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In situ investigation of an organic micro-globule and its mineralogical context within a Ryugu “sand” grain

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113

114 **ABSTRACT**

115 The Hayabusa2 mission from the Japan Aerospace Exploration Agency (JAXA) returned to
116 Earth samples of carbonaceous asteroid (162173) Ryugu. This mission offers a unique
117 opportunity to investigate in the laboratory samples from a C-type asteroid, without physical or
118 chemical alteration by the terrestrial atmosphere. Here, we report on an investigation of the
119 mineralogy and the organo-chemistry of Hayabusa2 samples using a combination of micro- and
120 nano- infrared spectroscopy. Particles investigated with conventional FTIR spectroscopy have
121 spectra dominated by phyllosilicate related absorption, as observed for samples of CI-
122 chondrites, selected ungrouped carbonaceous chondrites, and selected hydrated
123 micrometeorites. Ryugu samples show smaller sulfates related absorption than CI-chondrites.
124 Our samples that were only briefly exposed to the Earth atmosphere show absorptions related
125 to molecular water, revealing fast terrestrial contamination of the spectral signature at 3- μ m.
126 Overall, our FTIR data are in agreement with other work done on Ryugu samples, revealing a
127 low degree of mineralogical variability across Ryugu samples. AFM-IR mapping of the grains
128 show the presence of a micrometer-sized organic globule in one of our analyzed grains. The
129 AFM-IR spectra obtained on this globule is similar to IR spectra obtained on IOM suggesting
130 that it is constituted of refractory organic matter. This globule may host silicate in its interior,
131 with a different mineralogy than bulk Ryugu phyllosilicate. The shape, presence of peculiar
132 silicate, and the nature of organic constituting the globule point toward a pre-accretionary origin
133 of this globule and that at least part of Ryugu organics were inherited from the protosolar
134 nebulae or the interstellar media. Altogether, our results further the similarities of Ryugu
135 samples to CI-chondrites.

136 Keywords: Ryugu, Organic globule, Atomic Force Microscopy-Infrared spectroscopy (AFM-
137 IR), NanoIR3s

138

139 INTRODUCTION

140 In late 2020, samples of the dark asteroid Ryugu (Cb spectral type) were returned to Earth
141 after a >5 billions of kilometres trip made by the Hayabusa2 spacecraft, built by the Japan
142 Aerospace Exploration Agency (JAXA). Early investigations of the samples revealed that
143 Ryugu particles share many characteristics of chemically primitive but also highly aqueously
144 altered CI-group of carbonaceous chondrites (Yokoyama et al., 2022; T. Nakamura et al., 2022;
145 Noguchi et al., 2022; Yada et al., 2022). Therefore, the Hayabusa2 samples offer the unique
146 opportunity to investigate exceptionally fresh CI material. Hayabusa2 samples were protected
147 from interaction with the oxidizing terrestrial atmosphere from capsule recovery to curation
148 process, and they were also protected from thermal and mechanical modification during
149 atmospheric entry.

150 The relation to CI-meteorites was drawn from chemical, mineralogical and isotopic
151 similarities (Yokoyama et al., 2022; T. Nakamura et al., 2022; Yada et al., 2022; Noguchi et
152 al., 2022; Naraoka et al. 2023, Yabuta et al. 2023, Dartois et al. 2023). CI chondrites show an
153 interplay of ingredients down to the sub-micrometer scale (Tomeoka and Buseck, 1988, Le
154 Guillou et al., 2014), which requires analytical techniques with sub micrometer spatial
155 resolution to separate their composition and understand their petrographic relations. Infrared
156 spectroscopy (IR) is an effective method and a non-destructive technique for molecular-atomic
157 scale vibrations of organic and inorganic compounds in extra-terrestrial materials (Kebukawa
158 et al., 2011; Orthous-Daunay et al., 2013; Beck et al., 2014; Phan et al., 2021). However,
159 conventional IR spectrometers use mirror-based optics to focus the beam on the sample and
160 thus the spatial resolution is limited by diffraction. This IR diffraction limitation can be
161 overcome by using AFM-IR (Atomic Force Microscopy-Infrared Spectroscopy), based on the
162 combination of infrared spectroscopy and atomic force microscopy to efficiently distinguish
163 spectral signatures of the different constituents (Dazzi & Prater, 2017; Mathurin et al., 2019).
164 This technique has been successfully applied to extra-terrestrial materials (Mathurin et al.,
165 2019; 2022; Kebukawa et al., 2018; Yesiltas et al., 2021; Phan et al., 2022; Noguchi et al., 2022;
166 Yabuta et al., 2023; Dartois et al., 2023).

167 Here we report our work to understand the mineralogy and petrography of fine-grained
168 Ryugu samples as part of the Preliminary Examination Team (Noguchi et al., 2023) using
169 photothermal AFM-IR spectroscopy. Across our investigations we gained insights into the
170 mineralogy and chemistry of phyllosilicates, and we report on the discovery of a “large”
171 organic-dominated globule.

172 MATERIALS AND METHODS

173 Fine-grained Ryugu C0105 samples

174 After their arrival on Earth in December 2020, the Ryugu samples were transported from
175 JAXA's Extraterrestrial Sample Curation Center in Sagamihara, Japan to the Mineralogy and
176 Petrography fine-grain (Sand) initial analysis team at Kyoto University (Noguchi et al., 2023).
177 Two grains of Ryugu from chamber C (C0105-003200401 and C0105-00380010), designated
178 C0105-0032 and -0038 in the following text, were then sent to University Grenoble Alpes for
179 Micro-FTIR, AFM-IR and SEM-EDS analyses.

180 Ryugu fragments were tightly pressed between two diamond windows (type IIa diamond,
181 3 mm diameter and 500 μm thick), generating to thin and flat samples (1-5 μm thick, with a
182 typical area of 50 μm x 50 μm). One of the two windows was removed to avoid interference
183 and to minimize beam intensity loss during transmission mode measurements. This sample
184 preparation significantly reduced scattering artifacts and was well suited for conventional
185 micro-FTIR. These pressed samples were also used for AFM-IR measurements. Typically,
186 meteorite grains were prepared by crushing 10 – 20 μm fragments between two diamond
187 windows, while the Ryugu samples were collected at around 1-5 μm . Before AFM-IR analysis,
188 all samples were analysed using conventional micro-FTIR analysis, in order to select regions
189 of interests (ROI).

190 Methods

191 *Micro-FTIR spectroscopy*

192 The micro-infrared spectra were measured with a Bruker Hyperion 3000 infrared
193 microscope at the Institut de Planétologie et d'Astrophysique de Grenoble (IPAG, Grenoble,
194 France). Spectra were measured in transmission and obtained by putting the diamond window
195 in a custom-made environmental chamber, which expose the sample to secondary vacuum, and
196 elevated temperature if needed (up to 300°C). This procedure enables removal of molecular
197 water that can perturb the IR spectra in the 3- μm range (4000-3000 cm^{-1}), and also around 1630
198 cm^{-1} . Spectra were obtained for areas that are typically 50 μm x 50 μm .

199

200 *Atomic force microscope based infrared spectroscopy (AFM-IR) measurements*

201 AFM-IR analyses were performed on Ryugu samples after the micro-FTIR
202 measurements. IR images and absorption spectra were acquired using a nanoIR3sTM (Bruker)
203 located at IPAG. This system includes an atomic force microscope (AFM) probe, which can

204 scan the sample to generate its topographical image as well as measuring IR absorption by
205 detecting photo-thermal expansion (Dazzi & Prater, 2017). Detailed descriptions of the
206 NanoIR3sTM (Bruker) were provided in previous publications (e.g., Phan et al., 2022, 2023)
207 together with measurement of reference materials. Briefly, the excitation laser source is a
208 Carmina laser (from APE company) that covers a part of the mid-IR range, from 2000 to 700
209 cm⁻¹ with its OPO/DFG (Optical Parametric Oscillator and a Difference Frequency Generation)
210 architecture (APE GmbH, Germany), and infrared light in the 2700 – 4000 cm⁻¹ wavenumber
211 range is supplied by an optical parametric oscillator, Firefly (FF) IR laser (M squared lasers
212 limited, Glasgow, UK). Both contact mode (CM) and tapping IR mode (TM) were used for
213 spectroscopy and imaging measurements. The reference signal (incoming laser intensity) is
214 recorded prior to image and/or spectra collection, and laser alignment optimization is performed
215 before signal acquisition at different wavelengths (or wavenumbers) in the scanned range.

216 AFM-IR images were obtained using the APE laser in TM with a laser power of 8.81-
217 25% of its maximum and a pulse rate at 340 -380 kHz. These analytical conditions were
218 optimized by choosing the lowest laser power that would provide good quality spectra without
219 affecting the sample integrity. It is well known that laser irradiation can alter the structure of
220 macromolecular organics (in particular using highly focused beam like in Raman spectroscopy)
221 and the analytical protocol we used has been constructed and validated in our earlier work on
222 meteorites and coals (Phan et al., 2022; 2023). The images were collected in the range of 2000-
223 700 cm⁻¹ at infrared wavenumbers of 1720 cm⁻¹, 1600 cm⁻¹, 1450 cm⁻¹ and 1000 cm⁻¹, which
224 correspond to the carbonyl (C=O) stretching, sp² aromatic (C=C), methylene (CH₂) bending
225 and/or carbonate and/or NH₄⁺ bending mode, and silicate (Si-O) stretching, respectively.
226 Images were taken through each region of interest (ROI) from each section. In addition, AFM-
227 IR images in the range of 3800-2700 cm⁻¹ were acquired using the Firefly laser in CM, which
228 can be resolved into discrete bands including the stretching of -OH (3600 – 3700 cm⁻¹),
229 asymmetric stretching of CH₃ (2960 cm⁻¹), asymmetric stretching of CH₂ (2930 cm⁻¹),
230 symmetric stretching of CH₃ (2880 cm⁻¹) and symmetric stretching of CH₂ (2860 cm⁻¹) (Beck
231 et al., 2010; Dazzi & Prater, 2017; Jubb et al., 2019; Phan et al., 2022). To better visualize the
232 spatial distribution of different components, composite RGB color images were created by
233 superimposing three different absorption images using the Anasys software. Before overlaying
234 the images, each individual image was realigned to compensate for any small drifts between
235 AFM-IR image recordings. The scan speed of all maps was 0.1 Hz and the scan sizes were from
236 300 × 300 to 500 × 500 points depending the size of ROI.

