

# Contribution of Ryugu-like material to Earth's volatile inventory by Cu and Zn isotopic analysis

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# Contribution of Ryugu-like material to Earth's volatile inventory by Cu and Zn isotopic analysis

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#### 108 Abstract (162 words)

109 Initial analyses showed that asteroid Ryugu's composition is close to CI (Ivuna-like) 110 carbonaceous chondrites - the chemically most primitive meteorites, characterized by near-solar 111 abundances for most elements. However, some isotopic signatures (e.g., Ti, Cr) overlap with other 112 carbonaceous chondrite (CC) groups, so the details of the link between Ryugu and the CI chondrites are not fully clear yet. Here we show that Ryugu and CI chondrites have the same zinc 113 114 and copper isotopic composition. As the various chondrite groups have very distinct Zn and Cu isotopic signatures, our results point at a common genetic heritage between Ryugu and CI 115 116 chondrites, ruling out any affinity with other CC groups. Since Ryugu's pristine samples match 117 the solar elemental composition for many elements, their Zn and Cu isotopic compositions likely 118 represent the best estimates of the solar composition. Earth's mass-independent Zn isotopic 119 composition is intermediate between Ryugu/CC and non-carbonaceous chondrites, suggesting a 120 contribution of Ryugu-like material to Earth's budgets of Zn and other moderately volatile 121 elements.

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#### 123 Main text

124 Introduction. Ivuna-type (CI) carbonaceous chondrites (CCs) have elemental abundances that 125 are the closest to the composition of the solar photosphere (e.g., [1]) (the exceptions being H, C, 126 N, O, Li and the noble gases). Thus, the CIs are key reference samples for investigating how early Solar System processes shaped the compositions of the planets and their building blocks. The 127 128 return of the Havabusa2 spacecraft in December 2020, after two successful touchdown and 129 sampling events on the Cb-type asteroid (162173) Ryugu<sup>2,3</sup>, offers the unprecedented opportunity 130 to study volatile element fractionation processes using samples unaffected by terrestrial alteration, 131 in particular water incorporation. Initial studies on bulk chemical and isotopic compositions revealed similarities between Ryugu and CIs<sup>4-7</sup>. However, Ryugu samples exhibit slightly higher 132  $\Delta^{17}$ O than the average from other CI samples, Orgueil and Ivuna, which is interpreted in terms of 133 134 original heterogeneity between small samples, or contamination of the meteorites by terrestrial 135 water incorporated into the structure of the alteration minerals (e.g., phyllosilicates, sulfates, iron oxides and hydroxides), not adsorbed to the surfaces<sup>5</sup>. Similarly, although Ti and Cr isotope 136 137 compositions show that asteroid Ryugu formed in the CC reservoir, it was not possible to establish 138 a clear genetic link to just one of the CC groups because the Cr and Ti isotopic compositions of 139 Ryugu overlap not only with Ivuna-like (CI) but also with the Bencubbin-like (CB)<sup>5</sup>, Renazzo-like 140 (CR)<sup>5</sup> and High-iron (CH) groups. However, the low volatile contents of these three groups of 141 meteorites, as well as the metal-rich nature of the CB and CH chondrites, argue against any affinity with Ryugu<sup>5,6</sup>. Thus, because CI chondrites and Ryugu samples share the same Ti and Cr 142 nucleosynthetic signatures, as well as similar mineralogical and elemental compositions<sup>5,6</sup>, it has 143 been proposed that they formed contemporaneously from the same outer Solar System reservoir<sup>3,5-</sup> 144 7. 145

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147 Material akin to carbonaceous chondrites such as Ryugu and the parent body of the CIs could 148 have delivered significant fractions of the moderately and highly volatile elements present in inner 149 Solar System planets (e.g., 8-13). Because Ryugu samples have been handled carefully to avoid 150 possible contamination, they are ideally suited to estimate the solar composition and assess the 151 contribution of these outer Solar System objects to the inventory of volatile elements in the 152 terrestrial planets. Highly volatile and moderately volatile elements are defined as elements with 153 50% condensation temperatures (T<sub>c</sub>) <665 K and 665–1135 K, respectively, under canonical nebular gas conditions at 10<sup>-4</sup> bar (e.g., 14). Zinc and Cu are ideal elements to investigate volatility-154 155 related processes, such as volatile element loss, during planetary accretion<sup>15</sup>, and are classified as 156 moderately volatile elements (MVE) (with T<sub>c</sub> of 726 K and 1037 K, respectively)<sup>14,16</sup>. 157 Carbonaceous chondrite groups display distinct Zn and Cu isotopic mass fractionation effects (e.g., 158 17-21), defining a trend from CIs to CKs (CK = Karoonda-like), with the CIs being the most 159 volatile-rich and isotopically heaviest (for both Zn and Cu) of the CC groups. We have measured 160 the Zn and Cu isotopic compositions of Ryugu samples to (i) verify the link between Ryugu and 161 CI chondrites for moderately volatile elements, and (ii) assess the contribution of Ryugu-like 162 material to the inventory of moderately volatile elements in Earth.

