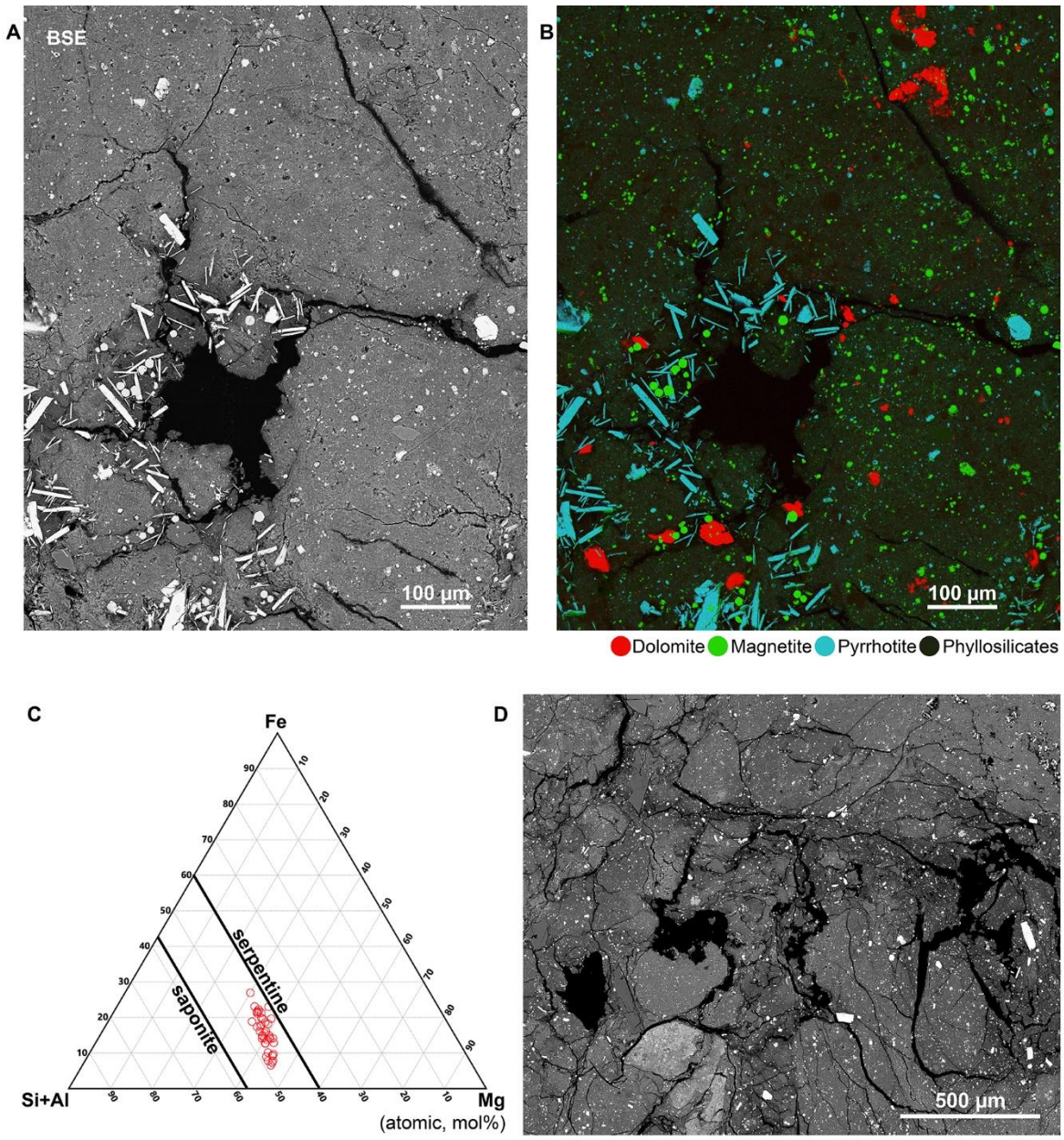

Fig. 1. Petrography of the Ryugu sample. (**A**) Backscattered electron (BSE) image of Ryugu sample A0058-C1001 (*12*). The black space in the figure is a pore. (**B**) Combined elemental map of the same sample, with characteristic X-rays of Ca Kα, Fe Kα, and S Kα lines assigned to RGB color channels as indicated in the legend. Carbonate (dolomite), sulfide (pyrrhotite) and iron-oxide (magnetite) minerals are embedded in a matrix of phyllosilicates, and in some cases precipitated in small veins. The sulfide texture is similar to that in the ungrouped chondrite Flensburg (*52*). (**C**) Ternary diagram between Fe, Mg, and Si+Al showing bulk chemical compositions of phyllosilicates in A0058-C1001. Black lines are compositions of solid solution for serpentine and saponite. Each open red circle shows bulk chemical composition of phyllosilicates measured in various locations of panels A and B, each location being 5–10 µm square. We chose each size to exclude minerals other than phyllosilicates in the area. The bulk compositions differ from place to place, with a distribution indicating that the phyllosilicates consist of serpentine and saponite with variable Fe/Mg ratios. Uncertainties on each measurement are smaller than the symbol size. (**D**) BSE image of Ryugu sample C0002-C1001, showing brecciated matrix. The texture is similar to CI chondrites (*53*).