237 Local AFM-IR spectra were also obtained for two grains, C0105-0032 and C105-0038
238 pressed grains. For C0105-0032, the spectra were acquired in TM using the APE laser, while
239 for C0105-0038, the spectra were acquired in CM using both the APE in the range 2000-700
240 cm^{-1} and the Firefly laser in the range 3800-2700 cm^{-1} . To avoid damaging the samples and
241 obtain high-quality spectra, the incident laser power was kept to 1.22-5.03% of its maximum
242 and the pulse rate was maintained at 240-300 kHz (Phan et al., 2022; 2023). The IR spectra
243 were optimized at a constant laser power level for each wavenumber, with the laser power
244 recorded with an IR sensitive photodetector. Each AFM-IR spectrum was obtained at selected
245 points with a wavenumber spacing of 4 cm^{-1} and we have used co-averages of 3 spectra and 5
246 spectra for the APE and Firefly laser, respectively. For the spectral range of 2000 – 700 cm^{-1} , a
247 gold-coated semi-tap probe (PR-EX-TnIR-A-10, 75 ± 15 kHz, 1-7 N/m) was used to avoid
248 artifact effects due to the silicon IR absorption and allow to work both CM and TM. For the
249 spectral range of 4000 – 2700 cm^{-1} , the images and spectra are acquired in CM with “pure
250 contact” model PR-EX-nIR2-1, a resonant frequency of 13 ± 4 kHz and a spring constant of
251 $0.07 - 0.4 \text{ N m}^{-1}$.

252

253 *Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) measurement*

254 After AFM-IR analysis, the samples were coated with a thin gold (Au) film for
255 observation with a scanning electron microscope in secondary and backscattered electron
256 modes. A JEOL JSM-7000F scanning electron microscope (SEM) equipped with an energy
257 dispersive spectroscopy (EDS) (USA, Inc, Peabody, MA) was used at the Consortium des
258 Moyens Technologiques Communs (CMTC, University Grenoble Alpes, France). EDS maps
259 of carbon (C), oxygen (O), silicate (Si), aluminum (Al), iron (Fe), nickel (Ni) and sulfur (S)
260 were collected at the acceleration voltage of 10kV and the beam current of 30 nA. EDS spectra
261 were also collected to drive more details on the global composition of each section (Supporting
262 Information).

263

264 **RESULTS**

265 **Grain C0105-0032**

266 Using the tapping IR mode (TM), we studied the spatial distribution of organic and
267 mineral infrared signatures throughout the entire surface of the C0105-0032 and C0105-0038.
268 A $5 \mu\text{m} \times 5 \mu\text{m}$ ROI of C0105-0032 was analyzed with a higher spatial resolution of 500×500

269 points (e.g., spatial resolution imaging of ~ 10 nm) (Fig. 1A). AFM-IR images obtained at
270 different wavelengths show the distribution of different vibrational bonds: carbonyl (C=O) (in
271 red, at 1720 cm^{-1}), aromatic (C=C) (in pink, at 1600 cm^{-1}), carbonate (CO_3) or CH_2 bending
272 mode groups (in blue at 1450 cm^{-1}), sulfate (SO_4) (in yellow, at 1100 cm^{-1}), and phyllosilicate
273 (Si-O) (in green, at 1000 cm^{-1}) (Fig. 1B-F). Figure 2B-C shows a color composite RGB map
274 (1720 , 1600 and 1450 cm^{-1} IR intensity) and individual absorption map at 1450 , 1100 and 1000
275 cm^{-1} , together with the locations where full spectra were collected in the $2000 - 700\text{ cm}^{-1}$ range.

276 These maps enable to identify different domains (Fig. 1-2). Overall, the most widespread
277 absorption is the band at around 1000 cm^{-1} , which can be attributed to Si-O stretching in
278 phyllosilicates (green area in Fig. 2B and 2C). This observation agrees with the fact that Ryugu
279 fine-grained samples mineralogy is dominated by phyllosilicates (Noguchi et al., this volume).
280 Isolated blue and violet (Fig. 2B and 2C) areas are also observed in the RGB maps, and are
281 interpreted to be micro to sub- μm sized carbonate grains.

282 Only a few areas are red in Fig 2A can be explained by pure organics. The map obtained
283 at 1720 cm^{-1} , intended to probe the C=O mode, shows a strong correlation to carbonates
284 signatures. Several areas appear yellow in Fig. 2C, meaning that they display particularly strong
285 signatures around 1100 cm^{-1} , which may be interpreted by the presence of sulfate.

286 In order to gain further insights in the constituents of our Ryugu grains we collected an
287 array of more than 100 single-point AFM-IR spectra in the $2000 - 700\text{ cm}^{-1}$ range (in tapping
288 IR mode), that can be compared to μ -FTIR spectra of the grains as well as to reference spectra
289 of possible mineral components (e.g., saponite, dolomite, calcite) and the Orgueil CI chondrite
290 (Phan et al., in prep) (Fig. 2D). We averaged 90 spectra, exhibiting a similar signature (P spectra
291 in Fig. 2D) and compared them to 13 different spectra obtained at locations marked P1-P10 and
292 C1-C3. The average spectra (P) in the green region have a strong and narrow absorption at 1000
293 cm^{-1} , similar to FTIR spectra observations, which are attributed to phyllosilicate (Si-O), and the
294 best spectral analogue to date is a saponite spectra (Beck et al., 2014), with possible contribution
295 from serpentine (Dartois et al., 2023).

296 The C2 and C3 spectra also display strong absorption at 1440 cm^{-1} and 880 cm^{-1} band
297 attributed to carbonate (Fig. 2D). Carbonates were found in mm-sized grains (Nakamura et al.,
298 2023) and smaller isolated or aggregated grains (Yabuta et al., 2023; Dartois et al., 2023) of a
299 few to $\sim 30\text{ }\mu\text{m}$ size. Dolomite is the dominant carbonate in the Ryugu coarse samples (1-8 mm)
300 which were formed by aqueous alteration reactions at low temperature, high pH and water/rock

301 ratios <1 (Nakamura et al., 2023). Porous dolomite and magnetite that occur in some frothy
302 layer are thought have been modified by space weathering processes (Noguchi et al., 2023).

303 Interestingly, spectrum C1 in the redder location in Fig. 2B reveals faint but distinct
304 peaks at 1720 and 1600 cm^{-1} attributed to C=O and C=C present together with the strong peak
305 at 1000 cm^{-1} implying the presence of organic matter associated with Mg-rich phyllosilicate
306 (Fig. 2D). A diffuse organic component within the phyllosilicate matrix may be present in the
307 grain, but in tapping IR mode, these faint organic signatures are generally absent from the AFM-
308 IR spectra (Fig. 2D-E) (Phan et al., 2022; 2023). In addition, spectra obtained at the P1- P10
309 that have different absorption at 1100 and 860 cm^{-1} , probably due to different types of sulfate
310 and/or silicate (Madejová et al., 2017) (Fig. 2E).

311

312 **Grain C0105-0038**

313 The grain of C0105-0038 (Fig. 3A) was fractured into several smaller grains, then crushed
314 between two diamond windows (Fig. 3B), and the micro-FTIR spectra measured are displayed
315 in Fig. 3C. The Ryugu bulk samples infrared transmission we obtained appear similar to those
316 measured for CI chondrites such as Orgueil or Ivuna (Nakamura et al., 2023; Yokoyama et al.,
317 2022). A band at 3690 cm^{-1} is observed, corresponding to an -OH stretching mode in a Mg-rich
318 phyllosilicate. This band is weak in Fig. 3C since the pressed sample was particularly thin. In
319 the 3000 – 2800 cm^{-1} range several bands are observed with peaks at 2952, 2925, 2873 and
320 2857 cm^{-1} . These peaks are attributed to the asymmetric and symmetric stretching modes of the
321 CH_3 , CH_2 and CH groups, related to complex interactions between overtones and fundamental
322 vibrations. Spectra obtained in all sections reveal the presence of a sharp feature at 1000 cm^{-1}
323 that can be attributed to phyllosilicate. Unlike the other samples, grain 4 (G4) presents a strong
324 signature at 1440 and 880 cm^{-1} that can be attributed to carbonate bending and in-plane mode,
325 respectively (Phan et al., 2022).

326 A $20 \times 20 \mu\text{m}^2$ area of grain 3 (G3) (red spectra in Fig. 3) was imaged in AFM-IR tapping
327 mode (Fig. 4). Different from C0105-0032 grain, this grain does not display a signature around
328 1100 cm^{-1} , meaning that sulfate is absent. Similarly, AFM-IR intensity was measured at 1720,
329 1450 and 1000 cm^{-1} , corresponding to carbonyl (C=O), carbonate (CO_3) and phyllosilicate (Si-
330 O) (Fig. 4C-E). These maps and the associated RGB composite map we produced (Fig. 4F)
331 show an intense signal at 1000 cm^{-1} throughout the sample (green) that can be attributed to
332 phyllosilicate. This map also shows grains with strong AFM-IR intensity in all three

333 wavelengths (bright green in the RGB composite), that are interpreted to be phases with high
334 refractive index (Fe-oxides, metal and sulfides) which was confirmed by SEM imaging and is
335 corroborated by other studies (Dartois et al., 2023). Several small grains appear in blue in this
336 map, and are interpreted to be small carbonate grains.

