



Title	Carbonate record of temporal change in oxygen fugacity and gaseous species in asteroid Ryugu
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1 **Carbonate record of temporal change in oxygen fugacity and gaseous species in asteroid**
2 **Ryugu**

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93

94 **The Hayabusa2 spacecraft explored asteroid 162173 Ryugu and brought its surface materials to**
95 **Earth. Ryugu samples resemble Ivuna-type (CI) chondrites – the most chemically primitive**
96 **meteorites – and contain secondary phyllosilicates and carbonates, which are indicative of**
97 **aqueous alteration. Understanding the conditions (such as temperature, redox conditions, and**
98 **fluid composition) during aqueous alteration is crucial to elucidating how Ryugu evolved to its**
99 **present state, but little is known about the temporal changes in these conditions. Here we show**
100 **that calcium carbonate (calcite) grains in Ryugu and Ivuna samples have variable $^{18}\text{O}/^{16}\text{O}$ and**
101 **$^{13}\text{C}/^{12}\text{C}$ ratios that are respectively 24–46‰ and 65–108‰ greater than terrestrial standard**
102 **values, whereas those of calcium-magnesium carbonate (dolomite) grains are much more**
103 **homogeneous, ranging within 31–36‰ for oxygen and 67–75‰ for carbon. We infer that the**
104 **calcite precipitated first over a wide range of temperatures and oxygen partial pressures, and**
105 **that the proportion of gaseous $\text{CO}_2/\text{CO}/\text{CH}_4$ molecules changed temporally. By contrast, the**
106 **dolomite formed later in a more oxygen-rich and thus CO_2 -dominated environment when the**
107 **system was approaching equilibrium. The characteristic isotopic compositions of secondary**
108 **carbonates in Ryugu and Ivuna are not observed for other hydrous meteorites, suggesting a**
109 **unique evolutionary pathway for these asteroids.**

110

111 The Japan Aerospace Exploration Agency (JAXA) Hayabusa2 spacecraft explored the near-Earth
112 asteroid 162173 Ryugu and brought samples of its surface materials back to Earth^{1,2}. Ryugu has been
113 classified spectroscopically as a member of the C-complex of asteroids^{3,4}. It is a rubble pile asteroid
114 consisting of numerous rocky blocks that are the fragments resulting from the disruption of an original,
115 larger parent body⁵⁻⁷.

116

117 Previous work has reported that Ryugu materials underwent extensive aqueous alteration as the result
118 of water activity in the original parent body⁸⁻¹⁰ and are mainly composed of secondary minerals that
119 formed during the aqueous alteration: phyllosilicates, carbonates, sulphides, and oxides. On the other
120 hand, primary minerals like anhydrous silicates are rare⁹. These petrological characteristics are
121 comparable to those in the CI (Ivuna-type) chondritic meteorites, pointing to a kinship between Ryugu
122 and CI chondrites. The Ryugu's whole-rock chemical and isotope compositions confirm a close
123 affinity with CI chondrites^{8,11,12}.

124

125 Carbonates, the major Ca budget in Ryugu and CI chondrites¹³, are of particular interest because (i)
126 their chemical and isotopic compositions reflect the conditions of aqueous alteration, and (ii) their
127 grain size is commonly large enough to allow *in-situ* analysis by electron and ion microprobes¹⁴⁻¹⁷.
128 The C source of carbonates is unclear but was likely ices that included CO , CO_2 , and CH_4 , and/or
129 organic matter^{18,19}. These materials may have formed in the solar nebula or even the parental molecular

130 cloud of the solar system. Therefore, the C isotope compositions recorded by carbonates can help us
131 shed light on the physicochemical processes that operated in these environments.

132

133 In this study, we investigate the conditions of aqueous alteration and the origin of the materials
134 accreted by the Ryugu/CI parent bodies. To this end, we performed *in-situ* O and C isotope
135 measurements of calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) in Ryugu samples A0058, collected at
136 the first touchdown site, and C0002, from the second touchdown site, as well as the Ivuna meteorite.
137 The O isotope data of the A0058 and Ivuna dolomite are taken from a previous study⁸.

138

139 **Occurrences and isotope compositions of carbonate minerals**

140 Dolomite is the most abundant carbonate mineral in the analysed samples, and we found numerous
141 dolomite grains throughout the Ryugu and Ivuna matrices, whereas calcite is rare. No calcite grains
142 were observed in the Ryugu A0058 sample studied. Calcite was found only in limited areas (clasts) of
143 the Ryugu C0002 and Ivuna samples, occurring with primary anhydrous silicate minerals like Mg-rich
144 olivine and pyroxene (Fig. 1a). The calcite grains ($<10 \mu\text{m}$ in size) are usually smaller than the
145 dolomite grains (several tens of μm) (Fig. 1b). The dolomite has compositional variation and complex
146 zoning within grains (Extended Data Fig. 1). We also found breunnerite ($\text{Mg}(\text{Fe},\text{Mn})(\text{CO}_3)_2$) grains,
147 for which we did not measure isotope compositions because of the lack of a suitable standard material
148 for isotope analysis.