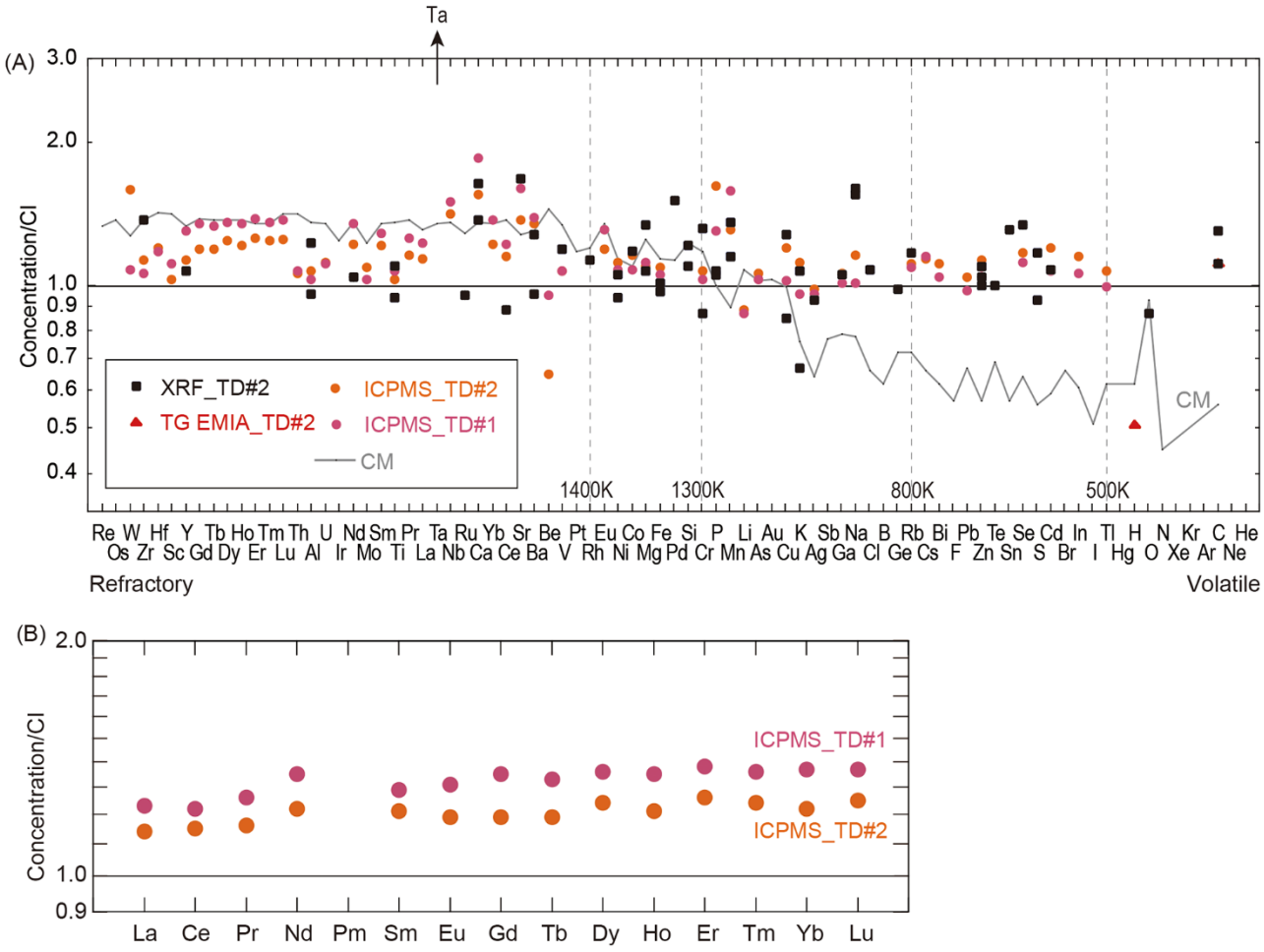

Fig. 2. Elemental abundances of Ryugu. (A) Measured abundances of elements in Ryugu, normalized to CI chondrite values (*49*), plotted on a logarithmic scale and as a function of 50% condensation temperature (i.e., volatility) (*49*). There is no systematic trend with condensation temperature. Black squares are results from our XRF analysis (*12*). Pink and orange circles are from our ICP-MS analysis (*12*). Red triangles are from our TG-MS and EMIA-Step analyses (*12*). In the legend, TD#1 and TD#2 indicate samples from the first and second touchdown sites, respectively. The high abundance of tantalum is indicated by upward arrow, which is due to contamination by the Ta projectiles used in the sampling process (*12*). The grey line shows representative values for CM (Murray-type) chondrites (*49*). The horizontal black line is the 1:1 ratio. The vertical dashed lines show specific condensation temperature thresholds, as labeled. (B) Rare Earth element abundances, plotted in order of atomic number and on a logarithmic scale. For both panels, numeric values and uncertainties are provided in data S2. Uncertainties are mostly much smaller than the variations between the samples and techniques.

