



Carbonates in Ryugu and Bennu with MicrOmega: Insights into Aqueous Alteration on Primitive Asteroids

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Abstract

Aqueous alteration was one of the earliest geological processes in the solar system and significantly shaped the mineralogical diversity observed in primitive minor bodies. Carbonate minerals are reliable tracers of the physicochemical conditions during alteration processes on early planetesimals. We present a comprehensive characterization of carbonates in the returned samples of asteroids Ryugu and Bennu, performed using the MicrOmega near-infrared hyperspectral microscope. We identify two major carbonate species, dolomite ($\text{CaMg}(\text{CO}_3)_2$) and breunnerite ($(\text{Mg,Fe})\text{CO}_3$), with similar relative abundances and mean elemental compositions on both asteroids, indicating analogous aqueous alteration pathways on their parent bodies. A general spatial separation of dolomite and breunnerite is observed, indicating that at size scales of 10–100 μm , alteration conditions favored the precipitation of one species over the other. We interpret this as evidence for a spatially heterogeneous local water–rock ratio, suggesting that a high local water–rock ratio suppresses the formation of dolomite, instead favoring precipitation of breunnerites. Based on relative carbonate abundances, we conclude that chambers A (sampling the surface) and C (predominantly sampling the subsurface) of the Ryugu sample contain different mixtures of lithologies with different alteration degrees.

Unified Astronomy Thesaurus concepts: Asteroids (72); Planetesimals (1259); Solar system formation (1530)

Materials only available in the online version of record: machine-readable table

1. Introduction

Aqueous alteration profoundly shaped the primordial solar system, fundamentally altering the composition of planetesimals from their initially accreted state within the solar nebula. Driven by radiogenic heating from the decay of short-lived isotopes (R. E. Grimm & H. Y. McSween 1989; T. Lichtenberg et al. 2016), this process triggered a cascade of mineralogical transformations that resulted in a wide variety of secondary minerals (A. J. Brearley 2006), including phyllosilicates

(K. Tomeoka & P. R. Buseck 1988; K. Howard et al. 2011), sulfides (D. S. Lauretta et al. 2000; M. Kimura et al. 2011), carbonates (M. Endress & A. Bischoff 1996; S. De Leuw et al. 2010), and oxides (J. F. Kerridge et al. 1979). These secondary mineral assemblages, record the conditions of alteration (e.g., precursor mineralogy, temperature, pressure, and fluid composition). Through their detailed analysis, we can reconstruct the early alteration history of asteroid parent bodies.

CI chondrites are the closest analogs to the initial elemental composition of the solar nebula (E. Anders & M. Ebihara 1982; J. Barrat et al. 2012), making them invaluable samples for understanding the building blocks of the solar system. By constraining their primary mineralogy and subsequent alteration, we have gained crucial constraints for early solar system



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processes, such as the timing and conditions of planetesimal alteration and the delivery of volatiles to the inner solar system (e.g., J. F. Kerridge et al. 1979; C. M. O. Alexander et al. 2012; E. Tonui et al. 2014). However, CI chondrites are rare and rapidly affected by terrestrial weathering through oxidation and hydration (M. Gounelle & M. E. Zolensky 2001; A. King et al. 2020), limiting the conclusions we can draw from them.

In 2020, JAXA's *Hayabusa2* mission returned 5.42 g of samples from the carbonaceous asteroid (162173) *Ryugu*. Sample examination revealed a close similarity to CI chondrites in elemental compositions (T. Yokoyama et al. 2023, 2025), modal mineral abundances (E. Nakamura et al. 2022), isotopic composition (T. Hopp et al. 2022; T. Yokoyama et al. 2023), and petrography (A. Yamaguchi et al. 2023). In 2023, NASA's OSIRIS-REx mission returned 120 g of samples from carbonaceous asteroid (101955) *Bennu* (D. S. Lauretta et al. 2024). While remote-sensing studies suggested CM chondritic composition (B. E. Clark et al. 2011; V. E. Hamilton et al. 2019), laboratory analyses revealed a similarity to CI chondrites (D. S. Lauretta et al. 2024). These samples provide excellent opportunities to study primitive materials without the detriment of terrestrial weathering.

The MicrOmega instrument is a near-infrared (NIR) hyperspectral microscope developed at Institut d'Astrophysique Spatiale (IAS) in Orsay, France, and operated in collaboration with the Institute of Space and Astronautical Science (ISAS) at the Extraterrestrial Sample Curation Center in Sagami-hara, Japan, where it is one of the few instruments to analyze the entirety of the returned *Ryugu* samples. The instrument is mounted in an N_2 -purged chamber and separated from the sample chamber by an NIR-transparent sapphire window, enabling sample analysis without exposure to the terrestrial atmosphere without exposure to the terrestrial atmosphere (C. Pilorget et al. 2022; T. Le Pivert-Jolivet et al. 2023; D. Loizeau et al. 2023; C. Pilorget et al. 2024). Thanks to a cooperation with NASA, JAXA has further acquired 0.5% (0.6 g) of the returned *Bennu* mass, which are now studied with MicrOmega in the same facility as the *Ryugu* samples (R. Fukai et al. 2025; C. Pilorget et al. 2025).

In this study, we investigate the abundance and speciation of carbonates in *Ryugu* and *Bennu* with MicrOmega, following up on first results on *Ryugu* presented in D. Loizeau et al. (2023) by extending the analysis to a larger fraction of *Ryugu* samples and to the comparison between the two rubble-pile asteroids. Carbonate minerals are among the most abundant secondary minerals in CI chondrites, making up 5 vol%, and occur surrounded by oxides, sulfides, and phosphates due to their common formation through aqueous alteration (K. Fredriksson & J. F. Kerridge 1988; M. Endress & A. Bischoff 1996). Chronological information from short-lived radionuclides suggests that carbonates formed early and throughout the alteration history, making them reliable tracers of aqueous alteration in CI chondrites (W. Fujiya et al. 2013; C. M. O. Alexander et al. 2015).

In Section 2, we describe the reference and MicrOmega data acquisition and the carbonate identification process. In Section 3, we describe the compositional and spatial distribution of carbonates identified in the two asteroids. In Section 4, we interpret their similarities and differences in the context of aqueous alteration on the parent bodies of *Ryugu* and *Bennu*. We draw conclusions in Section 5.

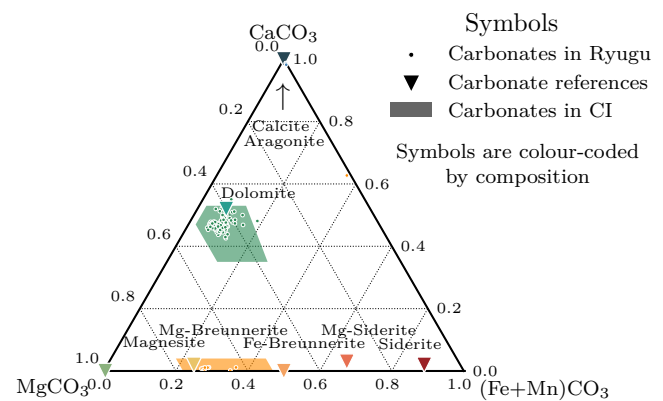


Figure 1. Elemental composition of carbonates identified in CI chondrites (shaded areas; from M. Endress & A. Bischoff 1996 and K. Fredriksson & J. F. Kerridge 1988) and *Ryugu* (dots; from W. Fujiya et al. 2023; A. Yamaguchi et al. 2023, and N. T. Kita et al. 2024). Triangles give the composition of the references; refer to Table 1.

2. Methodology

This section describes the carbonate reference data and MicrOmega science data used, followed by the algorithm for carbonate identification in the asteroidal samples.

2.1. Reference Spectra of Synthetic Carbonates

A variety of carbonate minerals have been identified in CI chondrites and *Ryugu*, including dolomite ($CaMg(CO_3)_2$), breunnerite ($(Mg,Fe)CO_3$), and calcite ($CaCO_3$; K. Fredriksson & J. F. Kerridge 1988; M. Endress & A. Bischoff 1996; D. Loizeau et al. 2023). Figure 1 shows the compositional spread of these species in CI chondrites and *Ryugu* in the $CaCO_3$ - $MgCO_3$ - $FeCO_3$ system. Note that cation substitution between Fe and Mn is common (L. M. Anovitz & E. J. Essene 1987). Four lattice vibration modes of the CO_3 group—symmetric stretching (ν_1), out-of-plane bending (ν_2), asymmetric stretching (ν_3), and in-plane bending (ν_4)—define their spectral properties in the NIR and mid-infrared (MIR) ranges. In the MicrOmega spectral range (0.99–3.65 μm , see Section 2.2), a suite of combination and fundamental bands of these modes produce a characteristic doublet feature around 3.4 μm . The relative contributions and minima of these bands are sensitive to the carbonate's cation composition (J. L. Bishop et al. 2021).