149

150 The O and C isotope compositions of the Ryugu and Ivuna carbonates are similar (Table 1). The $\delta^{18}\text{O}$
151 values of the calcite in C0002 and Ivuna (+24 to +46‰) show a grain-to-grain variation larger than
152 those of the dolomite in C0002, A0058, and Ivuna (+26 to +31‰) ($\delta^i\text{O}$ in ‰ =
153 $[(^{i}\text{O}/^{16}\text{O})_{\text{sample}}/(^{i}\text{O}/^{16}\text{O})_{\text{VSMOW}} - 1] \times 1000$; $i = 17$ or 18 and VSMOW is the terrestrial standard material,
154 Vienna standard mean ocean water) (Fig. 2a). The simple average of the $\Delta^{17}\text{O}$ values, the deviation
155 from the terrestrial fractionation line defined as $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$, of the C0002 and Ivuna
156 calcite is $+1.37 \pm 0.40\text{‰}$ (2SE, $N = 17$). The $\Delta^{17}\text{O}$ values of the C0002, A0058, and Ivuna dolomite
157 are systematically lower than those of the calcite, and the average $\Delta^{17}\text{O}$ value of the dolomite ($+0.26$
158 $\pm 0.23\text{‰}$, 2SE, $N = 16$) is closer to the whole-rock values of three Ryugu samples⁸ ($+0.61 \pm 0.28\text{‰}$,
159 2SD; Fig. 2b). The previously measured O isotope compositions of the A0058 and Ivuna dolomite are
160 in good agreement with those of the C0002 dolomite measured in this study⁸.

161

162 Like the $\delta^{18}\text{O}$ values, the dolomite in A0058, C0002, and Ivuna has a relatively narrow range of $\delta^{13}\text{C}$
163 values from +67 to +75‰ ($\delta^{13}\text{C}$ in ‰ = $[(^{13}\text{C}/^{12}\text{C})_{\text{sample}}/(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}} - 1] \times 1000$; VPDB is the
164 terrestrial standard material, Vienna Pee Dee belemnite) (Fig. 3). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the
165 dolomite are broadly consistent with the bulk $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbonates, including calcite,

166 dolomite, and breunnerite, in CI chondrites (Ivuna and Orgueil) determined on whole-rock samples¹⁸,
167 corroborating the observation that dolomite is the major carbonate mineral. On the other hand, the
168 $\delta^{13}\text{C}$ values of the calcite in C0002 and Ivuna are highly heterogeneous from grain to grain, ranging
169 from +65 to +108‰, and they are commonly higher than those of the Ryugu and Ivuna dolomite (Fig.
170 3). These variations have also been reported for other Ryugu samples²⁰, confirming that our results
171 represent the isotopic characteristics of Ryugu carbonates. For calcite grains on which we conducted
172 multiple measurements, the $\delta^{13}\text{C}$ values in each grain are identical within uncertainties of $\sim 5.1\%$. Thus,
173 the heterogeneity of $\delta^{13}\text{C}$ values within individual calcite grains is likely no larger than 10‰, which
174 is much smaller than the heterogeneity of $>40\%$ between grains.

175

176 **Isotope signatures of the Ryugu and CI carbonates**

177 If the carbonates were in O and C isotopic equilibrium with the aqueous fluid when they precipitated,
178 their O and C isotope compositions would have been determined by the mass dependent equilibrium
179 isotopic fractionation between carbonates and water for O, and that between carbonates and dissolved
180 CO_3^{2-} (and other dissolved C-bearing chemical species) for C. The magnitude of this equilibrium
181 isotopic fractionation depends on temperature²¹. Thus, the O and C isotope compositions of the
182 carbonates would reflect those of water and CO_3^{2-} as well as their formation temperatures. Assuming
183 equilibrium, the temperature of dolomite-magnetite precipitation in the Ryugu A0058 sample analysed
184 previously is estimated to be 37 ± 10 °C (ref.⁸), while the inferred alteration temperatures of CI
185 chondrites range up to 150 °C (ref.²²). The equilibrium O isotopic fractionation between water and
186 calcite leads to the enhancement of $\delta^{18}\text{O}$ values in calcite relative to water by approximately +38, +28
187 and +13‰ at 0, 40, and 150 °C, respectively²³. Thus, the $\delta^{18}\text{O}$ variation of $\sim 22\%$ observed in the
188 Ryugu calcite (Fig. 2) is potentially explained by formation temperatures that varied from 0 to 150 °C
189 assuming a fixed $\delta^{18}\text{O}$ value of water.

190

191 However, this argument does not necessarily mean that variable formation temperature is the sole
192 explanation for the observed $\delta^{18}\text{O}$ variation of the calcite. Indeed, the lack of a simple correlation
193 between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values (Fig. 3) implies that variable formation temperatures alone cannot
194 explain the observed $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ variations because the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of carbonates should
195 co-vary with their formation temperatures¹⁸. Rather it seems likely that the $\delta^{18}\text{O}$ value of water and/or
196 the $\delta^{13}\text{C}$ value of CO_3^{2-} varied spatially and/or temporally. A previous study used clumped isotope
197 thermometry for carbonates in Mighei-type (CM) chondrites and demonstrated that the $\delta^{18}\text{O}$ values of
198 water are variable between samples¹⁶.

199

200 Mass balance calculations^{24,25} and the O isotope composition of the putative, early solar system
201 water^{26,27} suggest that prior to the onset of alteration, water in the CI and other carbonaceous chondrites

202 had a significantly higher $\Delta^{17}\text{O}$ value, and possibly $\delta^{18}\text{O}$ value, than the anhydrous silicates²⁸. Thus,
203 as alteration progressed, the $\Delta^{17}\text{O}$ value, and possibly the $\delta^{18}\text{O}$ value, of the altering fluid would have
204 decreased^{24,25}. The $\Delta^{17}\text{O}$ values of the carbonates and fluid will be identical at equilibrium, and thus,
205 the $\Delta^{17}\text{O}$ values of the carbonates are a measure of the degree of progress of water-rock interactions.
206 The $\Delta^{17}\text{O}$ values of the dolomite in the Ryugu and Ivuna samples are systematically lower than those
207 of the calcite, and the Ryugu and Ivuna carbonates show resolvable $\Delta^{17}\text{O}$ variations beyond
208 uncertainties (Fig. 2b). Therefore, the calcite with systematically higher $\Delta^{17}\text{O}$ values formed from less
209 “evolved” fluids, and crystallized earlier than the dolomite. The fact that calcite is more prevalent in
210 less-altered areas, as shown by primary anhydrous silicates, suggests that Ca was more easily leached
211 during incipient aqueous alteration than Mg, allowing the formation of calcite before dolomite.