337 Interestingly, a small circular area in the right bottom corner of the map shows a strong
338 signature at 1720 cm^{-1} (Fig. 4C and 4F) corresponding to C=O in organic matter. An array of
339 50 spectra was collected in the green zone (Si-O array) and one spectrum (A1) was obtained on
340 the “red globule” in the RGB composite map (Fig. 4B and 4F). In addition to the organic
341 globule, organic signatures are present as a diffuse component within the phyllosilicate
342 (Average Si-O spectra), as evidenced from the presence of aromatic (C=C) band at 1600 cm^{-1}
343 (Fig. 4G) and a small feature around 1720 cm^{-1} . In the average spectra of “green” areas, a broad
344 band around 1000 cm^{-1} is present, similar to results obtained from grain C0105-0032, and
345 attributed to Si-O in phyllosilicates. Note that in the phyllosilicate-rich areas, the water bending
346 mode at 1630 cm^{-1} can contribute to some extent to this spectral region. While Ryugu grains
347 analyzed following an air-shutoff procedure do not show strong evidence for molecular water
348 (Nakamura et al., 2023), our samples that were exposed to air probably experienced re-
349 hydration to some extent.

350 The A1 spectrum obtained on the red globule shows three distinct peaks at 1720, 1600
351 cm^{-1} and 1450 cm^{-1} attributed to the C=O, C=C and CH_2 bending mode in organic matter (Fig.
352 4G). This spectrum is reminiscent of infrared spectra obtained on insoluble organic matter
353 (Orthous-Daunay et al., 2013; Quirico et al., this volume), or organic particle found in Orgueil
354 (Phan et al., 2022) (Fig. 4G).

355 Comparison to μ -FTIR spectra obtained on the same grain, reveals a good consistency
356 between local AFM-IR and conventional μ -FTIR spectra (Fig. 4G). The μ -FTIR spectra (in
357 black) can be well explained by a mixture of average AFM-IR phyllosilicate spectra, and
358 carbonates (to explain the 1450 cm^{-1} slightly more elevated in the FTIR spectrum of the grain
359 than in the average AFM-IR spectrum of phyllosilicates) and the different probe depths of the
360 two techniques.

361 While no phyllosilicate signal was detected in the globule area, the AFM-IR spectra
362 reveal a broad absorption massif with a maximum around 1050 cm^{-1} . The fact that no signal
363 was detected in the AFM-IR map is related to the fact that AFM-IR maps are obtained in tapping
364 mode, more sensitive to the surface, while AFM-IR spectra are obtained in contact mode, that
365 probes a larger volume of sample. The different shape of the $1000\text{-}1050\text{ cm}^{-1}$ band between the

366 organic globule and typical Ryugu phyllosilicate is related to the presence of a different type of
367 silicate (amorphous?) or contribution from organic vibration to this spectral region.

368 To further elucidate the mineralogy and structure of the organic matter in this area, we
369 collected AFM-IR maps of a $3 \times 3 \mu\text{m}^2$ area (Fig. 5A) around the organic globule at wavelengths
370 similar to those used for the larger area (1720, 1600, 1450, and 1000 cm^{-1} shown in Fig. 5B-E).
371 As can be seen in Fig. 5F, this region shows a significant contribution from the Si-O stretching
372 of the phyllosilicates in the 1000 cm^{-1} map, but these contributions are absent in the central
373 organic-rich area. Conversely, the central part corresponding to the organic globule shows a
374 strong 1720 cm^{-1} absorption related to C=O. The region also shows infrared absorptions at 1600
375 cm^{-1} , 1450 cm^{-1} as shown in Fig. 5C-D, which are spatially correlated and can be attributed to
376 aromatic (C=C) or/and water molecules, and aliphatic organic compounds, respectively. In
377 addition, the IR maps also show areas with strong and correlated intensity at 1600 cm^{-1} , 1450
378 cm^{-1} , and 1000 cm^{-1} , which may reveal the presence of high refractive index Fe-bearing
379 minerals such as Fe sulfide and Fe-Ni sulfides (Dartois et al., 2023), as shown in the Fe, Ni, S,
380 and BSE EDS images obtained after the AFM-IR measurement (Fig. S-1 and S-2).

381 The micro-globule apparent in the 1720 cm^{-1} absorption image, is circular, and has a
382 diameter of $\sim 1 \mu\text{m}$ (Fig. 5F). This globule was further investigated with full AFM-IR spectra
383 (Fig. 6) at the locations indicated in the AFM composite images (Fig. 6A-B). The first spectrum
384 at the central globule location (A1) reveals two distinct peaks and shows a higher aromatic peak
385 intensity (C=C) at 1600 cm^{-1} and less carbonyl (C=O) at 1720 cm^{-1} than in the bulk organic
386 particles we analyzed in Orgueil (Fig. 6C) (Phan et al., 2022). The weak peak at 1450 cm^{-1} is
387 attributed to the CH_2 bending mode, carbonate or NH_4^+ bending mode, which are all in this
388 spectral area. Although the sample IR images show no signal at 1000 cm^{-1} (Fig. 5E), the contact
389 IR spectrum reveals a prominent peak at 1050 cm^{-1} that has moved from the phyllosilicate
390 position at 1000 cm^{-1} (Fig. 4G and Fig. 6C-D), following results obtained in our first
391 investigations of the globule.

392 A series of spectra were collected in the globule from the center outward (labeled A1-A8
393 and B1-B8) in positions shown in the AFM and RGB images (Fig. 6 A-B) to better understand
394 the variation of the organic and silicate structure inside and outside the organic globule. The
395 spectra obtained are consistent with the presence of macromolecular organics as part of the
396 globule. As can be seen, the CH_2 and CH_3 bending modes (1450 and 1380 cm^{-1}) or the broad
397 congested band $\sim 1250 \text{ cm}^{-1}$ (C-O, C-C, OH, etc.) appear in all spectra within the globule (e.g.,
398 A1-A6 and B1-B4) and are consistent with observation of IOM in chondrites using

399 conventional μ -FTIR spectroscopy (Kebukawa et al., 2011; Orthous-Daunay et al., 2013). In
400 these spectra we also confirm the presence of the broad absorption massif with a maximum
401 around 1050 cm^{-1} . Looking at the relative intensity of the C=O and C=C modes, the organic
402 structure appears to be increasingly less aromatic while the silicate peak shape becomes thinner
403 from the center outward (Fig. 6C-D).

404 **DISCUSSION**

405 **Infrared mineralogy and comparison with other extra-terrestrial materials**

406 The silicate mineralogy of Ryugu fine-grained samples is dominating by a mixture of
407 “coarse”- and “fine”- grained phyllosilicates, with chemical compositions intermediate between
408 saponite and serpentine (Noguchi et al., this volume). The presence of saponite and serpentine
409 domains was confirmed by High-Resolution bright field TEM (Noguchi et al., this volume).
410 Serpentine and saponite are expected to have different mid-infrared spectra in the $10\text{-}\mu\text{m}$ range
411 where Si-O stretching occurs, at least in the case of well-crystallized serpentines (Beck et al.,
412 2014, Dartois et al., 2023). Interestingly, the serpentine-rich CM chondrites like ALH 83100
413 have infrared spectra in the $10\text{-}\mu\text{m}$ range clearly distinct from CI-chondrites (Fig. 7), meaning
414 that even low-crystallinity serpentines, generally dominate the mineralogical composition in
415 CM chondrites, can be distinguished from saponite; accordingly, a band is more in line with
416 serpentine measurement. Based on IR, the mineralogy of our Ryugu “sands” seem related to
417 saponite, rather than serpentine or a mixture of both.

418 Ryugu samples from the IOM and stone team were investigated with similar techniques
419 by Dartois et al. (2023). In their work, the spectral range covered is similar to that in our study,
420 (slightly broader in Dartois et al. (2023) as it goes down to 100 cm^{-1}). A difference between
421 these two works is that, in our case, FTIR measurements were done in a custom-made
422 environmental cell enabling exposure of the sample to vacuum and gentle heating (80°C). This
423 procedure enables to remove weakly bonded water molecules. Overall, the FTIR spectra we
424 obtained on fine-grained samples from the sand-team are highly similar to those obtained by
425 Dartois et al. (2023), and the AFM-IR images and spectra obtained in both works are in
426 agreement. Therefore, the combination of our work and Dartois et al. (2023) reveals a certain
427 homogeneity of Ryugu mineralogy over a range of grain sizes.

428 Spectra of CI chondrites show a shoulder around 1200 cm^{-1} that can be related to the
429 presence of sulfates, and this shoulder is absent from Ryugu samples. At least a fraction of
430 sulfates minerals in CI chondrites are interpreted to be of terrestrial origin (Gounelle &

431 [Zolensky, 2001, 2014; Nakamura et al., 2023; Viennet et al., 2023](#)) and samples from Ryugu
432 are fresher in that sense. Still, we observed that one of the samples studied shows signature of
433 small sulfate grains ($<1 \mu\text{m}$) than can be interpreted as products from the fast terrestrial
434 oxidation of iron sulfides. The signatures of carbonates at 880 and 1450 cm^{-1} present in the
435 spectra of the ungrouped carbonaceous chondrites Tarda and Tagish Lake ([Fig. 7](#)), are absent
436 in the spectra of the Ryugu grain shown in [Figure 7](#), but carbonates were identified with AFM-
437 IR and in other grains with μ -FTIR analyses.