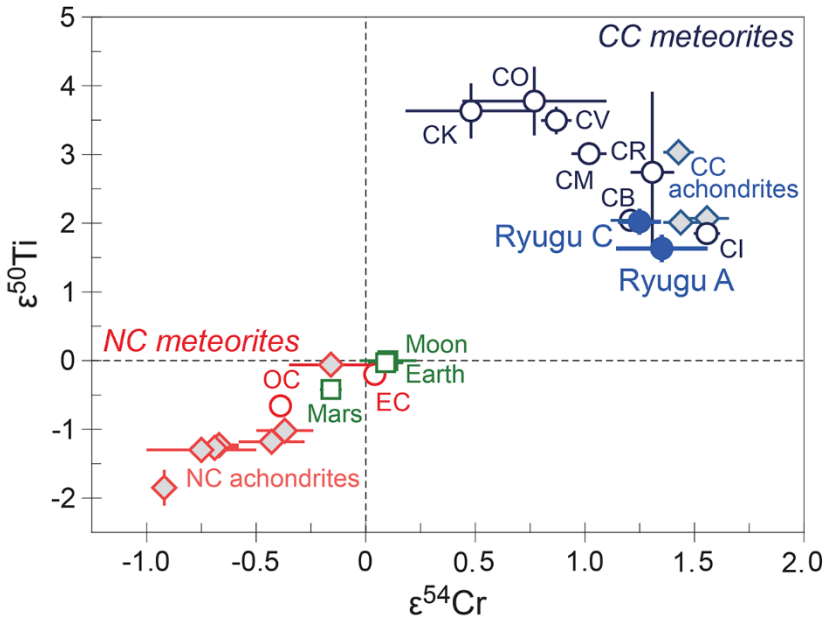

Fig. 3. Ti and Cr isotopes for Ryugu and other Solar System materials. Data are shown in epsilon notation, as defined by eqs. S1 and S2. The Ryugu samples (filled blue circles) are most similar to the CB and CI chondrites, in the CC meteorites region. CC: carbonaceous (dark blue symbols); NC: non-carbonaceous (red symbols). CI, CM, CO, CV, CK, CR, CB: named groups of carbonaceous chondrite meteorites, OC: ordinary chondrite meteorites, EC: enstatite chondrite meteorites (all empty circles). The CC achondrites and NC achondrites (filled diamonds) are differentiated stony meteorites that have Ti and Cr isotopic compositions similar to CC and NC meteorites, respectively. Values for Earth, the Moon and Mars are shown for comparison (empty green squares). Error bars are 2 standard deviations of the mean. Data are from (*21*, *54*, *55*), except Ryugu (this work). Numeric values are listed in data S3.