212

213 Like O isotopes, the C isotope compositions of carbonates are determined not only by their formation
214 temperatures but also by the $\delta^{13}\text{C}$ values of dissolved CO_3^{2-} . The C isotope composition of CO_3^{2-}
215 could have varied due to (i) Rayleigh-type isotopic fractionation as a result of the preferential escape
216 of ^{12}C -rich gaseous species like CH_4 (ref.¹⁶), (ii) the progressive formation of carbonates, i.e.,
217 fractional crystallization, (iii) the mixing of two or more C reservoirs with distinct $\delta^{13}\text{C}$ values that
218 supplied CO_3^{2-} (ref.¹⁹), and (iv) the change in the chemical speciation of the C-bearing gaseous species,
219 such as CO_2 , CO , and CH_4 , due to varying O and H partial pressures. Rayleigh-type isotopic
220 fractionation was not the primary mechanism for producing the observed $\delta^{13}\text{C}$ variation because it
221 would have resulted in higher $\delta^{13}\text{C}$ values in the dolomite, which formed from the more evolved fluids
222 than the calcite, whereas the opposite is observed. The influence of fractional crystallization during
223 carbonate formation was also minimal because the rare calcite that formed early presumably when a
224 larger CO_3^{2-} pool was available displays a larger $\delta^{13}\text{C}$ variation than the more common dolomite,
225 which is opposite to what one would expect in this scenario.

226

227 A previous study advocated that the observed $\delta^{13}\text{C}$ variation resulted from the mixing of C reservoirs
228 with distinct $\delta^{13}\text{C}$ values reflecting the spatially heterogeneous distribution of different C reservoirs¹⁹.
229 Possible C reservoirs include C-bearing gaseous species such as CO_2 , CO , and CH_4 , originally accreted
230 in ices, and organic matter, and the previous study invoked CO_2 -bearing ices as a ^{13}C -rich reservoir¹⁹.
231 However, the mixing timescales of gaseous species in the Ryugu/CI parent asteroids would have been
232 short unless the permeability was extremely low. Therefore, the spatially heterogeneous distribution
233 of C reservoirs would have not persisted for long. Furthermore, it is unclear why the calcite has
234 commonly higher $\delta^{13}\text{C}$ values than the dolomite, and calcite with lower $\delta^{13}\text{C}$ values is generally absent.

235

236 **Temporal change in oxygen fugacity and gaseous species**

237 Instead of spatial heterogeneity, the temporal variation in the $\delta^{13}\text{C}$ values of the C reservoirs and their

238 chemical speciation likely occurred due to a change in O partial pressure, or more precisely, O fugacity
239 (f_{O_2}), which is O partial pressure corrected for nonideal gas behaviour. Oxygen fugacity varied along
240 with the production of H_2 via the oxidation of Fe in metal and silicates by H_2O and the subsequent
241 escape of H_2 from the system, perhaps by diffusion or by making fractures in the parent body²⁹. Thus,
242 f_{O_2} was determined by the relative rates of the production and escape of H_2 ; in this scenario, f_{O_2} would
243 have at first decreased and then increased. In the case of CM chondrites, the amount of Fe^{3+} in their
244 matrices increases with increasing alteration³⁰, which is in line with this scenario.

245

246 The Fe and Mn abundances of terrestrial carbonates that reflect the Fe^{2+} and Mn^{2+} activities in fluids
247 have been used to infer the redox conditions under which they precipitated³¹. However, the Fe and Mn
248 abundances of Ryugu and Ivuna carbonates were likely controlled not only by redox conditions but
249 also by the amounts of these cations leached from primary minerals during the progressive aqueous
250 alteration³². Therefore, the zoning of Fe and Mn observed in the dolomite grains may not be a direct
251 proxy for the temporal change in f_{O_2} . Instead, here we propose that the $\delta^{13}C$ values of Ryugu and
252 Ivuna carbonates represent a record of such temporal f_{O_2} variation.