Based on these previous studies, we selected a suite of carbonate reference spectra representing two solid solution series: calcite-magnesite and magnesite-siderite. The spectra were obtained from synthetic carbonates with known elemental compositions, characterized in J. L. Bishop et al. (2021). While the authors provide multiple spectra for each carbonate species, encompassing variations in grain size and minor elemental variability, the differences between these spectra are typically smaller than the spectral variations introduced by other factors in MicrOmega measurements, such as the inherent spectral variability of the *Ryugu* samples caused by intimate mixing of materials within the MicrOmega pixel footprint (e.g., dolomite clast containing phyllosilicate matrix, magnetite, and sulfide, as can be seen in Figure S6a in A. Yamaguchi et al. 2023), varying degrees of crystallinity, and photometric effects at small spatial scales. For each species, we thus choose only the reference corresponding to the smallest available grain size ($\leq 45 \mu m$), matching the

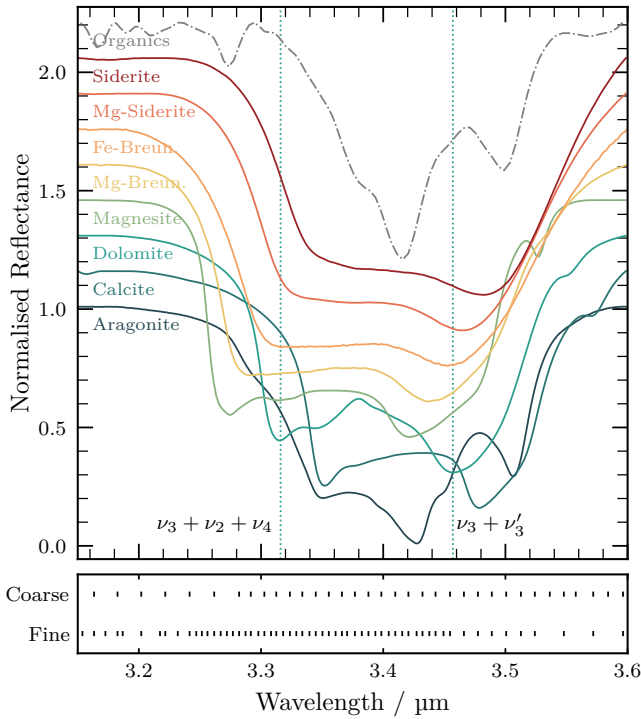


Figure 2. Reflectance spectra of synthetic carbonates and organic signature used in this work. The spectra are continuum-removed, normalized to uniform band depth, and vertically offset for comparability. Vertical lines indicate combination bands in dolomite (J. L. Bishop et al. 2021). The lower part indicates the coarse and fine wavelength sampling modes of MicrOmega used in this study.

MicrOmega pixel size scale of $22.5 \mu\text{m}$. We complement this selection with two spectra of breunnerites from H. H. Kaplan et al. (2020) and D. Loizeau et al. (2023), and a carbonate that is not regarded in J. L. Bishop et al. (2021). Figure 1 shows that the Mg/Fe ratios of these breunnerites varies considerably, making their spectral differences (shift of band minima) appreciable. As CH bands of aliphatic organic compounds are also active in the $3.4 \mu\text{m}$ region, we further add an organic signature measured in Ryugu from Z. Dionnet et al. (2023). All reference spectra are plotted in Figure 2 and further information is given in Table 1.

2.2. MicrOmega Spectra of Ryugu and Bennu

In the spatial domain, MicrOmega acquires images of a $5 \times 5 \text{ mm}^2$ field of view (FoV) in a 256×250 pixel grid with a pixel scale of $22.5 \mu\text{m}$. In the spectral domain, it covers the range from 0.99 to $3.65 \mu\text{m}$ with a resolution of typically 20 cm^{-1} (2 to 14 nm) by use of an acousto-optical tuneable filter (J.-P. Bibring et al. 2017). The majority of measurements regarded in this study were acquired with either a coarse or a fine sampling around $3.4 \mu\text{m}$, shown in the lower part of Figure 2. Each measurement produces a hyperspectral cube of (x, y, λ) data. Sample analysis is performed in an ultraclean chamber under a N_2 -purged atmosphere to prevent alteration by telluric H_2O and O_2 . Samples are observed from nadir under illumination at an incidence angle of 35° and under different azimuth angles (typically 0° , 90° , 180° , and 270°), allowing to illuminate regions that under other geometries may be shadowed. For more information, we refer the reader to J.-P. Bibring et al. (2017), L. Riu et al. (2018), and C. Pilorget et al. (2022).

Table 1
Literature Reference and Composition of Reference Minerals Used in This Work

Species	Ca	Mg	Fe	RELAB ID	References
Aragonite	1.00	0.00	0.00	BKR1JB1459A	(B21)
Calcite	0.98	0.02	0.00	BKR1JB1460A	(B21)
Dolomite	0.52	0.40	0.08	BKR1JB1461A	(B21)
Magnesite	0.00	0.99	0.01	BKR1JB0946A	(B21)
Mg-Breun.	0.02	0.74	0.24	...	(L23)
Fe-Breun.	0.02	0.49	0.49	...	(K20)
Mg-Siderite	0.03	0.32	0.66	BKR1JB1462A	(B21)
Siderite	0.02	0.06	0.92	BKR1JB1463A	(B21)
Organics	...	...	...	...	(D23)

Note. The references are K20—H. H. Kaplan et al. (2020), B21—J. L. Bishop et al. (2021), L23—D. Loizeau et al. (2023), and D23—Z. Dionnet et al. (2023).

The *Hayabusa2* mission returned a total of 5.42 g of Ryugu material, split over chambers A (surface sample; 3.24 g) and C (at least in part subsurface sample after artificial cratering; 2.03 g), with minor amounts in chamber B (T. Yada et al. 2022). Between 2020 December and 2024 June, MicrOmega has imaged the entire returned mass as bulk samples and about half in more detail in smaller “sub-bulks” and as individual grains. Compared to our previous study of carbonates (D. Loizeau et al. 2023), which regarded measurements up to 2021 December, we here regard all measurements up to 2024 June.

In 2024 August, NASA delivered $\sim 0.6 \text{ g}$ of Bennu samples to JAXA’s Extraterrestrial Sample Curation Center (T. Yada et al. 2024). These samples are representative of the overall Bennu sample, containing grains from both inside and outside the sample container. Since 2024 September, we are analyzing bulk samples (having split the 0.6 g sample into five bulks ORX-19000 to ORX-59000), followed by extraction and analysis of individual, millimeter-sized grains of Bennu with MicrOmega under identical measurement conditions as Ryugu. Enhancements to the analysis facilities now enable moving the sample dish between MicrOmega and a Fourier-transform infrared (FTIR) spectrometer (JASCO IRT-5200) while keeping it in the N_2 -purged environment and minimizing any disturbance to the grains inside. The FTIR provides a higher spectral resolution and coverage between 2 and $12 \mu\text{m}$ with a typical spot size between 50 and $100 \mu\text{m}$, allowing for an independent and complementary measurement of selected grains. The analysis here regards the sub-bulk samples only.

2.3. Carbonate Detection and Characterization

We can divide the problem of detecting carbonate signatures into two parts: (1) detecting a carbonate-rich pixel and (2) characterizing the carbonate species in that pixel. Due to its high spatial resolution, the Ryugu spectra in an individual MicrOmega pixel display at times large degrees of high-frequency noise and photometric effects, exceeding the difference in the carbonate reference spectra. To mitigate this, for each pixel, we average the spectrum with those of its direct neighbors, giving an analysis size scale of approximately $35 \mu\text{m}$, based on the retained $22.5 \mu\text{m}$ instrument pixel scale and applied smoothing kernel of $67.5 \mu\text{m}$ width in a rolling 3×3 grid. The following analysis is carried out on these averaged spectra.

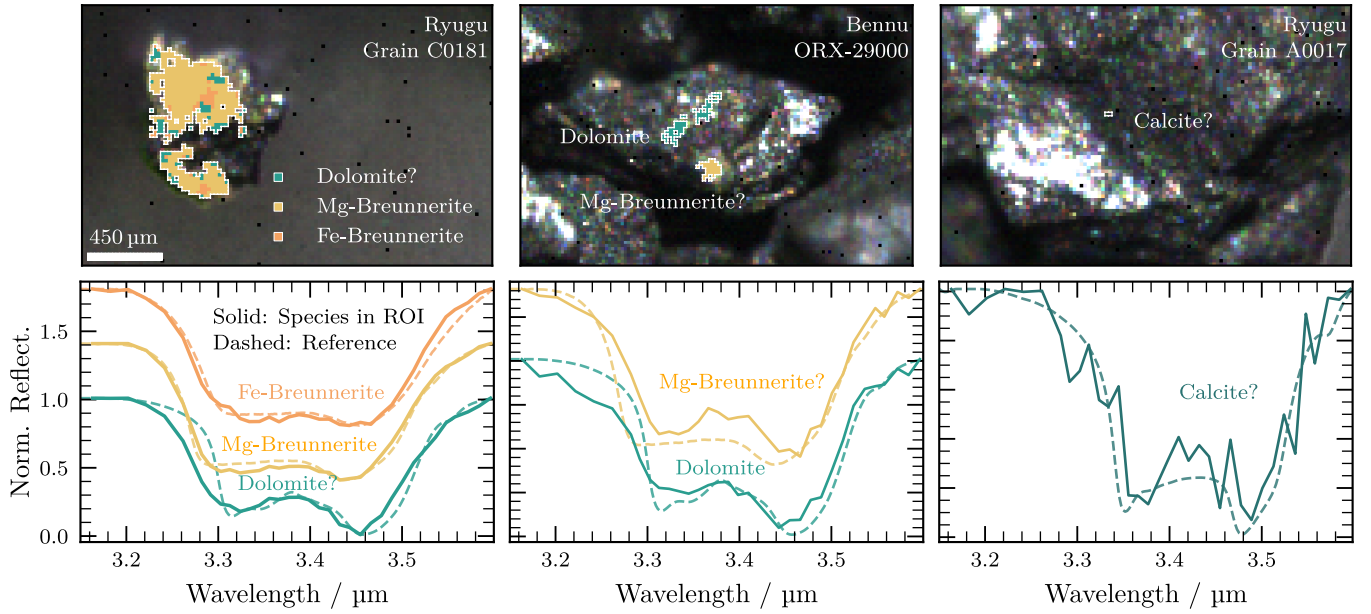


Figure 3. The top row shows false-RGB images of the samples acquired with MicrOmega. Carbonate-rich pixels are colored-in based on the most-likely carbonate composition for the respective pixel. Below the RGBs, we show the mean spectrum of all pixels associated with the dominant carbonate species in the measurement and the respective reference spectrum. The spectra are continuum-removed and vertically shifted for readability. The false-RGB channels represent the mean absorption around 2 μm , 3.4 μm , and 2.72 μm , respectively. The size scale is the same in all images.