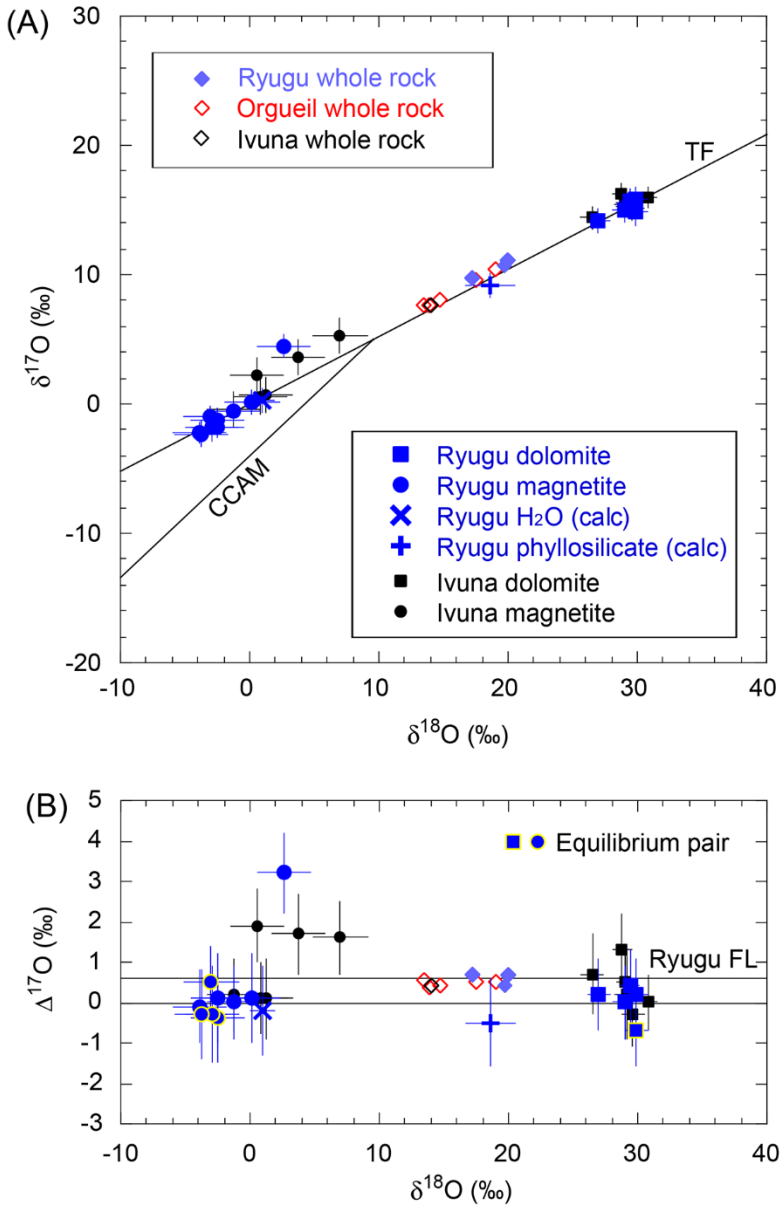

Fig. 4. Oxygen isotopes in Ryugu, Ivuna, and Orgueil. (A) $\delta^{17}O$ as a function of $\delta^{18}O$. Data are shown in δ notation, defined as the permille deviation from standard mean ocean water, see eq. S3. TF: terrestrial mass fractionation line, corresponding to mass-dependent isotope fractionations on Earth. CCAM: carbonaceous chondrite anhydrous mineral line, corresponding to the mass-independent isotope fractionations observed in refractory inclusions in chondrite meteorites. The Ryugu samples (solid blue symbols) are similar to the CI chondrites (black symbols for Ivuna, red for Orgueil). Oxygen isotopic compositions of H_2O (cross symbol) and phyllosilicates (plus symbol) in samples of Ryugu were calculated from values of dolomite and magnetite (blue symbols rimmed by yellow line in panel B), from locations shown in fig. S1. (B) $\Delta^{17}O$ as a function of $\delta^{18}O$. The Δ notation is defined as the permille deviation from the TF line, see eq. S4. Ryugu FL: mass-dependent fractionation line of Ryugu, derived by fitting a linear model to the Ryugu whole rock data (*12*). In both panels, the error bars are 2 standard deviations. Numeric values are provided in data S4.