438 Overall, from an infrared point of view, the clay mineralogy of Ryugu is similar to other
439 CI chondrites, some lithologies of Tagish Lake, and some other samples belonging to the
440 magnetite- and ^{17}O -rich group of carbonaceous chondrites ([Fig. 7, Hewins et al., 2021](#)). It is
441 interesting to note that these meteorites, in addition to having some commonalities from a
442 chemical point of view, also present some similarities in the clay mineralogy. We also present
443 in [Figure 7](#), a typical spectrum obtained on a fine-grained hydrated micrometeorite from
444 ([Battandier et al., 2018](#)). We can observe in this graph that hydrated micrometeorites are similar
445 to Ryugu samples and CI chondrites, and clearly distinct from CM chondrites ([Fig. 7](#)). The
446 similarities between Ryugu, CI chondrites, hydrated IDPs and micrometeorites are also
447 discussed in [Noguchi et al. \(this issue\)](#).

448

449 **An organic micro-globule**

450 While organic globules had been observed in different types of meteorites (e.g. [Claus](#)
451 [and Nagy, 1961; Alexander et al., 2017](#)), the discovery of an organic globule analyzed *in situ*
452 (without liquid or acid extraction) and on a fresh meteorite fall (Tagish Lake) provided clear
453 and non-ambiguous evidence for an extra-terrestrial origin of at least some of the globules
454 ([Nakamura et al, 2002](#)). While these structures are often referred to as “nano”-globules, their
455 size range goes up to more than a micrometer in diameter ($140\text{-}1700 \text{ nm}$ in [Nakamura et al.,](#)
456 [2002; 150 nm to 1150 nm](#) in [De Gregorio et al., 2013](#)). We will refer here to the term globule
457 to describe a spherical organic grain ($>100 \text{ nm}$), that may contain a mineral grain in its interior
458 (and in that case it is equivalent to a spherical coating). The globules can be solid or hollow,
459 and may present some layering in their interior ([Vollmer et al., 2020a](#)). They are made of H, O
460 and N bearing organic carbon and can be host to isotopic enrichment for C, N or H, but not
461 systematically and variably ([Nakamura-Messenger et al., 2006; De Gregorio et al., 2013;](#)
462 [Vollmer et al., 2020b](#)). For example, some nanoglobules from ALH 77307, Murchison and
463 Orgueil were not isotopically enriched ([De Gregorio et al., 2013](#)). They were also found to have

464 different organo-chemistry, with some globules enriched in aromatic moieties, while others
465 having a composition more similar to insoluble organic matter (IOM) (De Gregorio et al.,
466 2013). In the case of Ryugu sample, a carbon nano-globule was observed by Ito et al. (2022),
467 which was hosting a silicate phase in its interior. Hollow and solid nanoglobules have also been
468 observed in IOM samples extracted from Ryugu grains, and showing both aromatic-rich and
469 IOM compositions (Yabuta et al., 2023).

470 **Physical properties of this “lentil” globule**

471 The AFM-IR probe configuration in our measurements is not able to distinguish
472 whether the globule we observed is solid or hollow (Fig. 5F). We note, however, that based on
473 the combined 3D view of AFM topography and RGB composite maps, the globule is not flat
474 or spherical but “lentil” shaped (Fig. 5F). The AFM topographical image shows its apparent
475 diameter is around 1- μ m, while the physical height of the shape protruding from Ryugu
476 phyllosilicates matrix is only around 100 nm. This “lentil” shape could be related to sample
477 preparation, but we would rather expect a flat surface in that case. This shape may represent the
478 original structure of the globule, but most of it is buried in the surrounding matrix. An
479 alternative possibility is that the globule was hollow, with a spherical shape and collapsed at
480 some point.

481 After our investigations on the globule in the 7-13 μ m range with the APE laser source,
482 we attempted to characterize its aliphatic linkage using the Firefly laser source (2.5-4 μ m). For
483 hardware reason, chemical mapping using this laser source was only possible using AFM
484 contact mode, and not tapping mode like for the APE source. This mapping led to the disruption
485 of the globule and the organics that were constituting the globule were somehow spread over
486 the surface (See SI, Fig. S-3 and S-4). We also note that the areas for which APE spectra were
487 collected (in contact mode) are visible in the AFM-IR map obtained after spectral
488 measurements (Fig. 5B). The three small pits are due to the indentation of the globule by the
489 AFM-tip. This attests that the globule is somehow weak in physical nature.

490

491 **The nature of organic matter in fine-grained samples and in the globule**

492 Organic compounds were investigated by several techniques in Ryugu samples and
493 revealed a direct link between macromolecular organic matter in C-type asteroids and that in
494 primitive carbonaceous chondrites. Basically, four main chemical forms of carbon have been
495 observed in Ryugu grains as diffuse, highly aromatic, aromatic and IOM-like organic matter.

496 Particles and globules tend to show more highly carbonyl and aromatic compositions, while
497 diffuse organics more dispersed throughout the sample resemble IOM-like organic matter
498 (Yabuta et al., 2023, Rhonda et al., this volume). In the present study, both organic globule and
499 diffuse organics in fine-grained Ryugu were observed by AFM-IR measurements. The spectral
500 range covered by the APE laser can in principle be used to obtain information on the aromaticity
501 of the organic compounds, provided that the contribution of carbonates to the 1450 cm^{-1} feature
502 (CH_2 group) is negligible. In that case, the ratio of the 1450 and 1650 cm^{-1} (aromatic C=C) band
503 can be used as a semi-quantitative tracer of aromaticity. Nevertheless, molecular water in the
504 phyllosilicate may lead to a spectral superposition between the organic C=C and C=O bands
505 and the water bending mode around 1630 cm^{-1} , which can be removed by heating the sample
506 in vacuum with conventional μ -FTIR (Beck et al., 2010; Orthous-Daunay et al., 2013) but
507 cannot be removed with our AFM-IR setup.

508 In the case of two C0105 grains, diffuse organics seem to be present based on the AFM-
509 IR maps but the spectral range where the doublet of bands at 1720 and 1600 cm^{-1} occurs
510 (attributed to C=O and C=C) is perturbed by the water bending mode. The intensity ratio of
511 C=O and C=C is significantly lower than that of Ryugu IOM from μ -FTIR spectra (Quirico et
512 al., this volume) (Fig. 8), suggesting a contribution of water to the C=C position near 1600 cm^{-1}
513 or that diffuse organics are less carbonylated than IOM. Peak fitting by Dartois et al. (2023)
514 to disentangle between molecular water and C=C signatures seems to show that at least some
515 grains have a contribution from aromatic-rich organics in this spectral range.

516 Aliphatic organics are present in Ryugu fine-grained samples as evidenced by the modes
517 around 3.4-3.4 μm seen in our conventional μ -FTIR spectra, which cannot be due to globules
518 given their rarity, and which has been observed through STEM-EELS-EDS (Yabuta et al.,
519 2023). This diffuse aliphatic organic fraction is similar to that of Orgueil (Guillou & Brearley,
520 2014; Phan et al., 2022). It has been suggested that some of these compounds may be hosted
521 within the interlayer space of phyllosilicates (Viennet et al., 2023). The comparison between
522 spectra of intact Ryugu grains and IOM show that the CH_2/CH_3 ratio, determined from the ratio
523 of the antisymmetric stretching modes of the CH_2 and CH_3 chemical groups is higher for intact
524 grains compared to IOM (Dartois et al., 2023; Quirico et al., this volume) (Fig. S-4). This
525 supports the view that diffuse organic matter is a mix between IOM and soluble organic
526 molecules that are lost during the chemical extraction of IOM.

527 The AFM-IR spectra obtained on the globule are presented in Figure 6, while some
528 structural parameters ($\text{C=O}/\text{C=CC}$ and $\text{CH}_{2\text{bend}}/\text{C=C}$) derived from these spectra are shown in

529 [Figure 8A-B](#). At first glance, the spectra obtained on the globule are reminiscent of
530 measurements obtained on IOM samples ([Quirico et al., this volume](#)). A difference is the
531 presence of a broad absorption at 1050 cm^{-1} that we attribute to silicates under or inside the
532 globule (see discussion below). Some spectral variations were found inside the globule, with
533 an increase of the $\text{C=O}/\text{C=C}$ and $\text{CH}_{2\text{bend}}/\text{C=C}$ from the center to the exterior ([Fig. 8](#)) of the
534 globule. Overall these parameters are in line with values obtained for Ryugu's IOM ([Fig. 8](#)),
535 revealing that the organic chemistry of the globule is similar to IOM.

536 The IOM PET team analyzed in detail the organo-chemistry of refractory organics from
537 Ryugu samples, as well as their isotopic composition ([Yabuta et al., 2023](#)). Organic globules
538 were found and investigated by several techniques revealing the presence of both IOM-like and
539 aromatic globules, with grain size ranging typically 50-500 nm up to 2000 nm in diameter. The
540 globule we investigated here is therefore amongst the largest ones found in Ryugu so far. Both
541 IOM-like and aromatic globules were found in [Yabuta et al. \(2023\)](#), while the only globule we
542 detected is IOM-like. However, aromatic globules may be more difficult to detect with AFM-
543 IR due to the interference with molecular water, and the lack of 1720 cm^{-1} peak.

544

545 **Silicates inside the globule?**

546 The organic globule identified by [Ito et al. \(2022\)](#) in Ryugu samples revealed the
547 presence of a silicate particle in its interior. A carbon globule with a silicate core was also
548 observed in the CR2 chondrite NWA 801 ([Hashiguchi et al., 2013](#)) and in Renazzo-type CR
549 chondrites GRA 95229 ([Vollmer et al., 2020a](#)). In our case, while the AFM-IR maps obtained
550 in tapping mode revealed the absence of signal in the Si-O region in the globule, contact mode
551 spectra showed the presence of a broad band around 1050 cm^{-1} , probably due to silicate
552 signature for AFM-IR spectra obtained within the globule. Contact mode AFM-IR spectra may
553 probe a larger volume around several micrometers under the surface ([Mathurin et al., 2022](#)),
554 and may be picking signals from below or inside the globule. Given the diameter of the globule
555 and the spatial resolution of contact mode IR spectra ([Phan et al., 2022](#)), it is unlikely that this
556 silicate signature comes from the phyllosilicates on the side of the globule. It can also be noted
557 that this silicate signature is distinct from typical phyllosilicates signatures obtained from
558 Ryugu samples, with a broader shape and maxima of absorption around 1050 cm^{-1} . The spectra
559 obtained on the globule also show a feature around 800 cm^{-1} , not seen in other spectra obtained
560 on Ryugu. This band could be related to Si-O-Si bending in SiO_2 , or to $\text{Fe}^{3+}\text{-OH}$ in a
561 phyllosilicate ([Madejová et al., 2017](#)). The fact that this silicate signature is particular, and was

562 found only associated to the globule may suggest that this phase may be located inside the
563 globule. However, this argument remains circumstantial at best without excavation and direct
564 observation of the grain interior.