2.3.1. Detection

We employ two criteria to identify a carbonate-rich pixel. First, we use the linear combination of reflectance values between 3.22, 3.35, 3.48, and 3.6 μm defined in D. Loizeau et al. (2023) to quantify the absorption depth around 3.4 μm against a linear continuum. Second, for all pixels exceeding a depth threshold, we perform a χ^2 comparison with the reference spectra shown in Figure 2. We only regard the spectrum in the range of 3.15 and 3.6 μm . Prior to matching, we remove the continuum using a convex hull approximation and scale the spectrum snippet to a uniform band depth. We repeat the same preprocessing for all reference spectra, after resampling them to the same wavelength pattern as the MicrOmega measurement. We record the lowest χ^2 value and the corresponding reference spectrum as the best match.

The definition of the threshold depth and χ^2 values is a trade-off between purity and completeness of the final carbonate sample. Using a subset of grains with prominent carbonates, we define initial parameter thresholds, aiming to maximize the detected carbonates while minimizing false positives. We further vary the values based on the number of carbonate-rich pixel identified in a 5×5 grid around a given pixel, to reflect the increased probability that a pixel contains a carbonate if many of its neighboring pixels contain carbonates. The search algorithm iteratively scans all pixels in a given measurement until the number of carbonate-rich pixels converges.

2.3.2. Characterization

As we rely on a single spectral feature to identify carbonates, reliable characterization and distinction of different species is challenging. The following characterization algorithm is the result of numerous trial-and-error iterations. For each carbonate-rich pixel, we initially assign the carbonate with the lowest χ^2 value as the best match. We then group all pixels by their best match and compute their mean spectrum, under the assumption that the more pixels we average, the closer the mean spectrum

should resemble the reference spectra. If the mean spectrum does not match the reference within a threshold, we remove this association from all pixels and instead assign the second best match. Pixels that after a second iteration do not have a convincing match with a reference are rejected.

Finally, we visually confirmed all characterizations. This inspection showed that the band shape is highly variable, in particular the strength of the lower-wavelength shoulder and absorption, and less reliable for identification than the band minima. In an estimated fraction of $\sim 20\%$, we changed the algorithmically identified best match to a visually better fitting species. Figure 3 shows example carbonates in samples of Ryugu and Benu, including dolomites, breunnerites, and a possible calcite detection.

2.4. Definition of Carbonate Grains

To express carbonate presence in terms of physical grain size rather than individual pixel, we group neighboring pixel detections into contiguous regions of interest (ROIs). We consider two pixels to be neighboring if they are horizontally, vertically, or diagonally adjacent. Each ROI is assumed to represent a separate carbonate grain embedded in the matrix. Note that this must not always be the case: Ryugu grain C0181 in Figure 3 presents two separate ROIs that likely represent two extrusions of the same carbonate grain. However, establishing this requires nondestructive 3D analysis methods (e.g., Z. Dionnet et al. 2023; L. Jossé et al. 2025) and is beyond the feasible scope here.

Pixels within an ROI are not necessarily matched to the same carbonate species. This may be due to true compositional variability (e.g., zoning or touching grains) or spurious, as, e.g., shadowing or out-of-focus regions can lead to low signal-to-noise ratio (SNR) and false associations. To facilitate analysis, we assign each ROI to a specific species based on its most abundant species. In all cases, the dominant species exceed 50% of the total ROI size. The best-matching carbonate

is consistent between different measurements (e.g., under different azimuths) for the vast majority of ROIs, though inconsistencies at the pixel level may arise. Finally, we account for observations of the same grain in different measurements by visually cross-matching all ROIs, creating a record of carbonate detections across measurements (i.e., geometries). In the following, we only regard the largest detection in terms of pixel size for all unique carbonate grains. We will further refer to Ryugu and Benu grains as “particles” to avoid confusion with the term “carbonate grain.”

2.5. Validation with FTIR

In Appendix A, we validate the carbonate characterization done with MicrOmega with FTIR spectroscopy measurements for a selection of Benu particles.

3. Results

In total, we identified 1210 carbonate ROIs in Ryugu samples and 250 in Benu samples. After cross-identification of grains in different measurements, we identified 709 distinct carbonate grains in samples of Ryugu and 90 in samples of Benu. We provide a table of sample IDs and identified carbonate species for both Ryugu and Benu in a machine-readable format (refer to Table 2).

Carbonates in Benu had a higher number of repeated detections (average number of 2.8 detections per grain compared to 1.7 in Ryugu) as we performed extensive measurements with varying fields of view (FoVs) and azimuth angles of the same regions of the five sub-bulk samples upon receiving them in 2024 August. In this section, we discuss these grains in terms of their mineralogy, abundance, and spatial distribution. Where possible, we compare our results with the ones we previously reported in D. Loizeau et al. (2023), while also extending the analysis to additional aspects.

3.1. Speciation

In Figures 4 and 5, we show the number of distinct carbonate grains per species and equivalent diameter (diameter of circular grain with equal surface area) identified in Ryugu (split over chambers A and C) and Benu. The binning intervals are defined based on the pixel areas of the grains. For both asteroids, dolomite and Mg-breunnerite represent the majority of carbonates, with similar fractions in terms of number of identified grains: dolomite comprises 63% (67%) of grains in Ryugu (Benu), both Mg- and Fe-breunnerite 29% (29%), and calcite 7% (4%). The remaining 1% in Ryugu are associated to Mg-siderite. The speciation observed in Ryugu is consistent with our previous findings presented in D. Loizeau et al. (2023), while revealing higher fractions of breunnerites (previously 19%) and calcites (previously below 1%) in four times as many detected grains.

Figure 3 shows a candidate detection of a calcite grain. Due to their small sizes (generally smaller than $10\ \mu\text{m}$ across, refer to Section 3.3), these grains typically have large χ^2 values, indicating less similarity with the reference spectrum. We further note that calcite is likely much more abundant at size scales smaller than the pixel scale of $22.5\ \mu\text{m}$ here.

Given the low number of Mg-siderite candidate detections (only detected in Ryugu, five in chamber A, two in chamber C), we exclude these ROIs from the following analysis. While the spectra suggest an Mg-siderite composition, we cannot rule out that a

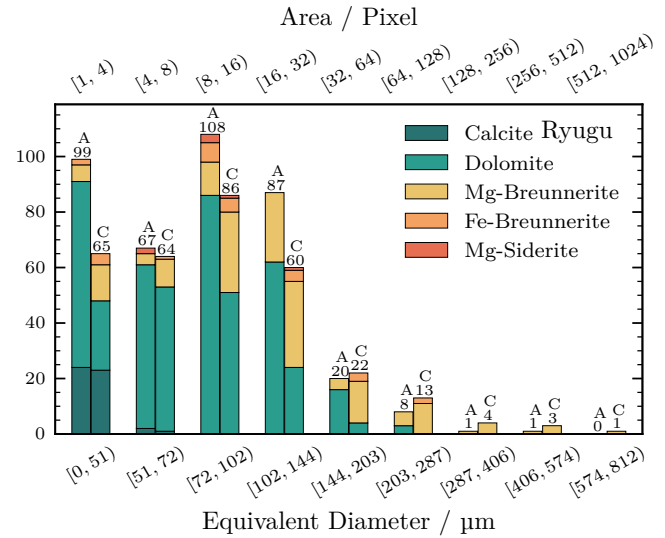


Figure 4. Species and size distribution of distinct carbonate grains in Ryugu samples, split over chambers A and C. The bars represent the number of individual grains. The carbonate area doubles for each interval from left to right. In the three largest size bins, all carbonates are Mg-breunnerites. Note that the ratio of searched material in chamber A vs. chamber C is 1.5:1.

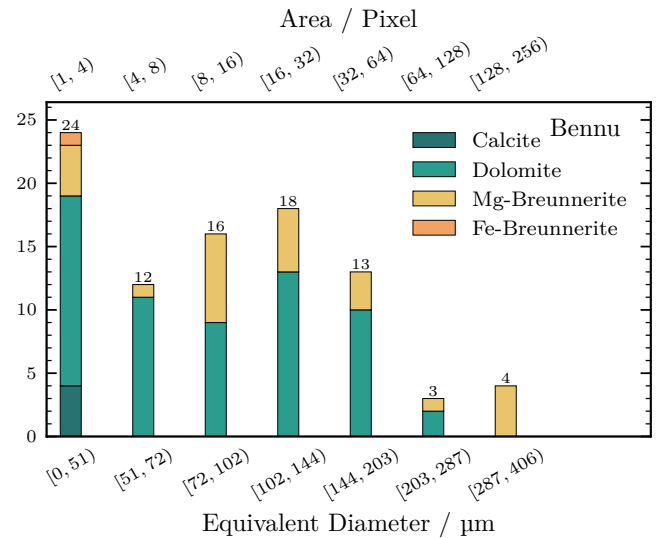


Figure 5. As Figure 4, showing the species and size distribution of carbonate grains in Benu samples.

misleading spectral appearance might arise in a few cases given the large number of spectra (order of 10^8) we have analyzed. Independent compositional verification of these ROIs would be valuable.