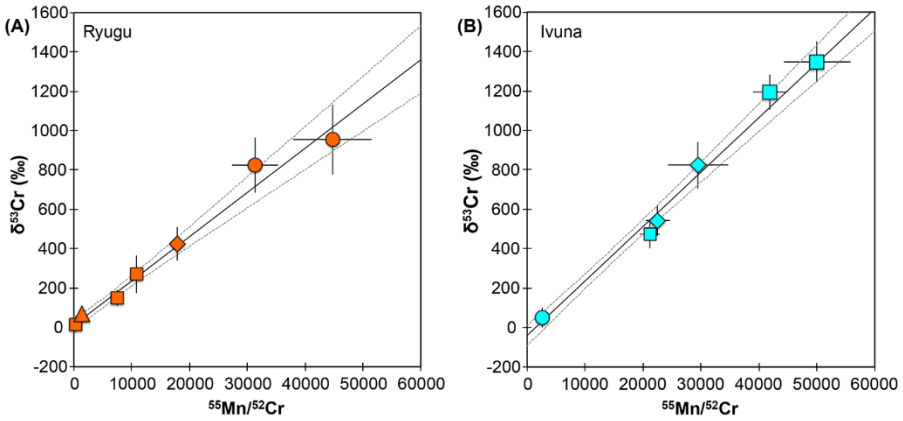

Fig. 5. ^{53}Mn-^{53}Cr isotopes measured from dolomite. Data are shown for samples of (A) Ryugu and (B) Ivuna. Each symbol shape corresponds to measurements of a single crystal. The solid straight lines are least squares regression lines fitted to the data, and the dashed curves show 2-sigma confidence limits (*12*). The regression for Ryugu (*12*) indicates that dolomite precipitation occurred $5.2^{+0.7}_{-0.8}$ million years after the birth of the Solar System (there are additional systematic uncertainties on this value, see text). Error bars are 2 standard deviations. Numeric values are provided in data S5.