565

566 **Possible formation mechanisms**

567 We typically surveyed an area of more than 2500 μm^2 fine-grained Ryugu samples with
568 AFM-IR, while the surface of the nanoglobule is of less than 1 μm^2 . Therefore, carbon-rich
569 globules are rare and the amount of C present in the form of globules is likely insufficient to be
570 the dominant reservoir of carbon in Ryugu samples, since the bulk organic C content is of about
571 3 wt.% (Yokoyama et al., 2022). Several possible formation mechanisms and formation
572 environments have been proposed for the carbon-rich globules encountered in carbonaceous
573 chondrites. They were summarized in the thorough investigation by De Gregorio et al. (2013).
574 The possible formation environments includes pre-solar, solar nebula or asteroidal. If pre-solar,
575 these globules may be inherited directly from the diffuse interstellar medium (DISM), where
576 carbonaceous compounds could form a shell surrounding an ice-silicate core (Greenberg et al.,
577 1995). In the solar nebula scenario, carbon globules may be the leftover of gas-phase or solid-
578 state chemistry in the solar parent molecular cloud or the protosolar nebula. Globular-shape
579 carbon-rich particle have been produced experimentally by two-step UV-irradiation of ice-
580 mixture (Piani et al., 2017) or warm plasma chemistry (Bekaert et al., 2018). However, the
581 capability of such mechanism to reproduce the peculiar structure of IOM remains to be assessed
582 (Quirico et al., 2020). A last formation environment that has been proposed for carbon-rich
583 globules is on the parent planetesimal, where their formation would be triggered by the presence
584 of liquid water on these objects. In the study of Cody et al. (2011), micrometer-sized globule
585 with morphologies reminiscent of meteorite observations were produced from the liquid-phase
586 polymerization of formaldehyde. Another possibility is that the presence of liquid water on the
587 asteroid could have induced mobilization of a diffuse organic fraction, and led to their
588 condensation locally. In that sense, the organic-globule would form as coatings surrounding a
589 pre-existing grain such as discussed by (Vollmer et al., 2020a).

590 In our study, only one globule was observed, but for the first time we were able to extract
591 the IR spectra of a single globule, *in situ*. Our observation reveals strong similarities with
592 insoluble organic matter, and that this globule is not particularly enriched in aromatic moieties.
593 This IOM-like chemistry is consistent with analyses on IOM extracted from the CI Orgueil by
594 De Gregorio et al. (2013), for which no aromatic globule was found unlike CR chondrites for

595 instance. In our work, we observed some chemical variability within the globule based on the
596 C=O/C=C ratio, where the outer part of the globule appears enriched in C=O. This may record
597 the history of the globule synthesis, or its chemical modification upon hydrothermal alteration.

598 The fact that the globule seems to be associated to a silicate phase distinct from the typical
599 phyllosilicates from Ryugu, as observed in [Ito et al. \(2022\)](#) and our study, suggests that the
600 globule was not produced on the asteroid; in the parent body mechanisms suggested in the
601 above paragraph, none would lead to preferential formation of the globule around a specific
602 type of silicates. One possibility is that the migration and coalescence of organic-compounds
603 occurred at the very beginning of the aqueous alteration process, and the presence of the coating
604 protected the silicate from conversion to phyllosilicates. While parent-body formation cannot
605 be strictly excluded, our preferred explanation is a pre-accretionary origin, but the exact
606 environment and synthesis mechanism remain elusive. The oxygen isotope of the silicates
607 associated to the carbon globule in the CR2 chondrite NWA 801 were measured by [Hashiguchi
608 et al. \(2013\)](#). Their results showed that oxygen isotopes in the silicate are similar to solar system
609 material, suggesting then a solar system origin for the globule. Similar work done on Hayabusa2
610 samples may help understand the formation environment of the carbon globules from Ryugu.

611

612 CONCLUSION

613 Here, we report on an infrared spectroscopy study of fine-grained particles from the
614 Ryugu asteroid, as part of the Hayabusa2 PET “sand” team. Infrared absorption properties were
615 obtained on grains at the 100 μm x100 μm scale using conventional FTIR, and at the sub- μm
616 scale using photo-thermal AFM-IR.

617 This work confirms that the mineralogy of Ryugu fine-grained material is dominated
618 by phyllosilicates. These phyllosilicates are Mg-rich and have infrared properties similar to
619 saponite, based on the 10- μm silicate absorption feature. They are clearly distinct from CM
620 chondrites, and similar to observations on other CI chondrites or selected ungrouped
621 carbonaceous chondrites, as well as to some hydrated micrometeorites. The sulfate signature
622 seen in CI chondrites are absent from our FTIR spectra of Ryugu samples. We also observe
623 carbonate ion signatures in the transmission FTIR spectra, and these ions are expected to be
624 present in a dolomite crystallographic structure.

625 Further investigations of the Ryugu “sands” mineralogy and organic compounds was
626 performed using AFM-IR, enabling to probe the sub- μm scale. We observe little variability of

627 the Si-O stretching, showing a relative homogeneity of the phyllosilicate from an IR perspective
628 at that scale. We observe the presence of small carbonate grains (100-500 nm) finely mixed with
629 the phyllosilicate. In one of the studied areas, small particles associated to a band at 1100 cm⁻¹
630 are present and interpreted to be terrestrial sulphate forming at the expense of S-bearing
631 opaques.

632 Analysis of organic signatures reveals the presence of a diffuse organic component, from
633 the presence of CH-modes, and we observe a single carbon-rich globule from AFM-IR mapping.
634 This globule is roughly 1- μ m in diameter and AFM-IR spectra obtained revealed the presence
635 of C=O and C=C, and CH₂-bend, in a similar way to IOM extracted from Ryugu samples. From
636 our study, carbon globule is rare in Ryugu and likely represent only a fraction of the carbon
637 budget in Ryugu; but detection biases may be present and inherent to our technique and sample
638 preparation protocol. This globule seems to be associated to silicate whose nature is different
639 from the typical Ryugu phyllosilicate. The presence of IOM like globules in Orgueil was
640 observed by [De Gregorio et al. \(2013\)](#) after acid-leaching. Our in-situ AFM-IR analysis reveal
641 the existence of such globule in a CI-related object. A pre-accretion scenario is favored for the
642 formation of this globule, but the exact formation environment, and mechanisms, remain
643 elusive.

644

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654 **Supplementary materials**

655 Supplementary data related to this article can be found in the Supporting materials part.

656

657 *Data Availability* – The data that support the findings of this study are available from the
658 corresponding author upon reasonable request.