While we obtained aragonite-like matches, we finally chose to discard all of them from the analysis due to the strong similarity with the spectral signature of organics in the regarded wavelength range (refer to Figure 2). Follow-up analyses are required to determine the crystal structure of Ca-carbonates (presenting as calcite or aragonites) in the samples. Furthermore, while a few MicrOmega observations matched the siderite reference, none of them passed visual inspection.

3.2. Composition

In Figure 6(a), we show the median spectra of all ROIs associated with calcite, dolomite, Mg-breunnerite, and

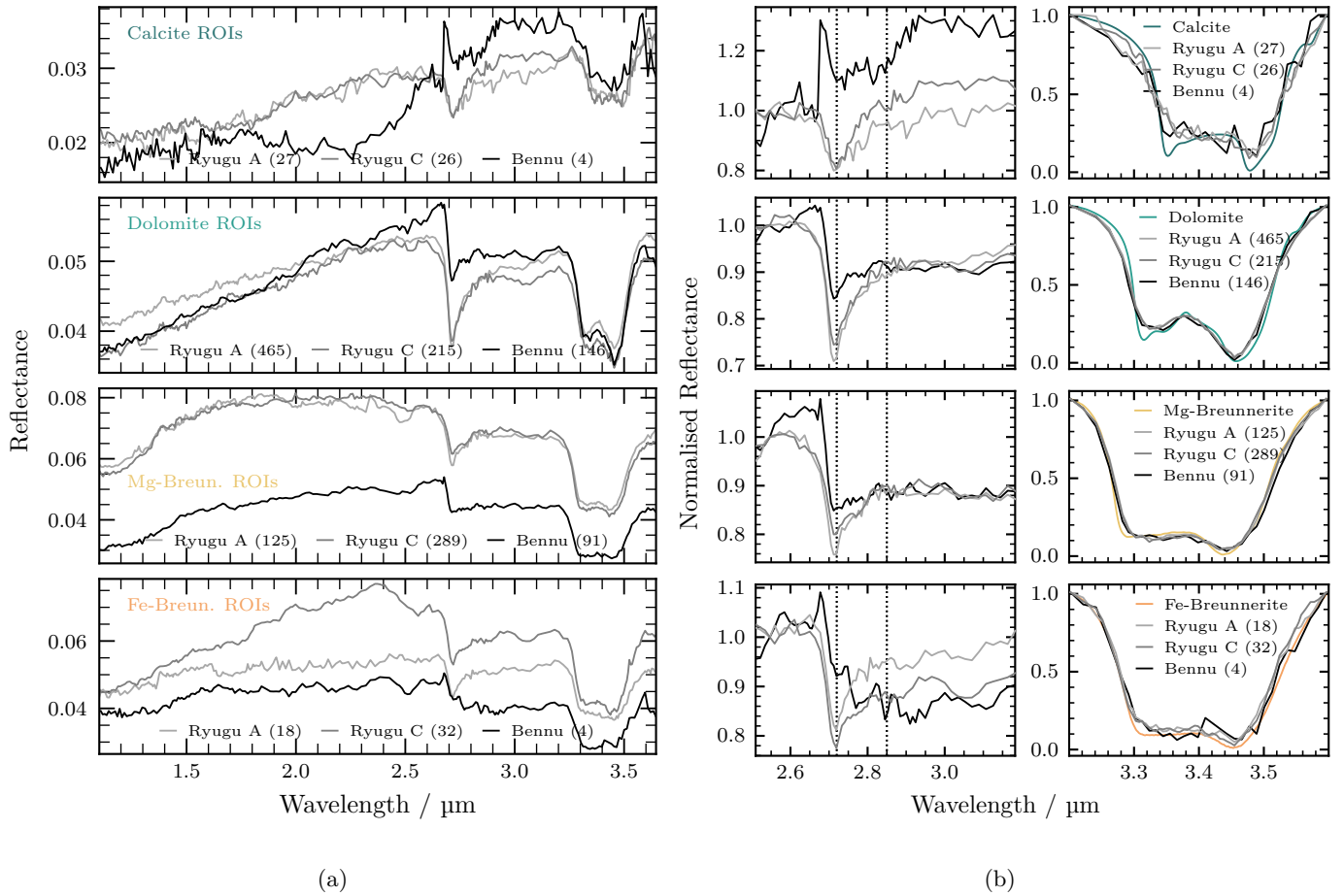


Figure 6. Median spectra of carbonate ROIs in Ryugu (chambers A and C separately) and Benu for four different carbonate compositions. The number in parentheses gives the number of averaged ROIs per spectrum. The left side shows the full spectra, the right side focuses on the 2.7 μm (normalized at 2.55 μm) and 3.4 μm (continuum-removed, scaled to uniform band depth) absorptions. Vertical dotted lines at 2.72 μm and 2.85 μm indicate typical band minima of Mg- and Fe-phyllosilicates, respectively.

Fe-breunnerite, separated into samples from Ryugu (split over chambers A and C) and Benu. Figure 6(b) presents the same spectra, focusing on the 2.7 and 3.4 μm bands and post-processed (normalization and continuum removal) for comparability. The legends in both figures indicate the number of ROIs represented by each spectrum.

The spectra show a highly similar carbonate mineralogy between the samples in chambers A and C of Ryugu. Band shape and minima of both the carbonate features at 3.4 μm and the 2.7 μm absorption of the surrounding matrix match well within sampling variability and measurement uncertainties (Figure 6(b)). The appearance of the carbonate features is further sufficiently different from that of the reference spectra that we rule out a bias in our detection method toward a narrow compositional range. We further note the drop-off toward 1.3 μm in the breunnerite ROIs in Figure 6(a), consistent with an Fe-rich composition (J. L. Bishop et al. 2021), which serves as independent verification of the matching algorithm as it did not take this spectral range into account. Minor differences among the median spectra of chambers A and C are apparent regarding the continuum slopes and absorption depths; however, these factors are susceptible to changes in the viewing geometry and less reliable compositional indicators.

In comparison to the references, the median dolomite spectra on the right-hand side in Figure 6(b) in Ryugu are slightly but consistently shifted toward shorter wavelengths,

indicating a more Mg-rich composition. Similarly, the Mg-breunnerite spectra are shifted toward longer wavelength with respect to the reference, indicating a more Fe-rich composition than that of the reference. These trends match the general compositional distributions reported for Ryugu (W. Fujiya et al. 2023; A. Yamaguchi et al. 2023; N. T. Kita et al. 2024) and observed in CI chondrites (K. Fredriksson & J. F. Kerridge 1988; M. Endress & A. Bischoff 1996), as shown in Figure 1. For calcites and Fe-breunnerites, discrepancies with the reference spectra are less suitable for interpretation given the high noise (calcites) and low number of grains (Fe-breunnerite).

Regarding Benu, we note a remarkable similarity in the median appearance of the carbonate absorption features to those in Ryugu across all four identified species (Figure 6(b)). While differences in the overall median ROIs spectra with respect to Ryugu are apparent in Figure 6, e.g., regarding the overall reflectivity of ROIs, we attribute them to differences in the surrounding matrix, further addressed in Section 3.7, and we conclude that carbonates in Benu have a similar mean composition to those in Ryugu and in CI chondrites.

3.3. Size Distribution

In both asteroids, breunnerites are on average the largest grains, followed by dolomites, while calcites are on average the smallest. For Ryugu, breunnerites (counting Mg- and Fe-

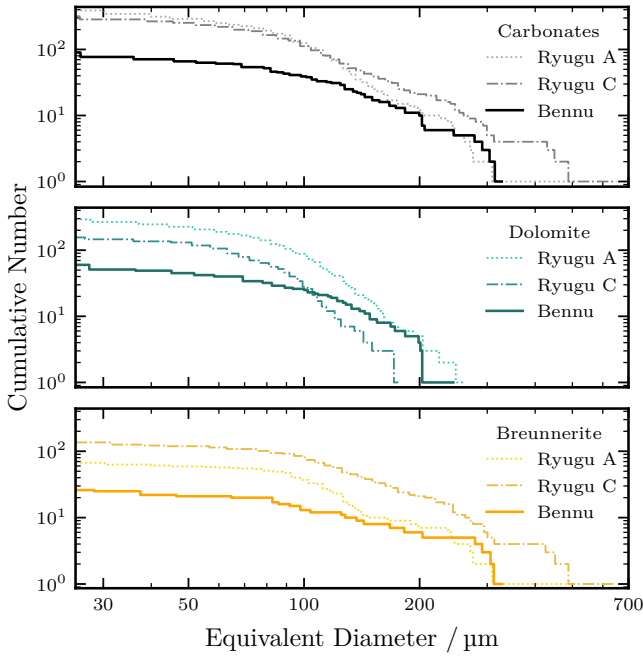


Figure 7. Size–frequency distribution of carbonate grains (top: all; middle: dolomites; bottom: breunnerites—Fe- and Mg-rich) in samples of Ryugu (split over chambers A and C) and Benu.