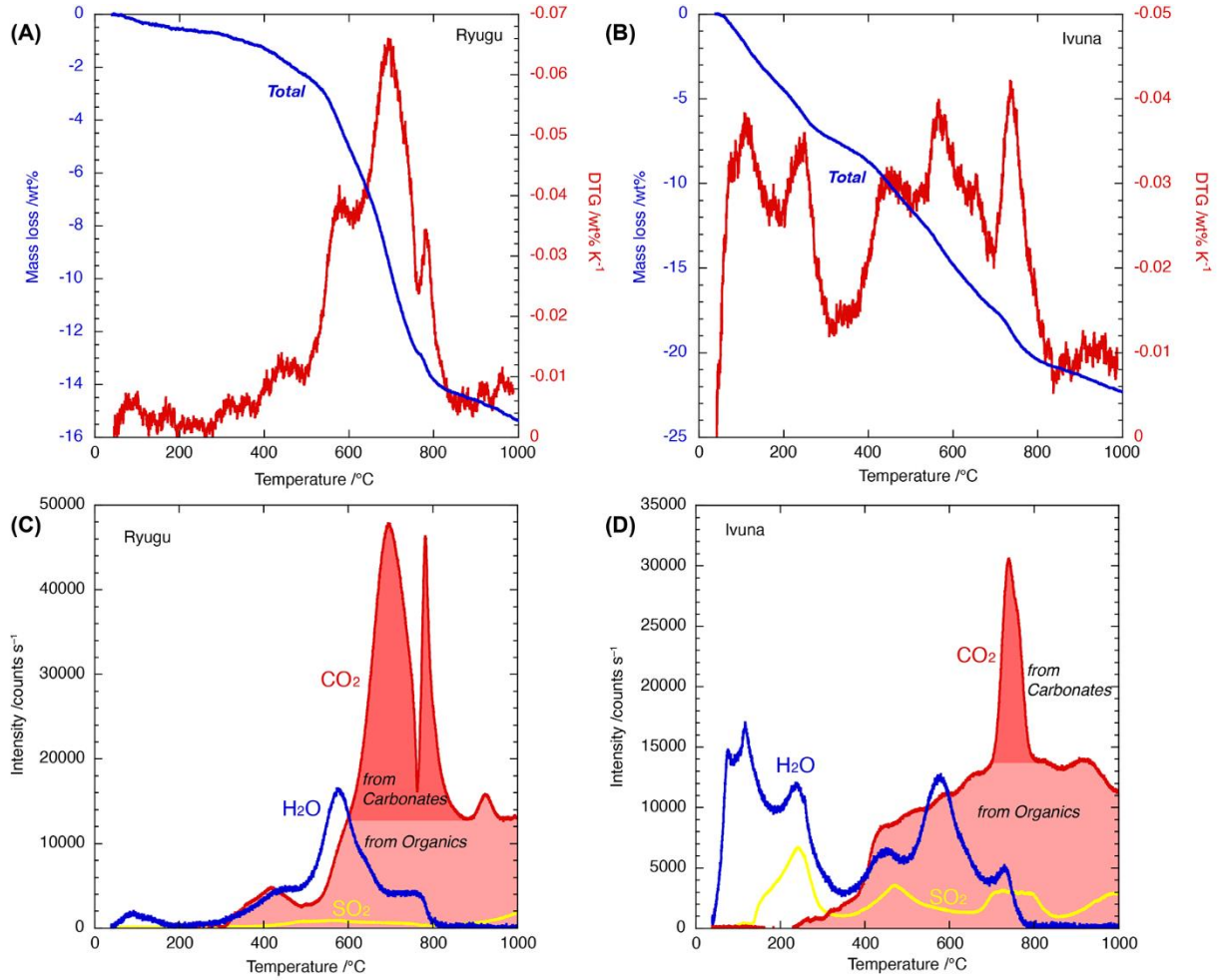

Fig. 6. Thermogravimetric analysis coupled with mass spectrometry (TG-MS) for Ryugu and Ivuna. Mass loss (blue, left axis) and differential of mass-loss (DTG; red, right axis) curves are shown for (**A**) Ryugu and (**B**) Ivuna. Derived mass intensity curves are shown for (**C**) Ryugu and (**D**) Ivuna. The H_2O trace (blue) is for mass-to-charge ratio (m/z) = 18, CO_2 (red line) for m/z = 44, SO_2 (yellow) for m/z = 64. Contributions of CO_2 are assigned to carbonates (red shading) and organics (pink shading). Numeric values are provided in data S7 (*12*).

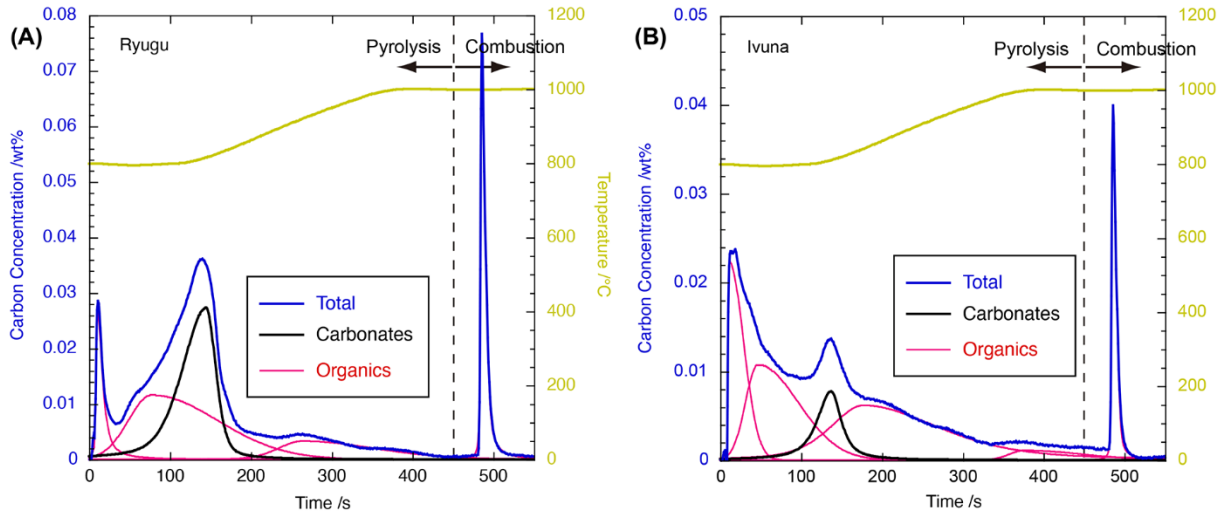

Fig. 7. Combination analyses of pyrolysis and combustion (EMIA-Step) for Ryugu and Ivuna. Carbon release curves are shown for (**A**) Ryugu and (**B**) Ivuna. The carbon concentration (blue, left axis) is plotted as a function of sample heating time (x-axis). The sample temperature (yellow, right axis) changes non-linearly with time. The dashed line at 450 s shows the boundary between conditions of pyrolysis and combustion (*12*). The integration under each blue curve corresponds to the total carbon released from the sample. These contributions are deconvolved and assigned to different carbonates (black) and organics (pink) in the sample (*12*); the integration under these curves correspond to inorganic and organic carbon concentrations, respectively. Numeric values are provided in data S8.

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Samples returned from the asteroid Ryugu are similar to Ivuna-type carbonaceous meteorites

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