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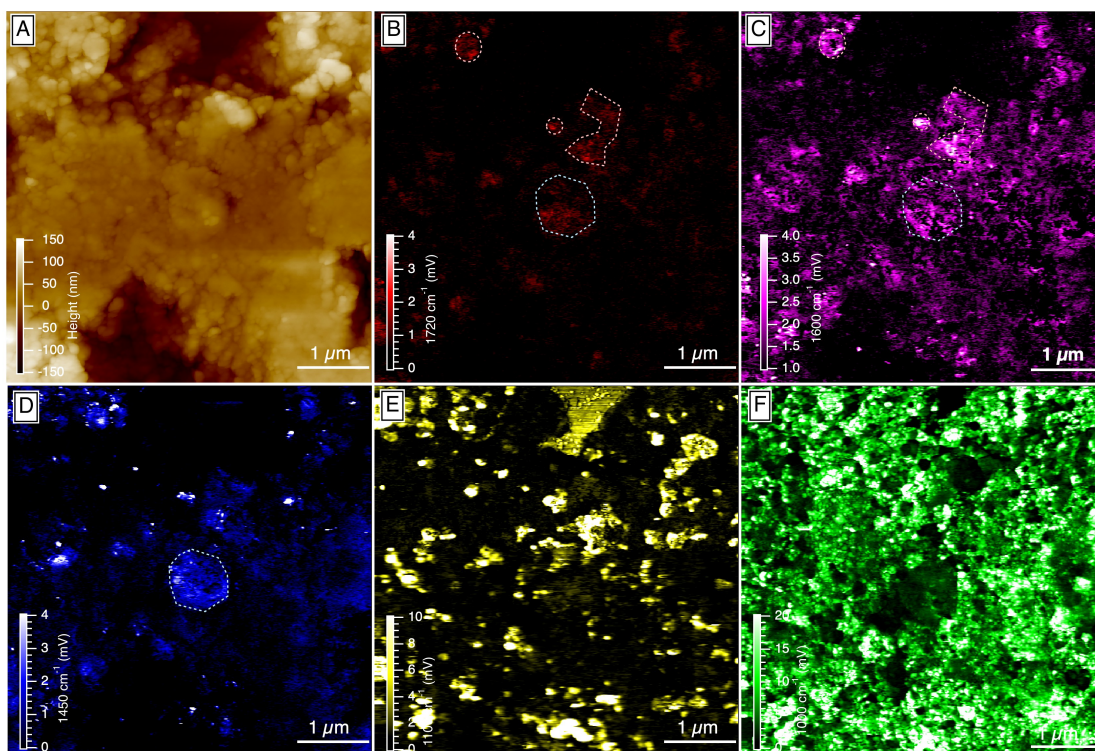
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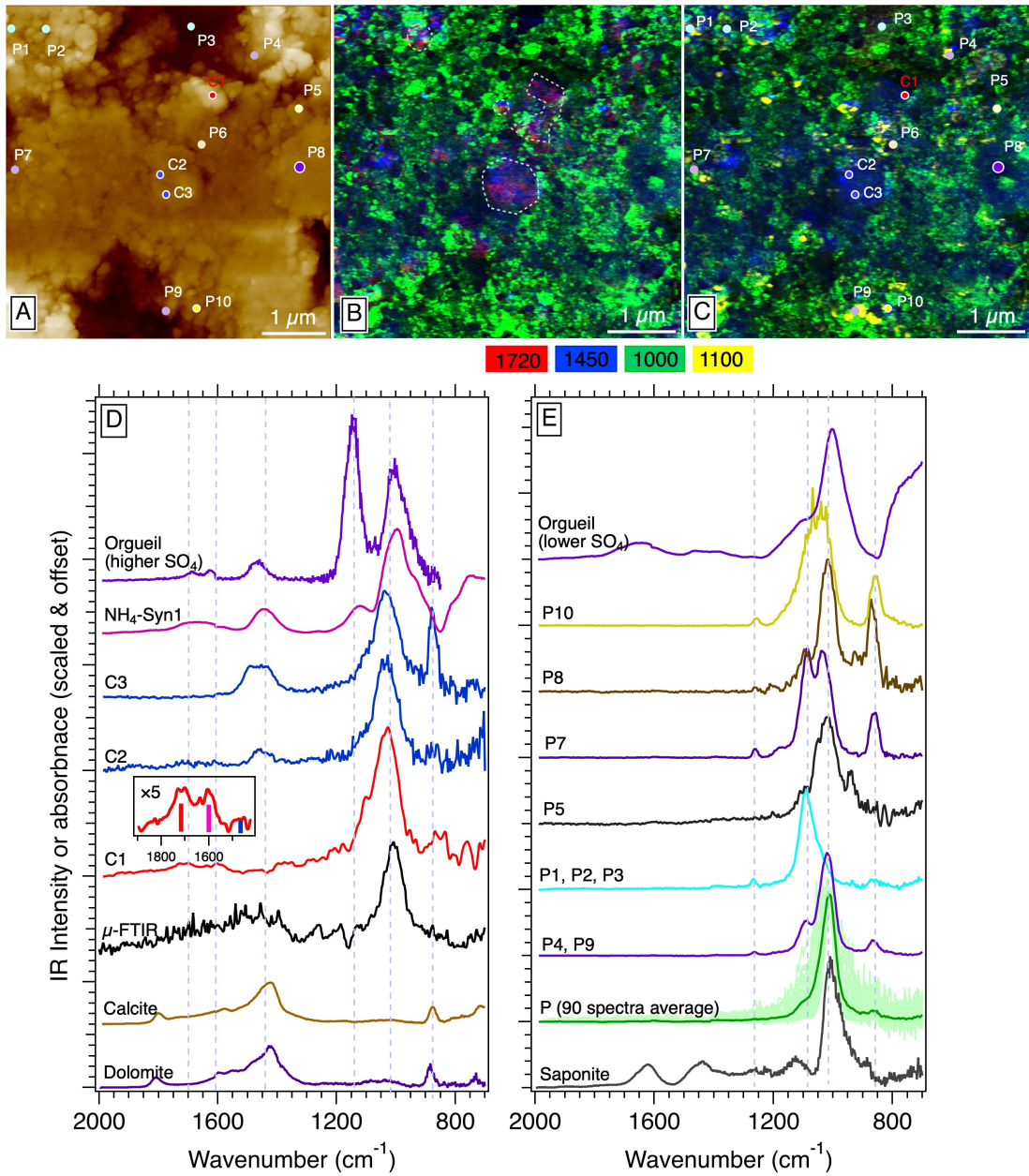
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923 **Figures**



924
 925 Figure 1. C0105-0032. (A) Topographic image (AFM) of the region of interest (ROI of 5×5
 926 μm^2); Chemical images of the absorption band at (B) C=O at 1720 cm^{-1} , (C) C=C and/or water
 927 at 1600 cm^{-1} , (D) Carbonate and/or CH_2 bending mode at 1450 cm^{-1} , (E) SO_4 and/or wing of
 928 Si-O at 1100 cm^{-1} and (F) Si-O at 1000 cm^{-1}
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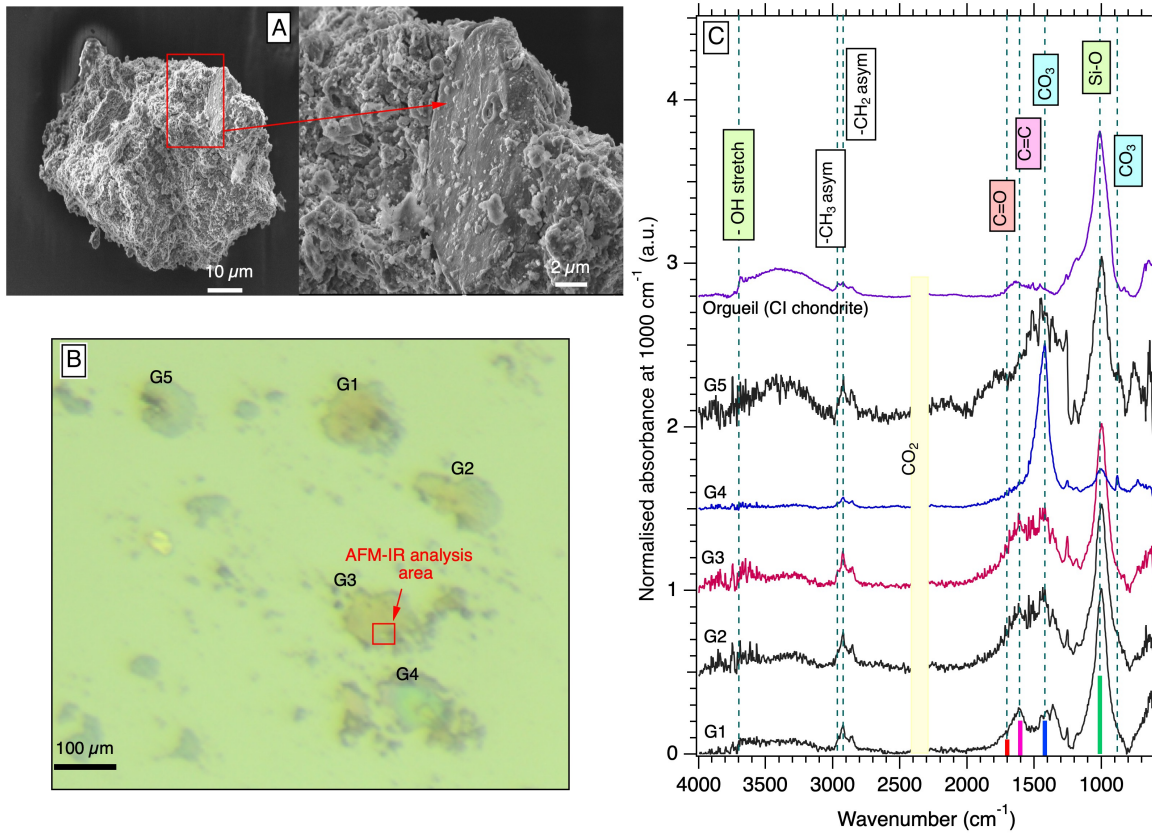


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932 Figure 2. C0105-0032. (A) Topographic image (AFM) with the single-point AFM-IR spectral
 933 positions surrounding the $5 \times 5 \mu\text{m}^2$ image (labeled C1: red point, C2, C3: blue point, P1-P10);
 934 (B) A composite image at 1720, 1000 and 1450 cm^{-1} , (C) A composite image at 1450, 1000 and
 935 1100 cm^{-1} ; (D) Comparison between the single-point AFM-IR spectra in carbonate-rich regions
 936 and the average $\mu\text{-FTIR}$ spectrum of same Ryugu grain, AFM-IR spectra of carbonate
 937 references (dolomite, calcite) and $\text{NH}_4\text{-Syn-1}$ (*Ammonium-mica-montmorillonite*); the AFM-
 938 IR spectra of Orgueil with high sulfate; (E) Comparison between AFM-IR spectra of
 939 phyllosilicate-rich regions, AFM-IR spectra of saponite and Orgueil with lower sulfate.