rich together) have median equivalent diameters of 108_{80}^{144} μm , where the sub- and superscripts give the first and third quartiles of the respective size distributions. Dolomites have equivalent diameters of 72_{51}^{98} μm . Calcite ROIs are typically one or two pixels in size, consistent with previously reported calcites of typically below 10 μm (e.g., W. Fujiya et al. 2023). The calcite signature does not strengthen in larger ROIs, indicating the grains are small and that any multipixel detections are artifacts of grains straddling the pixel grid. Calcites are often observed in clusters in CI chondrites and Ryugu (e.g., A. Yamaguchi et al. 2023, Figure S6g), meaning that a detection across one or more pixel may include multiple smaller grains that we cannot resolve at the MicrOmega pixel scale (M. Endress & A. Bischoff 1996). For Benu, we see similar though slightly larger size distributions, with 120_{80}^{183} μm for breunnerites and 87_{55}^{143} μm for dolomites. These size distributions are possibly skewed toward larger sizes, as smaller carbonate grains are often revealed during detailed studies of individual millimeter-sized Ryugu particles, which we did not include for Benu here. Overall, these size trends are in agreement with previously reported carbonate sizes in Ryugu (W. Fujiya et al. 2023; D. Loizeau et al. 2023; A. Yamaguchi et al. 2023), Benu (D. S. Lauretta et al. 2024), and CI Chondrites (E. Dufresne & E. Anders 1962; K. Fredriksson & J. F. Kerridge 1988).

A notable difference in the size distributions of both asteroids is the absence of large grains in Benu (refer to Figures 4 and 5). In the top part of Figure 7, we show the cumulative size–frequency distribution (SFD) of carbonate grains in Ryugu (split over chambers A and C) and Benu. Carbonates in Benu show a shallow slope, comparable to that of chamber C, with a drop-off around 150 μm in equivalent diameter. The drop-off indicates that larger carbonate grains are present on Benu and that their lack here is a sampling bias, likely due to the limited sample size (0.6 g) regarded here. In addition, large carbonates veins (centi- to decimeter

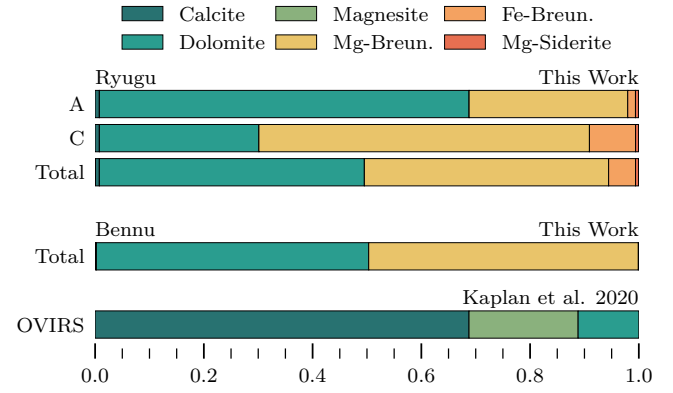


Figure 8. Relative abundance of different carbonates on Ryugu and Benu. The MicrOmega results are in terms of pixel area, the OVIRS results are in terms of number of carbonate spectra.

size) have been detected on the surface of Benu with the OVIRS instrument (H. H. Kaplan et al. 2020), whereas no such veins have been detected on Ryugu (K. Kitazato et al. 2019).

The top part of Figure 7 further shows that carbonates in chambers A and C of the Ryugu sample present different SFDs. The middle and bottom parts show the SFDs of only dolomites and breunnerites (Mg- and Fe-rich). We see that chamber A is richer in dolomites, while chamber C has considerably more breunnerites. Both carbonates present different SFDs, leading to deviations in the SFDs of both chambers at larger equivalent diameters, where breunnerites dominate. We discuss possible origins of this difference in Section 4.

3.4. Relative Abundances

Determining absolute carbonate abundances in the samples is highly challenging as we have numerous repeated observations under different geometries and no means to reliably calculate the total surface area searched. Instead, Figure 8 shows the relative abundance of different carbonates in terms of pixel area for Ryugu (chambers A and C, and in total) and Benu (derived using MicrOmega observations here and using OVIRS data in H. H. Kaplan et al. 2020). We only consider grains below 256 pixels in size, excluding the two largest sized bins in Figure 4 to reduce the sampling bias and increase comparability with Benu.

Among the Ryugu samples, we note a difference in the dolomite–breunnerite ratio (considering both Mg- and Fe-breunnerite) between chambers A and C across all carbonate size ranges where both species are present. Chamber A has a consistently higher dolomite–breunnerite ratio as chamber C contains considerably more breunnerite, both regarding the total pixel area (Figure 8) and the number of unique grains (Figures 4 and 7). Regarding the latter, we find a dolomite ratio of 1.8:1 and a breunnerite ratio of 1:2 between chambers A and C. This is particularly noteworthy as the ratio of material analyzed from each chamber is about 1.5:1 A to C in terms of mass. Thus, chamber A presents a small excess in dolomite, while chamber C presents a significant excess in breunnerite. A similar discrepancy in the dolomite–breunnerite distributions between the chambers is apparent in D. Loizeau et al. (2023).

Regarding the total Ryugu sample, we find a dolomite–breunnerite ratio of approximately 1:1 in terms of pixel area. This is strikingly similar to the ratio found in the Benu

samples. Indeed, in this aspect, the difference between chambers A and C of the Ryugu sample is larger than that between the two asteroids. A difference between the asteroids is the relative fraction of Fe-rich breunnerite, of which we identify more in Ryugu than in Bennu.

On the other hand, Figure 8 shows that the carbonate abundances identified with MicrOmega in Bennu do not match the remote-sensing characterization by H. H. Kaplan et al. (2020) using OVIRS. In particular, we did not identify any magnesite and a significantly smaller fraction of calcites. While MicrOmega and OVIRS investigate different size scales (micro- to millimeter versus meter), this strong discrepancy is unexpected and warrants further investigation. To investigate a systematic origin, we applied our χ^2 comparison on the OVIRS spectra (provided by H. Kaplan), yielding a similar, calcite-dominated result. We further note that the difference in the distributions is not consistent with a systematic wavelength shift: calcite and magnesite present band minima at larger and smaller wavelengths, respectively, than dolomite and Mg-breunnerite, meaning that the species abundances cannot be reconciled with a constant shift in wavelength. The origin of this discrepancy between the remote-sensing and laboratory size-scale observations remains an open question.

3.5. Zoning

We inspected all carbonate grains in Ryugu and Bennu for zoning, i.e., zones of different composition within an inclusion. We identified a single case where the spectral difference between the zones was sufficiently convincing upon visual inspection: particle C0181 of the Ryugu samples, which shows increasing Fe content toward the grain centers (refer to left part of Figure 3). Furthermore, dolomite-like signatures are detected toward the edges or in shadowed regions, though the spectral match with the dolomite reference is less convincing regarding the band minima and may instead represent low-SNR breunnerite detections. All other grains were homogeneous within the compositional resolution provided by our reference spectra, in agreement with our previous work (D. Loizeau et al. 2023). In particular, we did not find any dolomite–breunnerite mixture grains.

3.6. Neighboring Grains

In addition to zoning, we also searched for multiple carbonate grains of present on individual particles of Bennu or Ryugu, under the assumption that they initially formed in close vicinity on their parent body. In Ryugu samples, where we identify carbonates on 107 particles, we find 11 particles with two or more dolomite grains and three particles with two breunnerite grains. On Bennu, visual inspection of the aggregate samples yielded six particles with one or more dolomites, and one particle with two breunnerites.

Regarding co-occurrence of different species, for Ryugu, as reported in D. Loizeau et al. (2023), we identify one particle (C0041) which has a large breunnerite grain on one side and a smaller dolomite grain on the opposite side. For Bennu, we similarly found one particle where dolomite and Mg-breunnerite may coincide, though the Mg-breunnerite grain is on the edge of the grain and thus slightly out of focus in the MicrOmega measurements (middle part of Figure 3), leaving some uncertainty in the characterization. Given the large number of search material, this rarity of co-occurrence of both species is striking.

As for zoning, we conclude that dolomites and breunnerites grains larger than $\sim 50 \mu\text{m}$ in equivalent diameter generally formed spatially separated on Ryugu and Bennu on $100 \mu\text{m}$ to millimeter size scales.

3.7. Surrounding Matrix

Carbonates in Ryugu are intimate mixtures with the surrounding matrix rich in phyllosilicates, as evidenced by the $2.7 \mu\text{m}$ absorption present in the ROI spectra (C. Pilorget et al. 2022; D. Loizeau et al. 2023). In Figure 6(b), we see that this absorption is also present in carbonates from Bennu. However, the absorption profiles differ significantly for both dolomite and breunnerite grains between the two asteroids. Carbonate grains on Bennu show a more profound absorption toward $3 \mu\text{m}$. In addition, the breunnerite grains show a diminished reflectance ($\sim 4\%$ instead of 7% at $1.4 \mu\text{m}$). We confirmed these band profiles with FTIR measurements, which did not indicate the presence of minerals beside carbonates and phyllosilicates, as shown in Appendix A. This absorption is thus still consistent with mixtures of a phyllosilicate-rich matrix and carbonates, though possibly with a contribution from interlayer water in the phyllosilicates (impact on spectrum comparable to that shown in Figure 1 in T. Le Pivert-Jolivet et al. 2025) or with different matrix component compositions with respect to Ryugu (e.g., different saponite/serpentine ratios, refer to Figure A1 in S. Rubino et al. 2020). We note that about 10% of Bennu carbonate grains show a sharper $2.7 \mu\text{m}$ absorption similar to that in Ryugu. Among these 10%, we did not observe a compositional trend in the carbonates.