253

254 To see how the $\delta^{13}C$ values of carbonates will change with varying f_{O_2} , we consider a rather simple
255 model, where gaseous CO_2 and CO and carbonates (and dissolved CO_2 , HCO_3^- , and CO_3^{2-}) are in C
256 isotopic equilibrium, and the CO_2/CO ratio increases, corresponding to an increase in f_{O_2} . In cometary
257 ices, CO_2 and CO are the most abundant C-bearing chemical species³³, and the Ryugu/CI parent bodies
258 would have accreted significant amounts of CO_2 - and CO -bearing ices if they formed in the distal
259 solar system^{11,28}. At the earliest stage of aqueous alteration, the CO_2/CO ratio may have been
260 characterized by that of the accreted ices, which may be around unity or higher as observed for
261 cometary ices^{33,34}. We assume that the $\delta^{13}C$ value of the bulk gas ($CO_2 + CO$), $\delta^{13}C_{bulk}$, is constant
262 regardless of the CO_2/CO ratio. Then, the $\delta^{13}C_{bulk}$ is given by mass balance as $\delta^{13}C_{bulk} = x \delta^{13}C_{CO_2} +$
263 $(1 - x) \delta^{13}C_{CO}$, where x is the mole fraction of CO_2 defined by $x = CO_2/(CO_2 + CO)$, $\delta^{13}C_{CO_2}$ and
264 $\delta^{13}C_{CO}$ are the $\delta^{13}C$ values of CO_2 and CO , respectively. Thus, using Δ defined by $\delta^{13}C_{CO_2} - \delta^{13}C_{CO}$,
265 $\delta^{13}C_{CO_2}$ and $\delta^{13}C_{CO}$ are given by $\delta^{13}C_{CO_2} = \delta^{13}C_{bulk} + (1 - x) \Delta$ and $\delta^{13}C_{CO} = \delta^{13}C_{bulk} - x \Delta$, respectively.
266 The Δ value is approximated by $1000 \ln \alpha$, where α is the C isotopic fractionation factor between CO_2
267 and CO defined by $(^{13}C/^{12}C)_{CO_2}/(^{13}C/^{12}C)_{CO}$ and is positive at all temperatures (+93, +76, and +48‰
268 at 0, 40, and 150 °C, respectively^{21,35}). Therefore, with increasing x (and f_{O_2}), both the $\delta^{13}C$ values of
269 CO_2 and CO will decrease monotonically, and the $\delta^{13}C$ values of carbonates will also decrease. Thus,
270 in this simple model, a $\delta^{13}C$ variation of carbonates comparable to the observation (~40‰) is expected
271 if the x value varies from 0.5 to 1 (Fig. 3). The redox states evolved within a few million years after
272 the birth of the solar system as inferred from the ^{53}Mn - ^{53}Cr chronometry of Ryugu/CI dolomite^{8,10,20,36}.
273 The presence of CH_4 , another possible reducing gas, does not change this conclusion because the

274 behaviour of CH₄ in terms of C isotopic fractionation against CO₂ is quite similar to that of CO (ref.²¹).
275 Our model where CO₂ and CO are in C isotopic equilibrium at low temperatures requires the presence
276 of as yet unidentified processes/catalysts. The isotopic equilibrium in thermally matured natural gases
277 has been recently discussed³⁷.

278

279 The characteristic $\delta^{13}\text{C}$ values of Ryugu and Ivuna carbonates are not observed for other aqueously
280 altered meteorites such as CM chondrites and the ungrouped carbonaceous chondrite Tagish
281 Lake^{19,38,39}, suggesting that the redox conditions as well as the thermal history and accreted materials
282 are unique to their parent bodies. For instance, the $\delta^{13}\text{C}$ values of CM calcite are variable like Ryugu/CI
283 calcite, but the highest reported value ($\sim+80\%$) in CM calcite is lower than that of Ryugu/CI calcite
284 ($+108\%$) (Extended Data Fig. 2). Furthermore, the $\delta^{13}\text{C}$ values of CM dolomite are also variable from
285 $\sim+40$ to $\sim+60\%$, which is in contrast to the homogeneous $\delta^{13}\text{C}$ values observed for Ryugu/CI dolomite.
286 Iron in CI chondrites is dominated by octahedral Fe³⁺ and indicates more oxidized conditions than CM
287 chondrites³⁰, which is consistent with the homogeneous $\delta^{13}\text{C}$ values of Ryugu/CI dolomite.

288

289 Because the $\delta^{13}\text{C}$ values of the Ryugu/CI dolomite are commonly lower and more homogeneous than
290 those of the calcite, the dolomite likely formed at higher $f\text{O}_2$ and/or temperature than the calcite. This,
291 combined with the O isotope signatures of the carbonates, implies that the calcite formed during
292 prograde alteration over wide ranges of $f\text{O}_2$ and temperature, whereas the dolomite formed later during
293 retrograde cooling when the aqueous fluids and silicates approached O isotopic equilibrium. Therefore,
294 when the dolomite formed, the $f\text{O}_2$ was likely high enough that the major gaseous C reservoir was CO₂
295 (i.e., $x \sim 1$). If correct, the $\delta^{13}\text{C}$ value of CO₂ in C isotopic equilibrium with the dolomite, which has
296 the average $\delta^{13}\text{C}$ value of $\sim+70\%$, would equal the $\delta^{13}\text{C}$ value of the bulk gas. Using the C isotopic
297 fractionation factor between dolomite and CO₂, $(^{13}\text{C}/^{12}\text{C})_{\text{dolomite}}/(^{13}\text{C}/^{12}\text{C})_{\text{CO}_2}$, of ~ 1.0092 at 40 °C or
298 ~ 0.9951 at 150 °C (refs.^{40,41}), the $\delta^{13}\text{C}_{\text{bulk}}$ ($= \delta^{13}\text{C}_{\text{CO}_2}$) value is estimated to be between $+61\%$ and
299 $+75\%$.

300

301 The above simple model implies a $\delta^{13}\text{C}$ value higher than $+60\%$ for C-bearing molecules originally
302 accreted in ices. Such ¹³C-rich compositions are not common among solar system materials other than
303 meteoritic carbonates and water-soluble organic compounds⁴². A similar level of ¹³C-enrichment ($\delta^{13}\text{C}$
304 $= +65 \pm 51\%$), albeit with large uncertainty, has been reported for CO₂ in the coma of 67P/Churyumov-
305 Gerasimenko⁴³. The mechanism to produce ¹³C-rich compositions is not well understood, but self-
306 shielding during CO photodissociation in the solar nebula or the parent molecular cloud of the solar
307 system is a possible mechanism⁴⁴⁻⁴⁶. Thus, the inferred ¹³C-rich composition of C-bearing molecular
308 ices would have resulted from such physicochemical reactions^{47,48}, and we concluded that the
309 Ryugu/CI parent bodies accreted materials that originated from these cold environments.