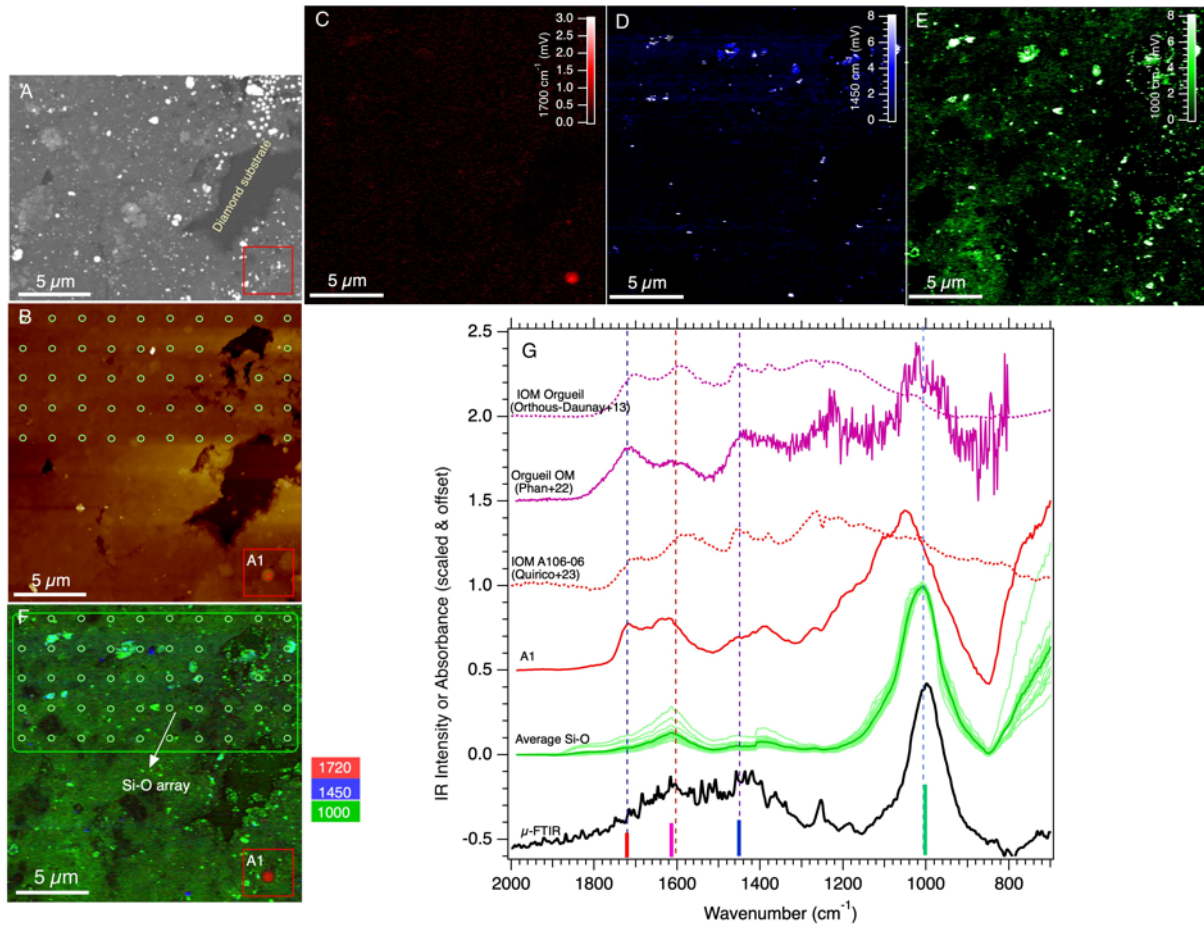
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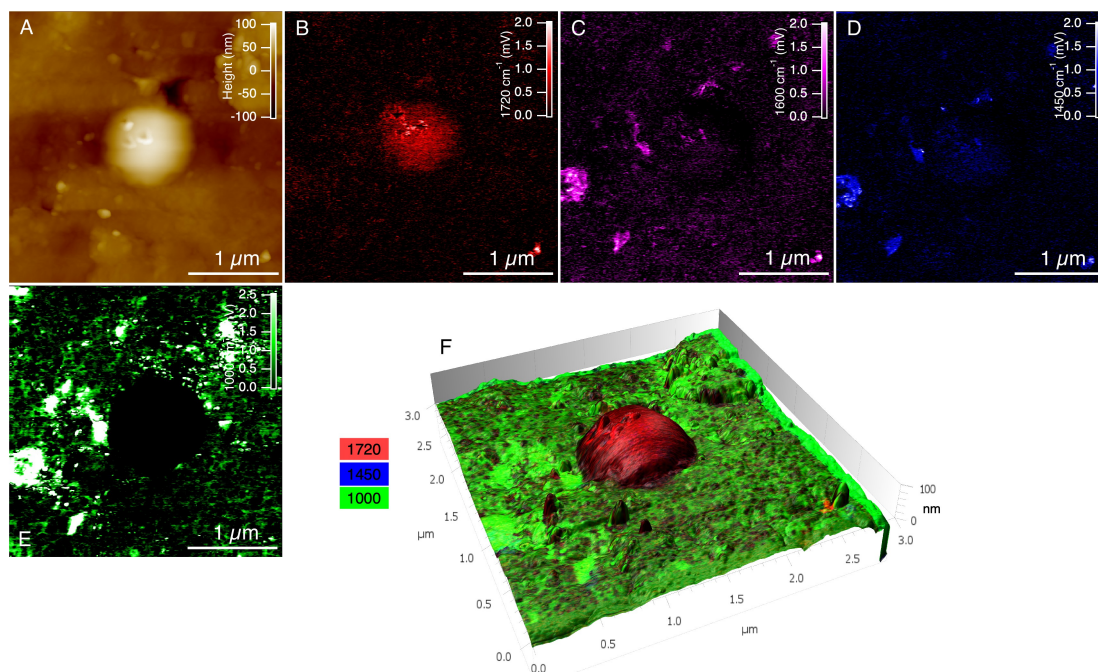
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943 Figure 3. C0105-0038. μ -FTIR spectra of Ryugu sample in different grains. (A) Back scattered
 944 electron (BSE) image showing the melted splash due to the space weathering (Noguchi et al.,
 945 2023). (B) Visible image of different fractured grains after crushing between two diamond
 946 windows (G1 – G5) for μ -FTIR analyze showing the location of the AFM-IR map (red square).
 947 (C) Different μ -FTIR spectra corresponding to G1 – G5 grains in the visible image (B) in
 948 comparison to μ -FTIR spectrum of Orgueil (CI chondrite).