We further use the band positions and shapes as indicators of the Mg/Fe ratio of the phyllosilicates in the surrounding matrix. On the left-hand side of Figure 6(b), we note that the phyllosilicates surrounding calcites in Ryugu and Bennu present an asymmetric absorption profile typical of a contribution around $2.85 \mu\text{m}$ and the presence of Fe-rich phyllosilicates. On the other hand, we observe no significant difference between the phyllosilicates surrounding dolomites and breunnerites in Ryugu, neither of which shows a clear $2.85 \mu\text{m}$ absorption. The $2.7 \mu\text{m}$ absorptions in Bennu are challenging to interpret given the strong absorption around $3 \mu\text{m}$.

4. Discussion

In this section, we evaluate the main MicrOmega results with respect to their implications for carbonate precipitation and aqueous alteration in the parent bodies of Ryugu and Bennu. We note that, given the resolution of the MicrOmega instrument, we consider the conclusions we draw to apply to Ryugu, Bennu, and their parent bodies in the $10\text{--}100 \mu\text{m}$ size scales. At smaller scales, local variability in the alteration environment may lead to different patterns.

4.1. Convergent Carbonate Precipitation Pathways in Ryugu and Bennu Parent Bodies

The MicrOmega measurements of the returned samples reveal that aqueous alteration on Ryugu and Bennu led to largely similar carbonate assemblages. On both asteroids, dolomite and breunnerite are the dominant carbonate phases, with calcite only present in minor amounts (Figures 4 and 5). Overall, the carbonate assemblages we observe resemble those found in CI chondrites in terms of species, relative abundances, and relative size distributions (Section 3.1 to

3.4; K. Fredriksson & J. F. Kerridge 1988; M. Endress & A. Bischoff 1996) and previous studies of Ryugu (W. Fujiya et al. 2023; D. Loizeau et al. 2023; A. Yamaguchi et al. 2023; N. T. Kita et al. 2024) and Bennu (D. S. Lauretta et al. 2024). We further show here that the mean compositions of dolomite and breunnerite in the two bodies match closely (Figure 6(b)), as do their relative abundances (Figure 8). Finally, both Ryugu and Bennu carbonate grains lack zoning detectable at the MicrOmega pixel scale ($22.5 \mu\text{m pixel}^{-1}$; Section 3.5), and dolomite and breunnerite generally do not coincide on individual particles (Section 3.6).

Nevertheless, subtle differences in the carbonate assemblages of both asteroids do exist. These include the relative ratios of Mg-rich to Fe-rich breunnerite (Figure 8), variations in the associated phyllosilicate absorption near $2.7 \mu\text{m}$ (Figure 6(b)), and the remote observation of decimeter-sized carbonate veins on Bennu (H. H. Kaplan et al. 2020) but not on Ryugu (K. Kitazato et al. 2019). These suggest localized variations in the alteration environment or subsequent geological evolution, but they do not fundamentally alter the conclusion of broadly convergent carbonate formation pathways.

This convergence in carbonate formation is notable given that, while largely similar, Ryugu and Bennu do present differences in bulk isotopic compositions (H, N, O), refractory element abundances, and total carbon content (E. Nakamura et al. 2022; H. Naraoka et al. 2023; T. Yokoyama et al. 2023; D. S. Lauretta et al. 2024). These underlying differences point to different formation environments or slightly varied accreted materials. The similarity in the resulting carbonates therefore suggests that the physicochemical factors governing carbonate precipitation during aqueous alteration were either similar on both parent bodies or that carbonate precipitation in low-temperature alteration environments leads to only a limited number of stable endpoints.

4.2. Local Water–Rock Ratio Heterogeneity Imposes Spatial Species Separation

A second main result from our analysis is the general spatial separation of dolomite and breunnerite observed in both Ryugu and Bennu (Section 3.6) on $100 \mu\text{m}$ to millimeter spatial scales. While exceptions occur at smaller scales (e.g., A. Yamaguchi et al. 2023, their Figure S6e, breunnerite in contact with dolomite, and T. J. McCoy et al. 2025, Figure 1b, breunnerite inclusion in dolomite), dolomites and breunnerites larger than $\sim 50 \mu\text{m}$ are generally not found in close vicinity. Similar spatial separation has also been noted in CI chondrites (K. Fredriksson & J. F. Kerridge 1988; M. Endress & A. Bischoff 1996).

This spatial separation has important physicochemical implications. While local factors (cation availability, temperature, water–rock ratio (W/R)) typically favor only one carbonate species at a time, evolving parent body conditions should produce locally mixed carbonates over time. The observed separation of dolomite and breunnerite implies that a spatially heterogeneous factor imposed local trends in the carbonate formation at size scales of $10\text{--}100 \mu\text{m}$ during their precipitation.

Early carbonate formation in parent bodies is triggered by supersaturation conditions in the alteration fluid (R. E. Grimm & H. Y. Mcsween 1989; M. Endress & A. Bischoff 1996; A. J. Brearley 2006; A. Morlok et al. 2006). Ca^{2+} is available early due to the rapid dissolution of calcium-bearing minerals

(e.g., calcium-rich material within chondrules, anorthite, calcium-aluminum-rich inclusions (CAIs)) during the initial stages of aqueous alteration (S. De Leuw et al. 2010). As a minor element, Ca^{2+} is likely heterogeneously distributed in the parent body over the analysis size scale of $10\text{--}100 \mu\text{m}$, as it is leached from Ca-silicates in minor accretion components like chondrules and CAI. Under the assumption of limited fluid circulation, supported by the observation of lithologies with varying W/R (e.g., T. Nakamura et al. 2023) and a heterogeneous distribution of secondary minerals over the Ryugu samples (T. Yokoyama et al. 2025), this spatial heterogeneity likely persisted over time. Therefore, in principle, dolomite–breunnerite separation could be explained by the different local availability of Ca^{2+} . However, while this would explain regions devoid of dolomite (in cases of low Ca^{2+} concentration), breunnerite should still precipitate in regions with dolomite (in cases of high Ca^{2+} concentration), as Mg^{2+} and Fe^{2+} are abundantly available. This is incompatible with MicrOmega observations.

An alternative hypothesis on the cause of the dolomite–breunnerite separation could involve local temperature variations. However, thermal evolution models for parent bodies generally show a temporal progression of heating and cooling throughout the interior (T. Nakamura et al. 2023). This would more likely produce zoned crystals or temporal overgrowths of different carbonate species, rather than general spatial separation.

Instead, we propose that the deciding factor was a locally heterogeneous W/R, which governed the concentration of ions available for precipitation (T. Nakamura et al. 2023). This scenario is based on the premise that the limited and possibly unevenly distributed fluid was progressively consumed by reactions with the rock. The local W/R would therefore dictate both the extent of element leaching from precursor minerals and the dilution of the resulting ions in solution, leading to distinct chemical pathways in different regions of the parent body. However, we note that this numeric model and our scenario as a whole do not consider kinetics and the interplay of different alteration factors in their full complexity.

At low W/R, the high concentration of readily leached Ca^{2+} favors initial precipitation of calcite. In regions with low initial W/R, alteration ceases and a lithology with few alteration products remains, as observed in both Ryugu and Bennu samples (W. Fujiya et al. 2023; D. S. Lauretta et al. 2024). In regions with intermittent initial W/R, the dissolution of Mg-Fe silicates (e.g., olivine, pyroxene) provides Mg^{2+} and Fe^{2+} in the fluid, raising the local $\text{Mg}^{2+}/\text{Ca}^{2+}$ sufficiently to favor dolomite precipitation. The exact precipitation scenario of dolomite in low-temperature environments is an open question (H. S. Santos et al. 2023), including the role of existing calcite crystals as possible nucleation sites for dolomite growth. The low abundance of calcite suggests that the majority of early-forming crystals is either dissolved or replaced during progressing alteration.

Finally, local volumes presenting high W/R do not see the precipitation of dolomite, as Ca^{2+} is sufficiently diluted in the fluid and supersaturation is not reached. Experiments (at temperatures above 100°C) show that dolomite precipitation kinetics are slowed at $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios above 5 (H. S. Santos et al. 2023). Higher W/R leads to more rapid leaching of Mg^{2+} , leading to $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios that favor breunnerite precipitation. In this scenario, a heterogeneous W/R distribution across the parent body, established early and maintained by limited

large-scale fluid mixing, would naturally lead to the observed spatial separation. This picture is consistent with the observed decrease in $\delta^{18}\text{O}$ isotopes of breunnerites compared to dolomites in Ryugu (N. T. Kita et al. 2024). However, as the authors note, these $\delta^{18}\text{O}$ isotope differences are also consistent with an increased precipitation temperature of breunnerites.