310

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319

320 **Author contributions**

321 W.F., N.K., K.N., N.S, and H.Y. designed this study and analysed the samples. W.F., N.K., K.N., C.A.,
322 and H.Y. were involved in data reduction and data interpretation. W.F. wrote the paper with support
323 and approval of all co-authors.

324

325 **Competing interests**

326 The authors declare no competing interests.

327

Table 1. $\delta^{18}\text{O}$, $\delta^{17}\text{O}$, $\Delta^{17}\text{O}$, and $\delta^{13}\text{C}$ values of carbonates in Ryugu and Ivuna samples.

Samples	$\delta^{18}\text{O}$ (‰)	2 σ	$\delta^{17}\text{O}$ (‰)	2 σ	$\Delta^{17}\text{O}$ (‰)	2 σ	$\delta^{13}\text{C}$ (‰)	2 σ
Ryugu C0002, calcite								
<i>Calcite#1a</i>	23.5	0.8	12.5	1.6	0.2	1.5	98.1	4.9
<i>Calcite#1b</i>	23.5	0.8	12.5	1.6	0.2	1.5	92.7	4.8
Calcite#1ave.	23.5	0.8	12.5	1.6	0.2	1.5	95.4	3.4
Calcite#2	38.4	0.6	22.2	1.1	2.2	1.1	101.7	4.8
Calcite#3-1	44.3	0.8	24.6	1.4	1.6	1.5	89.9	5.2
<i>Calcite#3-2a</i>	46.3	0.8	25.9	1.6	1.9	1.7	76.2	5.7
<i>Calcite#3-2b</i>	46.3	0.8	25.9	1.6	1.9	1.7	84.5	6.5
<i>Calcite#3-2c</i>	46.3	0.8	25.9	1.6	1.9	1.7	81.0	5.9
Calcite#3-2ave.	46.3	0.8	25.9	1.6	1.9	1.7	80.6	3.5
Calcite#3-3	44.5	1.2	24.9	1.5	1.8	1.4	84.1	6.2
Calcite#3-4	42.9	1.2	23.3	1.3	1.0	1.4	87.0	5.6
Calcite#4-1	n.d.		n.d.		n.d.		88.2	5.2
Calcite#4-2	n.d.		n.d.		n.d.		86.1	4.8
<i>Calcite#5a</i>	41.1	1.2	24.2	1.4	2.9	1.4	93.9	4.8
<i>Calcite#5b</i>	40.9	1.2	23.2	1.3	1.9	1.4	93.9	4.8
Calcite#5ave.	41.0	0.8	23.7	1.0	2.4	1.0	93.9	4.8
Ivuna, calcite								
Calcite#1	41.6	1.0	22.5	1.3	0.9	1.4	101.5	4.1
Calcite#2	41.5	1.0	23.4	1.3	1.8	1.4	104.8	4.8
Calcite#3	40.7	1.1	21.9	1.6	0.8	1.4	107.1	4.7
Calcite#5	33.9	1.0	20.0	1.3	2.4	1.4	81.4	3.8
Calcite#6	41.1	1.0	24.0	1.4	2.6	1.4	103.9	6.0
Calcite#7	38.0	1.0	20.2	1.4	0.4	1.4	98.0	5.1
Calcite#8-1	37.6	1.0	20.6	1.3	1.1	1.4	79.5	4.4
Calcite#8-2	37.0	1.0	20.0	1.3	0.8	1.4	89.0	5.2
<i>Calcite#9a</i>	36.0	1.0	20.2	1.3	1.5	1.4	106.6	5.8
<i>Calcite#9b</i>	36.0	1.0	20.2	1.3	1.5	1.4	109.9	5.1
<i>Calcite#9c</i>	36.0	1.0	20.2	1.3	1.5	1.4	106.7	4.8
Calcite#9ave.	36.0	1.0	20.2	1.3	1.5	1.4	107.8	3.0
<i>Calcite#10a</i>	43.6	0.6	22.3	1.5	-0.4	1.4	65.4	4.7
<i>Calcite#10b</i>	40.9	0.7	21.2	1.2	-0.1	1.2	65.4	4.7
Calcite#10ave.	42.2	0.5	21.7	1.0	-0.3	0.9	65.4	4.7