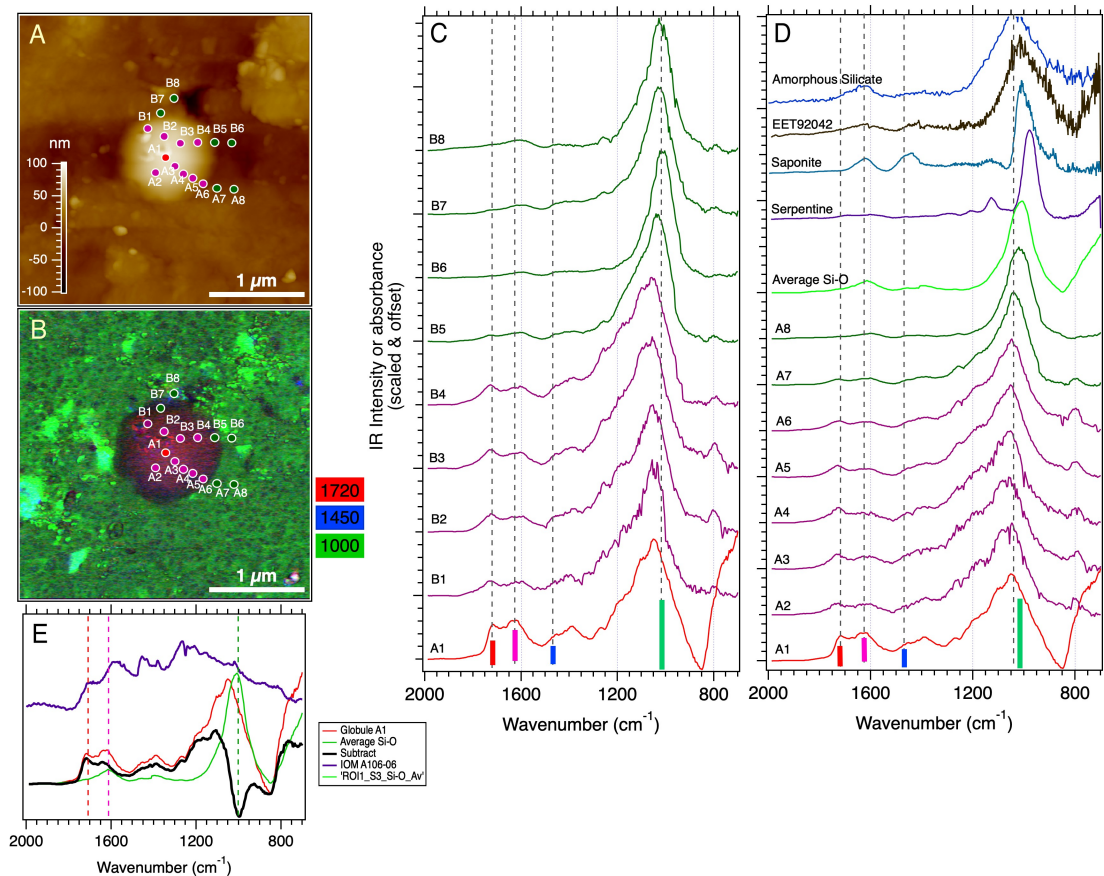


949

950 Figure 4. **C0105-0038** ($20 \times 20 \mu\text{m}^2$). (A) SEM image showing the region of AFM-IR
 951 measurements using the APE laser in the $2000 - 700 \text{ cm}^{-1}$ range. (B) Topographical image of
 952 the $20 \times 20 \mu\text{m}^2$ area. AFM-IR images collected at different absorption band at (C) C=O at
 953 1720 cm^{-1} (in red); (D) Carbonate and/or CH_2 bend mode at 1450 cm^{-1} (in blue); (E) Si-O at
 954 1000 cm^{-1} (in green) and (F) Composite RGB image in tapping mode of the three map: 1720,
 955 1000 and 1450 cm^{-1} , respectively with a small organic globule are visible in red square
 956 surrounded by a dominant phyllosilicate in green; (G) Comparison between AFM-IR single
 957 point spectra in the locations shown in (B) and (F), the μ -FTIR spectrum of Ryugu G3 grain,
 958 IOM Ryugu A106-06 (Quirico et al., this volume), IOM Orgueil (Orthous-Daunay et al., 2013)
 959 and the AFM-IR spectra of organic particles in Orgueil (Phan et al., 2022).
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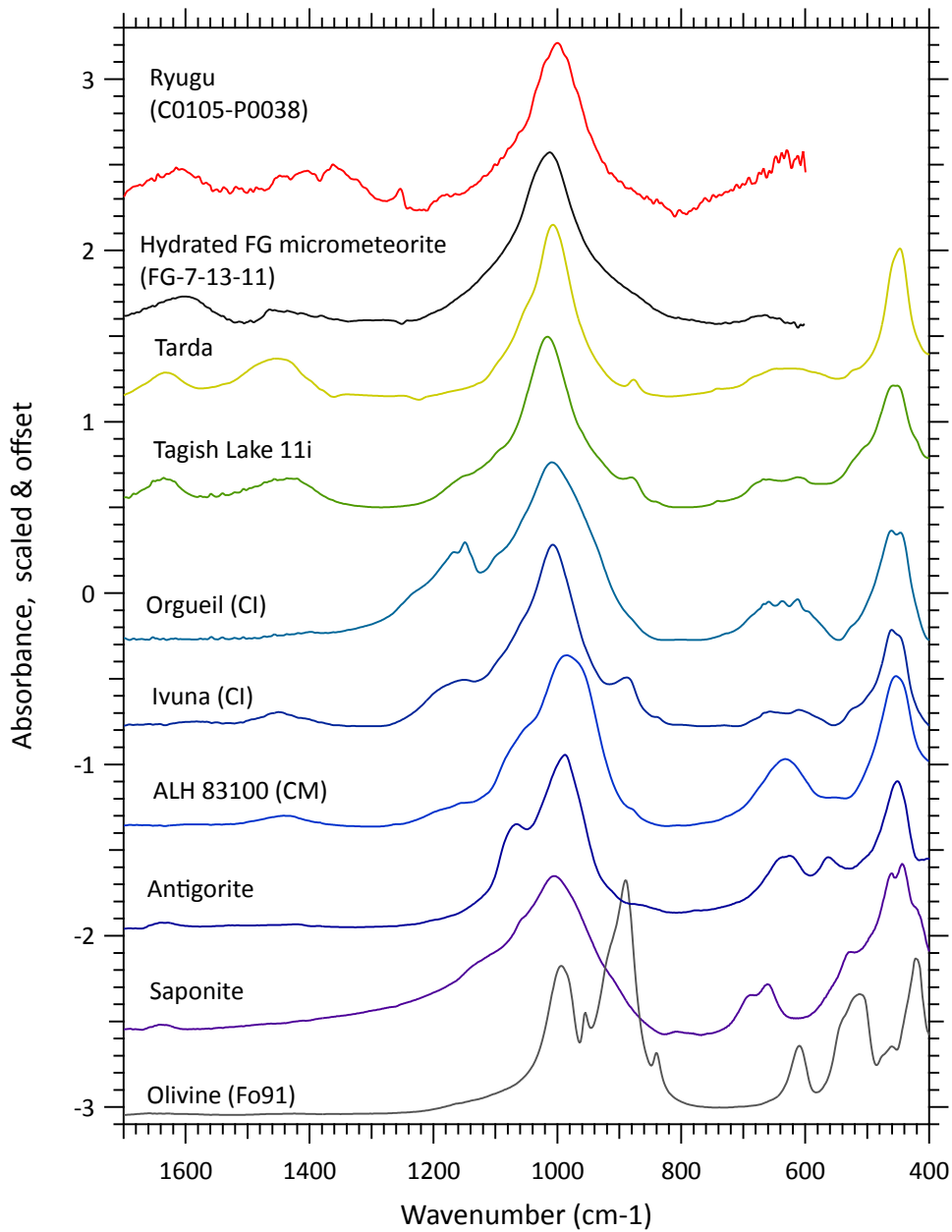


962
 963 Figure 5. **C0105-0038 ($3 \times 3 \mu\text{m}^2$)**. (A) Topographical image (AFM) showing some small spots
 964 damaged due to the physical contact of the AFM tip; Absorption images of the bands (B) C=O
 965 at 1720 cm^{-1} ; (C) C=C and water at 1600 cm^{-1} ; (D) $\text{CO}_3^{2-} / \text{CH}_2$ bending mode at 1450 cm^{-1} ; (E)
 966 Si-O at 1000 cm^{-1} ; (F) Composite 3D view of the RGB image derived from the three maps:
 967 1720 , 1000 and 1450 cm^{-1} , respectively, showing the “lentil” shape of the globule.
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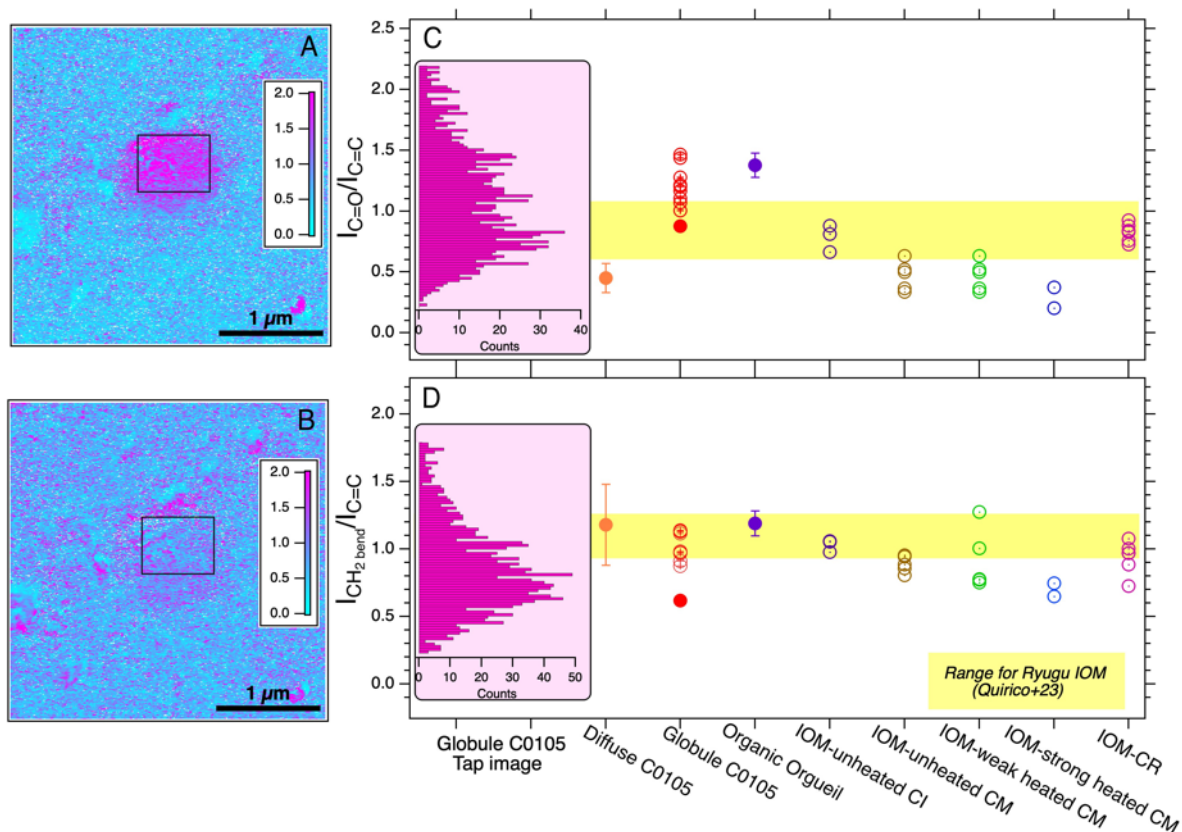
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970 Figure 6. C0105-0038-G3. (A) AFM and (B) Composite 2D view of the RGB image derived
 971 from three AFM-IR images at 1720 cm⁻¹, 1450 cm⁻¹ and 1000 cm⁻¹, respectively with the
 972 location of the single point AFM-IR spectra; (C) AFM-IR spectra performed in selected
 973 positions indicated in images (A)-(B) images (labeled B1-B8); (D) the AFM-IR spectra
 974 performed in selected positions shown on the (A)-(B) images (labeled A1-A8) from the centre
 975 to exterior of the organic globule, in comparison with mixture of saponite and carbonate,
 976 serpentine and amorphous silicate (anhydrous silicate) (Potapov et al., 2020) and AFM-IR
 977 spectrum of amorphous silicate in carbonaceous chondrite EET 92042 (Phan et al., 2022); (E)
 978 The subtracted spectrum between the organic globule (A1 spectrum) and the average Si-O
 979 spectrum, in comparison with μ -FTIR spectrum of IOM A106-06 (Quirico et al., this volume).



980

981 Figure 7. Comparison of the MIR spectra of Ryugu grain C0105-0038 to CI chondrites (Orgueil
 982 and Ivuna from Beck et al., 2014), ungrouped carbonaceous chondrites (Tarda and Tagish Lake
 983 from Gilmour et al., 2019), a CM chondrite and reference mineral phases (Beck et al., 2014).



984

985 Figure 8. C0105-0038. The AFM-IR ratio images showing (A) the I_{1720}/I_{1600} and (B) I_{1450}/I_{1600}
 986 ratio of interest region ($3 \times 3 \mu\text{m}^2$) for C0105-0038. Comparison of the peak intensity ratio of
 987 (C) C=O and C=C bands at 1720 and 1600 cm^{-1} , respectively and (D) CH_2 bending mode and
 988 C=C bands at 1450 and 1600 cm^{-1} , respectively, including: Histogram of the I_{1720}/I_{1600} ratio
 989 extracted from (A), Histogram of the I_{1450}/I_{1600} extracted from (B), the contact AFM-IR spectra
 990 of the organic globule in “bulk” Ryugu in C0105-0038, the AFM-IR spectra of the organic
 991 particle in Orgueil (Phan et al., 2022); the μ -FTIR spectra of IOM-like Ryugu from Quirico et
 992 al. (this volume) in yellow bar, and the μ -FTIR spectra of various IOMs in carbonaceous
 993 chondrites (Quirico et al., 2018).