An open question is the final sink of Ca^{2+} in regions of high W/R, where it initially does not get incorporated into dolomite. As carbonates are the main hosts of Ca in Ryugu and CI chondrites (E. Nakamura et al. 2022), the most likely sink is a late-stage carbonate formation, such as later generations of calcites or dolomites, or as impurities in breunnerite crystals. These late-stage carbonates could be smaller than the MicrOmega pixel resolution and thus have evaded detection here, or be highly localized in, e.g., impact fractures, leading to the formation of veins. In CM chondrites, where the most aqueously altered specimens also present a lack of dolomites, the dissolution of dolomites is accompanied by a late-stage formation of calcites (S. De Leuw et al. 2010). Another sink for Ca^{2+} is Ca-phosphate apatite; however, the scarcity of phosphorus relative to calcium suggests it is a minor one (E. Nakamura et al. 2022). Nevertheless, the presence of both apatite and hydrated ammonium-magnesium-phosphorus (HAMP) grains in Ryugu samples (E. Nakamura et al. 2022; C. Pilorget et al. 2024) show that Ca^{2+} concentrations varied locally, either spatially or over time, as apatites require Ca^{2+} for their formation while HAMPs require a fluid depleted in Ca^{2+} (C. Pilorget et al. 2024).

T. Matsumoto et al. (2024) and T. J. McCoy et al. (2025) both describe late-stage carbonate formation in highly alkaline brines due to freeze-out or evaporation of the alteration fluid, leading to the formation of sodium carbonates. In a similar manner, this late-stage evolution might lead to the formation of calcite along veins from impact fractures, as suggested to be present on Bennu (H. H. Kaplan et al. 2020).

4.3. Chambers A and C Sample Different Parent Body Lithologies in Varying Proportions

A striking outcome of our analysis, specific to Ryugu, is the significant difference in the dolomite–breunnerite ratio between Chambers A and C (Figure 8). Across the full range of measured inclusion sizes, breunnerite is more common in Chamber C than in Chamber A, while dolomite is more abundant in Chamber A (Figures 4 and 7). Notably, 8 of the 10 largest carbonate grains identified, all Mg-breunnerites, are located in the Chamber C samples.

We consider this difference to be intrinsic to the sampled material, rather than an artifact introduced during or post sample collection, given that the abundance inversion persists across all size ranges. Furthermore, in D. Loizeau et al. (2023), we show that the *Hayabusa2* sampling process of Ryugu did not fragment carbonate grains above $50\text{ }\mu\text{m}$ in equivalent diameter, based on the comparison of loose carbonate grains observed in the bulk sample and grains embedded into larger particles.

While Ryugu at meter-scale appears as a homogeneous mixture of remnants of its parent body (e.g., K. Kitazato et al. 2019; L. Riu et al. 2021), we thus conclude that it presents heterogeneity in mineral abundances, at least at the spatial scale of the *Hayabusa2* sampling. As the two chambers sample surface and subsurface material, we considered whether the heterogeneity derives from a processing of material on

Ryugu’s surface, e.g., space weathering (solar irradiation and micro-meteorite bombardment; T. Le Pivert-Jolivet et al. 2023) or elevated surface temperatures during perihelion passages of Ryugu (P. Michel & M. Delbo 2010). Both processes affect the surface uniformly; however, it is unclear how they would preferentially affect breunnerites over dolomites, and the presence of low-temperature alteration products suggests that Ryugu’s surface did not undergo significant heating (A. Yamaguchi et al. 2023).

Instead, we propose that chambers A and C sample different mixtures of parent body lithologies that experienced different dominant alteration conditions. Chamber C sampled material richer in a breunnerite-dominant lithology (indicative of higher W/R alteration), whereas chamber A sampled material richer in a dolomite-dominant lithology (intermediate W/R). This implies that neither chamber, individually, is fully representative of the bulk Ryugu material collected. The heterogeneity reinforces the concept of limited large-scale mixing during alteration on the parent body. Interestingly, the combined A + C sample approaches the relative carbonate abundances seen in the Bennu bulk sample (Figure 8), though the significance of this is uncertain given the sample mass difference and potential heterogeneity on Bennu itself.

5. Conclusion

We performed a detailed characterization of carbonate minerals in the returned samples from asteroids Ryugu and Bennu using the MicrOmega near-infrared hyperspectral microscope. Our analysis revealed remarkably similar carbonate populations on both asteroids, dominated by dolomite and breunnerite, with only minor occurrences of calcite. The mean spectral properties and relative abundances of these phases are comparable between the two bodies, suggesting convergent alteration pathways despite known differences in their bulk compositions and isotopic signatures. These assemblages closely resemble those found in CI chondrites.

A key finding is the clear spatial separation of dolomite and breunnerite grains observed consistently in samples from both asteroids at the analysis size scale of $10\text{--}100\text{ }\mu\text{m}$. We interpret this separation as evidence for the guiding influence of local W/R heterogeneity during aqueous alteration. Our proposed scenario suggests that intermediate W/R ratios favored dolomite precipitation, while high local W/R ratios suppressed dolomite formation and instead promoted the precipitation of breunnerite, leading to distinct formation zones. This W/R-driven mechanism provides a coherent explanation for the observed spatial patterns and aligns with isotopic constraints from the literature.

Furthermore, we identify significant differences in the dolomite–breunnerite ratio between Ryugu’s chamber A (surface) and chamber C (subsurface) samples. Chamber C exhibits a higher proportion of breunnerite across all investigated size ranges. This indicates that Ryugu possesses mineralogical heterogeneity at the sampling scale, possibly reflecting the mixing of distinct parent body lithologies that experienced different dominant W/R alteration regimes. Consequently, neither chamber’s sample set alone can be considered fully representative of the bulk returned material.

Taken together, our results highlight the critical role of local physicochemical conditions, particularly the W/R ratio, in governing carbonate speciation during aqueous alteration on primitive asteroids. Discrepancies with remote-sensing data,

particularly regarding calcite abundance on Benu, underscore the importance of multiscale analysis and warrant further investigation. Continued laboratory analysis of these unique samples, especially correlative studies at submicron scale, will further refine our understanding of the earliest fluid-driven processes that shaped planetesimals in the solar system.

Acknowledgments

We thank H. Kaplan for making the Fe-breunnerite reference spectrum and the OVIRS data available to us for this analysis. We further thank Z. Dionnet for providing the organics signature from the Ryugu sample.

Appendix A

Comparison of MicrOmega and FTIR Characterization

We use the FTIR spectrometer at the ISAS Curation Facility to verify the carbonate characterization achieved with MicrOmega for select ROIs in the bulk samples of Benu. Figure 9 shows the FTIR and MicrOmega spectra of two ROIs identified with MicrOmega in the bulk sample of Benu. Note that the FTIR spot and the identified ROI cover similar but not identical areas. Between 3.0 and 3.6 μm , we can compare the FTIR and MicrOmega measurements and the reference spectra that yields the closest match. For ROI 1, characterized as dolomite-like, the FTIR and reference match well in the overall shape, while the MicrOmega spectrum shows a less profound band at smaller wavelengths. A weaker $\nu_3 + \nu_2 + \nu_4$ contribution with respect to the reference spectra is a common occurrence in both Ryugu and Benu carbonate spectra, and we attribute this to crystal lattice impurities or effects due to the intimate mixture of carbonates with the surrounding matrix. For wavelengths longer than 3.6 μm , we show the FTIR spectrum and vibrational modes of magnesite and dolomite determined by J. L. Bishop et al. (2021) as vertical

lines. The frequencies of vibrational modes are characteristic of mineral composition, though their relative strengths are complex functions of the crystal structure. In the FTIR spectrum of ROI 1, we observe in particular the stretching vibrations ν_3 and ν'_3 , as well as its combination bands with the bending vibrations ν_1 and ν_4 . The combination of ν_3 and ν'_3 in addition to a contribution at 6.6 μm gives rise to a strong peak around 6.6 μm . While the ν_3 modes of magnesite and dolomite are too close together to be distinguished here, the ν'_3 mode and in particular the $\nu_3 + \nu_4$ combination band show strong tendencies toward a dolomite-like composition. The feature around 10 μm further shows significant contribution from the surrounding phyllosilicates in the matrix.

ROI 2 characterized as breunnerite-like, shows excellent agreement between the FTIR, MicrOmega, and the Mg-breunnerite reference spectra. We further show the references of magnesite and Fe-breunnerite in Figure 9 to highlight the small yet appreciable shift in wavelength of these species. At longer wavelengths, the FTIR spectrum is dominated by a feature around 6.6 μm , in part due to the ν_3 and ν'_3 modes of the grain. The low contribution around 10 μm underlines that only little matrix material is included in the FTIR spot. As for ROI 1, we base the MIR characterization principally on the ν_3 and ν'_3 modes and the $\nu_3 + \nu_4$ combination band. We observe a shift toward lower wavelengths (toward magnesite reference) as compared to ROI 1, consistent with an increase in Mg and the breunnerite-like characterization based on the MicrOmega spectrum.

In Figure 10, we show the spectra of several carbonate grains identified in the bulk sample of Benu. As in Figure 9, we compare MicrOmega and FTIR measurements. For several grains, we measured multiple FTIR spots to assess the spectral variability across the grain. As before, we conclude that the FTIR analysis supports the characterization carried out with MicrOmega.