Ryugu A0058, dolomite								
<i>Dolomite#5</i>	(27.0)	(0.9)	(14.2)	(1.0)	(0.2)	(0.9)	67.7	1.5
<i>Dolomite#5</i>	(27.0)	(0.9)	(14.2)	(1.0)	(0.2)	(0.9)	67.2	1.2
<i>Dolomite#5ave.</i>	(27.0)	(0.9)	(14.2)	(1.0)	(0.2)	(0.9)	67.5	1.0
<i>Dolomite#2</i>	(29.0)	(1.0)	(15.0)	(1.0)	(0.0)	(0.9)	74.8	1.5
<i>Dolomite#4</i>	(30.0)	(0.9)	(15.8)	(1.0)	(0.2)	(0.9)	72.1	1.3
<i>Dolomite#1</i>	(29.9)	(0.9)	(14.8)	(1.0)	(-0.7)	(0.9)	71.3	1.2
<i>Dolomite#3</i>	(29.5)	(0.8)	(15.7)	(1.0)	(0.4)	(0.9)	74.5	1.5
Ryugu C0002, dolomite								
<i>Dolomite#3a</i>	27.3	1.0	15.2	1.3	1.0	0.9	72.1	1.3
<i>Dolomite#3b</i>	28.1	1.0	14.7	1.3	0.1	0.9	72.1	1.3
<i>Dolomite#3ave.</i>	27.7	0.7	14.9	0.9	0.6	0.6	72.1	1.3
<i>Dolomite#4</i>	28.3	1.0	15.3	1.3	0.6	0.9	70.1	1.3
<i>Dolomite#1a</i>	28.6	1.0	15.6	1.3	0.7	0.9	68.1	1.3
<i>Dolomite#1b</i>	28.7	1.0	15.1	1.3	0.2	0.9	68.1	1.3
<i>Dolomite#1ave.</i>	28.7	0.7	15.4	0.9	0.5	0.6	68.1	1.3
<i>Dolomite#2a</i>	26.7	1.0	14.1	1.3	0.2	0.9	69.4	1.3
<i>Dolomite#2b</i>	27.7	1.0	14.1	1.3	-0.3	0.9	69.5	1.3
<i>Dolomite#2ave.</i>	27.2	0.7	14.1	0.9	0.0	0.6	69.4	0.9
Ivuna, dolomite								
<i>Dolomite#1</i>	(29.0)	(0.7)	(15.6)	(0.8)	(0.5)	(0.9)	68.1	1.3
<i>Dolomite#7</i>	(30.8)	(0.7)	(16.0)	(0.8)	(0.0)	(0.7)	68.6	1.1
<i>Dolomite#6</i>	(29.1)	(0.8)	(15.3)	(0.8)	(0.2)	(0.9)	72.3	1.2
<i>Dolomite#5</i>	(28.8)	(0.8)	(16.3)	(0.8)	(1.3)	(0.9)	67.2	1.2
<i>Dolomite#4</i>	(26.5)	(0.9)	(14.4)	(0.9)	(0.7)	(1.0)	68.3	1.3
<i>Dolomite#2a</i>	(29.6)	(0.9)	(15.1)	(0.9)	(-0.3)	(0.8)	67.4	1.3
<i>Dolomite#2b</i>	(29.6)	(0.9)	(15.1)	(0.9)	(-0.3)	(0.8)	65.6	1.3
<i>Dolomite#2c</i>	(29.6)	(0.9)	(15.1)	(0.9)	(-0.3)	(0.8)	67.4	1.3
<i>Dolomite#2ave.</i>	(29.6)	(0.9)	(15.1)	(0.9)	(-0.3)	(0.8)	66.8	0.7
<i>Dolomite#3</i>	(29.2)	(1.0)	(15.4)	(1.0)	(0.2)	(1.1)	68.8	1.2

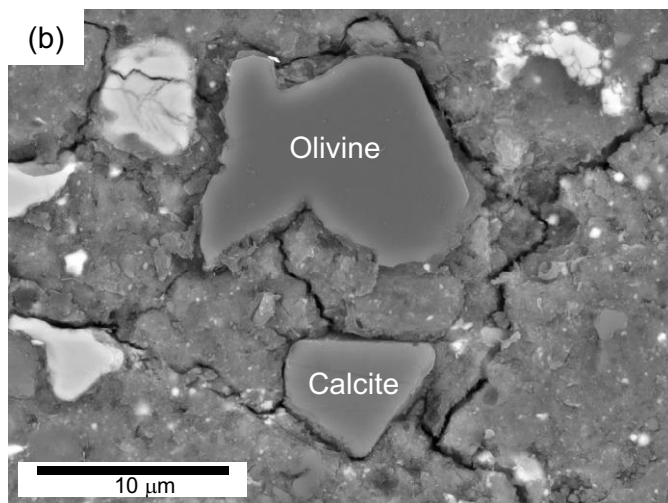
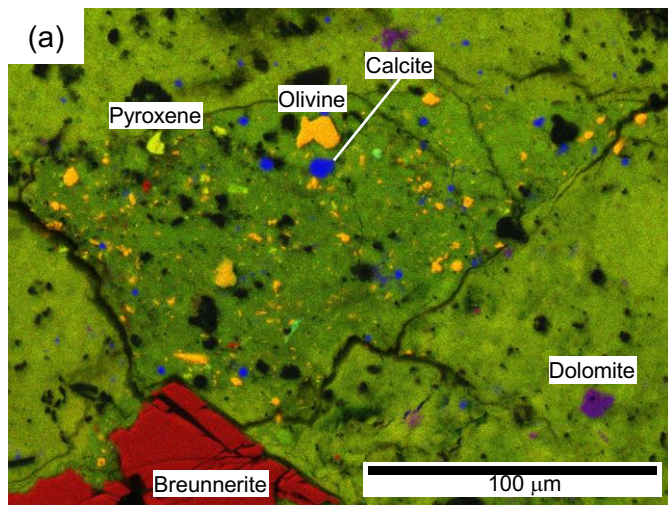
n.d.: Not determined.

The O isotope compositions of the Ryugu A0058 and Ivuna dolomite, shown in parentheses, are taken from Yokoyama et al. (2022) (ref.⁸)

2 σ errors are either external reproducibility (2SD) of standard measurements or internal precision (2SE) of the data within single measurements, whichever is the largest.

In case that we analysed single grains multiple times, as shown in *Italic*, we averaged the data and calculated the corresponding uncertainties by propagating individual errors.