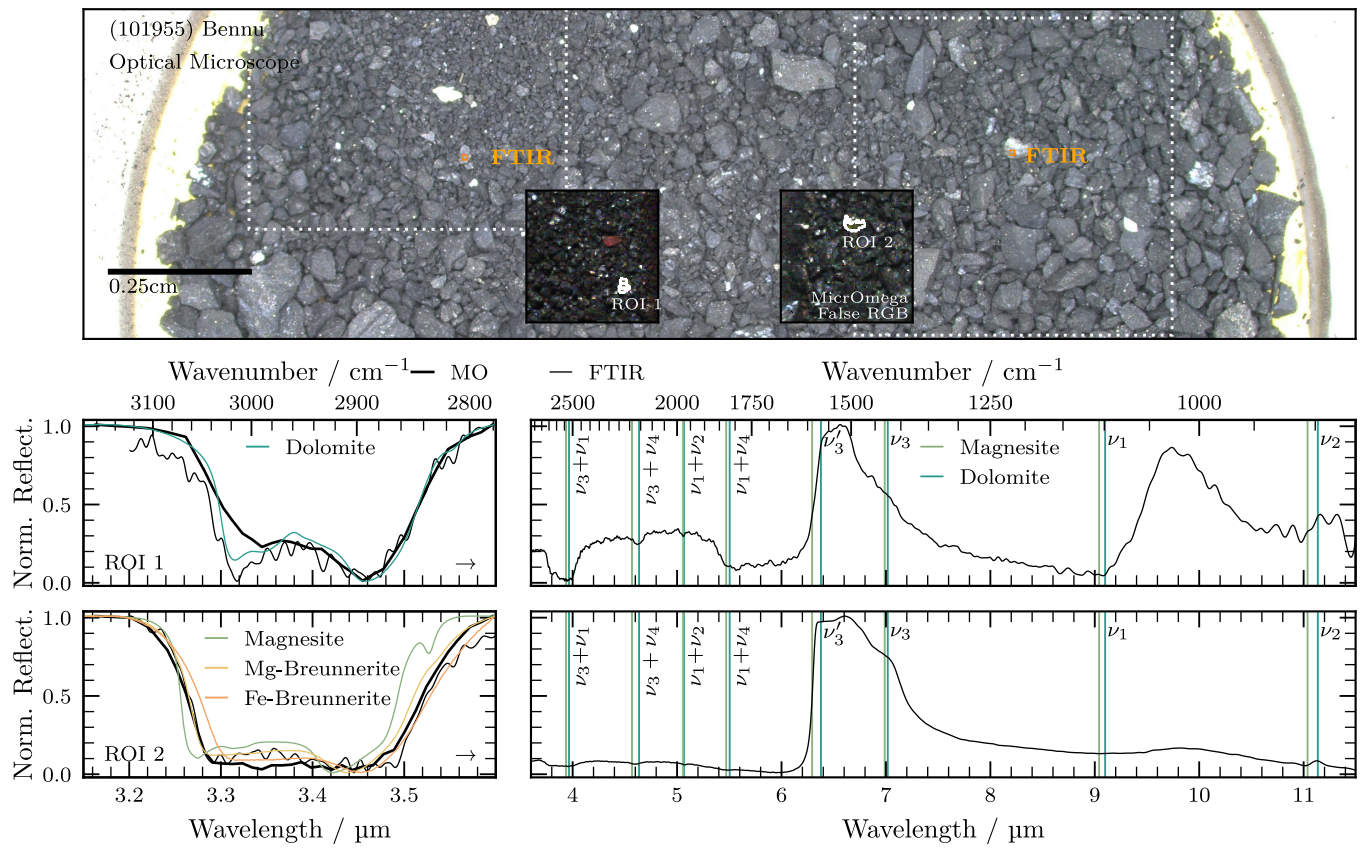


Figure 9. Identification of dolomite-like and breunnerite-like ROIs in bulk sample ORX-29000 of Benu. Top: optical microscope image of the sample. White, dotted rectangles give the MicroOmega footprint, approximately 0.56×0.57 cm. Orange squares indicate the spots that were analyzed with the FTIR (spot size of $100 \mu\text{m}$). The insets show false-RGB images of two MicroOmega measurements. The white contours labeled ROI 1 and ROI 2 show carbonate-rich areas that were automatically identified and characterized as dolomite-like and breunnerite-like respectively. Bottom: the MicroOmega (MO) and FTIR spectra of the two ROIs are shown for wavelengths below $3.6 \mu\text{m}$ in the left panel. For each ROI, we show the best-matching reference spectra (dolomite and Mg-breunnerite). For ROI 2, magnesite and Fe-breunnerite are further shown. For wavelengths above $3.6 \mu\text{m}$ (right panel), we depict the continuation of the FTIR spectra and reference vibrational modes of magnesite and dolomite from J. L. Bishop et al. (2021).

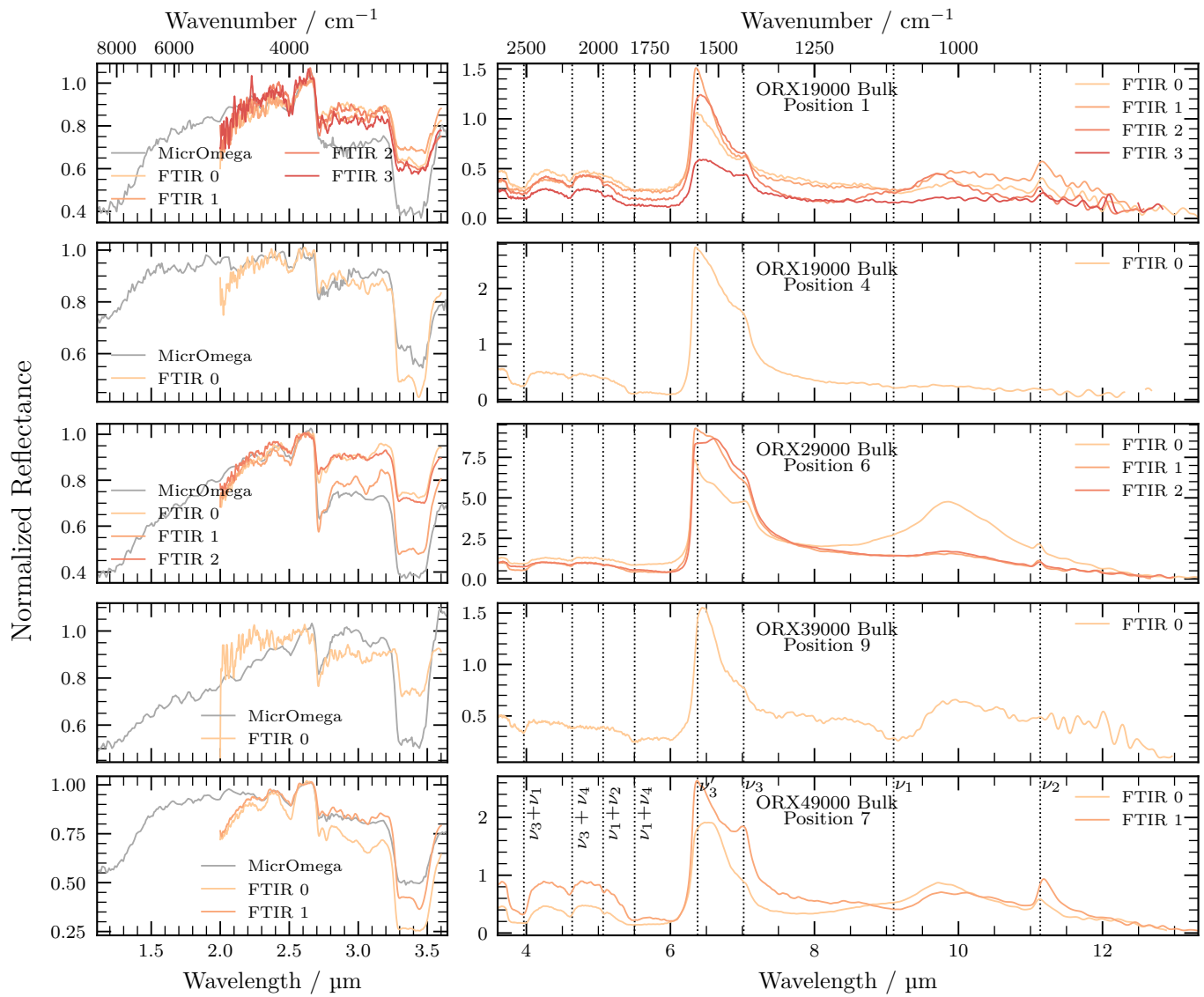


Figure 10. As for Figure 9, we show the FTIR and MicrOmega spectra of five different carbonate grains in the bulk sample of Benuu.

Appendix B

Table of Carbonate Detections in Ryugu and Benuu Samples

Table 2 summarizes the format of the table of carbonate detections in Ryugu and Benuu samples identified with

MicrOmega. The full table is provided in a machine-readable format. Sample IDs correspond to the JAXA curation designations for each sample.¹⁷

¹⁷ More information on each specific sample can be found at <https://darts.isas.jaxa.jp/app/curation/ryugu/> and <https://darts.isas.jaxa.jp/app/curation/benuu/>.

Table 2
Summary of Carbonate Detections in Ryugu and Benu Samples Identified with MicrOmega

Column	Unit	Description
asteroid	...	Asteroid that this sample belongs to. Either “ryugu” or “benu.”
sample_name	...	Name of sample in JAXA Curation catalog.
N_Calcite	...	Number of carbonate grains associated to calcite in sample.
N_Dolomite	...	Number of carbonate grains associated to dolomite in sample.
N_Mg-Breunnerite	...	Number of carbonate grains associated to Mg-breunnerite in sample.
N_Fe-Breunnerite	...	Number of carbonate grains associated to Fe-breunnerite in sample.
N_Mg-Siderite	...	Number of carbonate grains associated to Mg-siderite in sample.

Note. The table lists the sample ID, the number of identified carbonate ROIs, the total carbonate-bearing area across all ROIs, and the dominant carbonate composition identified in each sample.

(This table is available in its entirety in machine-readable form in the [online article](#).)

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