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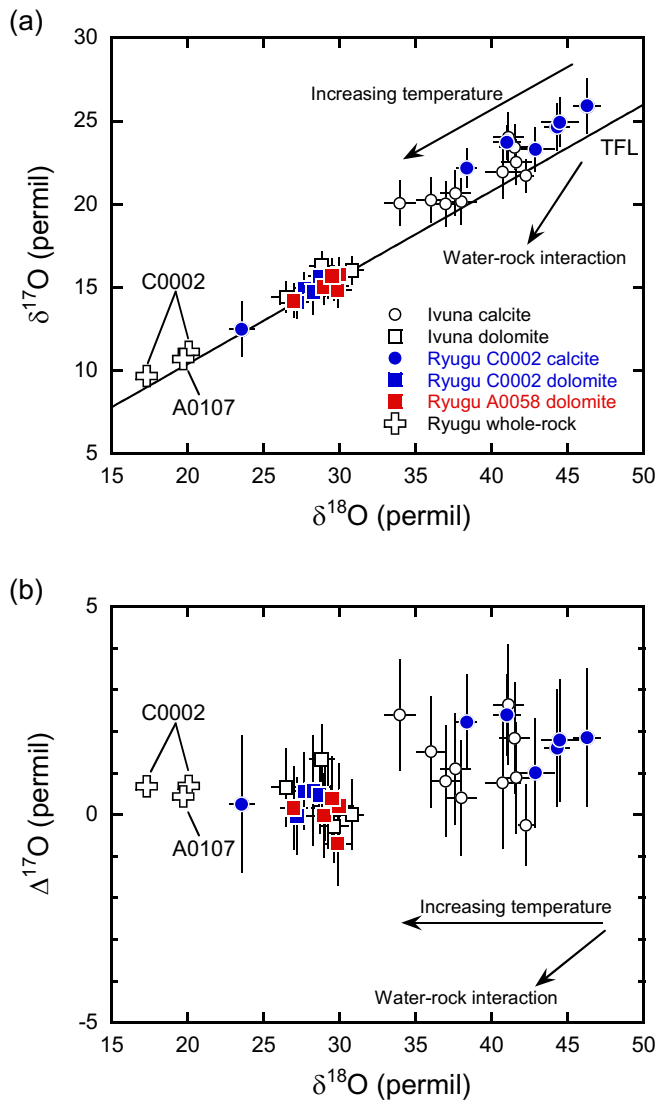
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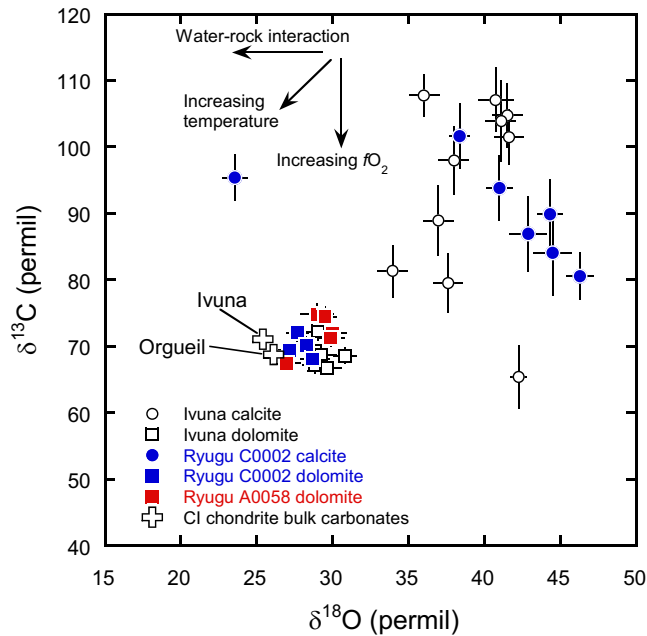
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Fig. 1. Calcite grains in the Ryugu C0002 sample. (a) Mg (red), Si (green), and Ca (blue) elemental maps showing the distribution of calcite grains. Calcite grains (blue) in the Ryugu and Ivuna samples can be found in limited areas with Mg-rich olivine (yellow) and pyroxene (light green). Purple grains are dolomite. The large red grain is breunnerite. (b) Backscattered electron image (BEI) of a calcite grain.



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337 **Fig. 2. Oxygen isotope compositions of the calcite and dolomite in Ryugu and Ivuna samples.** The
 338 whole-rock O isotope compositions of the Ryugu A0107 and C0002 samples are also shown for
 339 reference⁸. The changes in O isotope compositions due to variable formation temperatures and
 340 water-rock interaction are illustrated by arrows. (a) Oxygen three-isotope plot showing $\delta^{18}\text{O}$ vs. $\delta^{17}\text{O}$ values.
 341 TFL: Terrestrial fractionation line defined as $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$. (b) $\delta^{18}\text{O}$ vs. $\Delta^{17}\text{O}$ values. Data are
 342 presented as mean values $\pm 2\sigma$ errors which are either external reproducibility (2SD, $N = 6-20$
 343 depending on the measurement sessions) of standard measurements or internal precision (2SE) of the
 344 data within single measurements, whichever is the largest.



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Fig. 3. Comparison between C and O isotope compositions of the calcite and dolomite in Ryugu and Ivuna samples. Errors are 2σ (see also Table 1). The values of carbonates measured for whole-rock CI chondrites (Ivuna and Orgueil) are also shown for reference¹⁸. The changes in C and O isotope compositions due to variable formation temperatures and O fugacity, and water-rock interaction are illustrated by arrows. The calcite shows much larger variations in both C and O isotope compositions than the dolomite. Note that no simple correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values can be seen. Data are presented as mean values $\pm 2\sigma$ errors which are either external reproducibility (2SD , $N = 6\text{--}20$ depending on the measurement sessions) of standard measurements or internal precision (2SE) of the data within single measurements, whichever is the largest.

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463 **Methods**

464 **Isotope measurement using ion microprobe**

465 We produced the polished sections of Ryugu samples A0058-C1001 and C0002-C1001, and Ivuna
466 embedded in epoxy^{8,28}. The polished sections were coated with a thin (~5 nm) gold film using a Leica
467 EM ACE600 coater at Hokkaido University for backscattered electron (BSE) and X-ray imaging, and
468 elemental analysis before *in-situ* O and C isotope measurements. We observed their mineralogy and
469 petrology and located carbonate grains using a field-emission scanning electron microscope (FE-SEM;
470 JEOL JSM-7000F) equipped with an energy dispersive X-ray spectrometer (EDS; Oxford X-Max 150)
471 at Hokkaido University. The beam currents were ~2 nA and ~1 nA for the X-ray mapping and
472 quantitative analysis, respectively. Quantitative calculations were conducted using Oxford AZtec
473 software.

474

475 We selected five and four dolomite grains from the Ryugu samples A0058 and C0002, respectively,
476 and nine calcite grains from C0002 for isotope analyses. We also analysed seven dolomite grains and
477 ten calcite grains from Ivuna. Before the isotope analyses, the samples were coated again with an
478 additional thin (~65 nm) gold film.

479

480 We conducted the O and C isotope measurements of the selected carbonate grains using secondary ion
481 mass spectrometry (SIMS; CAMECA ims-1280HR) at Hokkaido University. Instrumental mass
482 fractionation (IMF) was corrected using the UWC3 calcite standard and a series of dolomite-ankerite
483 standards from the WiscSIMS laboratory for calcite and dolomite, respectively⁴⁹⁻⁵¹. Measurement
484 spots were observed using the FE-SEM after the SIMS measurements and data from spots with
485 inclusions or overlapping matrix minerals were rejected. The reported uncertainties (2σ) of isotope
486 compositions are the larger of the external reproducibility, i.e., 2 standard deviation (2SD) of standard
487 measurements or internal precision, i.e., 2 standard error (2SE) of data within single measurements of
488 unknown samples.

489

490 The procedures of O isotope measurement of dolomite were described by a previous study⁸. For O
491 isotope measurement of calcite, as previously described for the O isotope measurement of olivine²⁸,
492 secondary $^{16}\text{O}^-$, $^{17}\text{O}^-$, and $^{18}\text{O}^-$ ions produced by a Cs^+ primary ion beam (~30 pA, ~3 μm) were
493 simultaneously collected using Faraday cup (FC: $10^{11} \Omega$), electron multiplier (EM), and EM detectors,
494 respectively. Mass resolving power was >6000 sufficient to resolve $^{17}\text{O}^-$ from $^{16}\text{OH}^-$. The secondary
495 ion intensities of $^{16}\text{O}^-$ were $2\text{-}3 \times 10^7$ cps. The measurement time was 240 seconds. The $^{16}\text{OH}^-$ count
496 rate was measured immediately after each measurement, and we made a small tail correction on $^{17}\text{O}^-$;
497 its contribution to $^{17}\text{O}^-$ was typically less than ~0.1‰ and up to ~0.5‰ for a few analyses. The typical
498 uncertainties of $\delta^{17}\text{O}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ values were 1.4, 0.9, and 1.4‰, respectively.

499

500 For C isotope measurement of dolomite, secondary $^{12}\text{C}^-$ and $^{13}\text{C}^-$ ions produced by a Cs^+ primary ion
501 (~ 50 pA, ~ 2 μm) were simultaneously collected using FC (10^{12} Ω) and EM detectors, respectively. We
502 scanned the primary ion beam across 1×1 μm -sized areas to make the SIMS pits shallower and
503 suppress ratio drifts during measurements. Mass resolving power was ~ 4500 , sufficient to resolve $^{13}\text{C}^-$
504 from $^{12}\text{CH}^-$. The secondary ion intensities of $^{12}\text{C}^-$ were $5\text{-}6 \times 10^5$ cps. The measurement time was 480
505 seconds. The typical uncertainty of $\delta^{13}\text{C}$ values was 1.3%.

506

507 For C isotope measurement of calcite, secondary $^{12}\text{C}^-$ and $^{13}\text{C}^-$ ions produced by a Cs^+ primary ion
508 (~ 3 pA, ~ 1 μm) were simultaneously collected using two EM detectors. We scanned the primary ion
509 beam on 1×1 μm -sized areas. Mass resolving power was ~ 4500 . The secondary ion intensities of $^{12}\text{C}^-$
510 were $\sim 2 \times 10^4$ cps. The measurement time was 800 seconds. The typical uncertainty of $\delta^{13}\text{C}$ values
511 was 5.1%. The larger uncertainty of the calcite measurement was due to the smaller primary ion beam
512 intensity than for the dolomite measurement to analyse small calcite grains.

513

514 **Data availability**

515 All data generated or analysed during this study are included in this published article (and its
516 supplementary information files) and are available via Zenodo
517 (<https://doi.org/10.5281/zenodo.7957625>). As the initial analysis of Ryugu samples collected by the
518 Hayabusa2 spacecraft, the specimens analysed in this study were allocated to us by JAXA. The Ivuna
519 specimen used in this study was kindly provided by the Natural History Museum, UK.

520

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