163

164 **Results.** The Zn and Cu isotope compositions for four Ryugu samples (see **Methods section**), 165 together with six CC samples [Alais (CI), Allende A and B (CV), Murchison (CM), Orgueil (CI), 166 Tagish Lake (C2-ungrouped) and Tarda (C2-ungrouped)], were determined following the same 167 analytical protocol, and on the same samples as in [5] (**Table 1**). Most of these CC samples have 168 previously been characterized for their Zn and Cu isotopic composition<sup>17-19,21</sup>, except Tarda. The 169 isotopic compositions are given as the permil deviations from the JMC-Lyon Zn and NIST

170 SRM976 Cu standards:

171 
$$\delta^{x} Zn = \left[\frac{\binom{x_{Zn}}{64_{Zn}}Sample}{\binom{x_{Zn}}{64_{Zn}}JMC-Lyon} - 1\right] \times 1000$$
(1)

172 where x = 66, 67 and 68.

173 
$$\delta^{65} \text{Cu} = \left[ \frac{\binom{65}{\text{Cu}}\text{Sample}}{\binom{65}{\text{Cu}}\text{SRM976}} - 1 \right] \times 1000$$
(2).

During the course of this study, the two standards gave  $\delta^{66}$ Zn of 0.00 ± 0.005 ‰ (2SE; n = 163; JMC-Lyon) and  $\delta^{65}$ Cu of 0.00 ± 0.02 ‰ (2SE; n = 54; NIST SRM976). Zinc isotope measurements are also corrected for mass-dependent fractionation using the exponential law<sup>22</sup>, with the normalizing ratio of <sup>68</sup>Zn/<sup>64</sup>Zn of 0.3856<sup>23</sup>. Zinc isotopic anomalies are quantified using the epsilon notation relative to the JMC Lyon standard, as follows:

179 
$$\epsilon^{66} Zn_{C} = \left[\frac{\left(\frac{6^{6}Zn}{6^{4}Zn}\right)Sample}{\left(\frac{6^{6}Zn}{6^{4}Zn}\right)JMC-Lyon} - 1\right] \times 10^{4}$$
(3)

180 where c is the normalizing ratio  ${}^{68}$ Zn/ ${}^{64}$ Zn.

181

The Ryugu samples span a very limited range of mass-dependent Zn isotopic compositions with  $\delta^{66}$ Zn from +0.41 ± 0.06 ‰ to +0.45 ± 0.02 ‰ (2SD), with an average value of +0.43 ± 0.05 ‰ (2SD, n = 48) (Fig. 1a and Table 1). The  $\delta^{65}$ Cu values for Ryugu samples range from 0.00 ± 0.08 ‰ to +0.09 ± 0.05 ‰, (average value of +0.04 ± 0.11 ‰, n = 8, 2SD) (Fig. 1b and Table 1). Zinc and Cu abundances also span limited ranges from 338 ± 4 ppm to 383 ± 6 ppm (average 361 ± 40 ppm, n = 4, 2SD), and from 133 ± 2 ppm to 168 ± 1 ppm (average 147 ± 37 ppm, n = 4, 2SD), respectively (Table 2). These values are higher than the abundances reported for any CI chondrite,

189 consistent with other element abundances for Ryugu samples relative to CIs (Fig. 1, Table 2), 190 although Ryugu samples have lower H<sub>2</sub>O contents than CIs<sup>5</sup>. It is worth noting that the samples from both landing sites show identical  $\delta^{66}$ Zn values (Fig. 1a). In addition, the soluble organic 191 192 matter (SOM) extractions of samples C0107 and A0106, which was done prior to purification of 193 Zn and Cu, do not seem to have affected the Zn and Cu isotope compositions of the Ryugu samples (see Methods section). All the CCs measured in this study have  $\delta^{66}$ Zn and  $\delta^{65}$ Cu values, as well 194 195 as Zn and Cu abundances, that are consistent with previous studies (e.g., [17-21]), except for the 196 Cu isotopic composition for Allende A, which is more similar to CO chondrites (Figs. 1b and 2). 197 We note, however, that until now only one other measurement of Allende has been reported in the literature<sup>19</sup>, and so the difference could represent heterogeneity in the different analyzed fractions 198 199 of Allende in this study and in [19]. Similar sample heterogeneities for Cu isotopic compositions 200 have been reported for several fragments of Orgueil<sup>21</sup>. The Ryugu samples exhibit Zn and Cu 201 isotopic compositions that are similar to the Alais and Orgueil samples analyzed in this study (Figs. 202 1 and 2). This is consistent with previous work on the bulk elemental, isotopic, and mineralogical 203 properties of these samples, which reveal a genetic link between the Ryugu samples and CI 204 chondrites, implying formation from the same outer Solar System reservoir<sup>4-6</sup>.

205

Discussion. Earlier work has shown that bulk CC chondrites define negative correlations in plots of  $\delta^{66}$ Zn versus 1/Zn<sup>17,18</sup> and  $\delta^{65}$ Cu versus 1/Cu<sup>19</sup>. The variable degree of volatile element depletion among the different CC groups reflect mixing of chemically and isotopically distinct reservoirs during their accretion (e.g., 17-19,24,25). The CI chondrites, along with Ryugu, are the least volatile depleted and isotopically heaviest (for both Zn and Cu) of the CC groups, while the most volatile depleted chondrites, the CVs, are the isotopically lightest (this study; [17-21]) (**Figs.** 

212 1 and 2). The CC trend is interpreted as the result of mixing of volatile-rich material enriched in 213 heavy Zn and Cu isotopes and volatile-poor material enriched in light Zn and Cu isotopes (e.g., 214 [17-19]). Similar correlations are observed for other moderately volatile elements in CCs, such as Te<sup>25</sup> and Rb<sup>26,27</sup> and their associated isotope compositions, which is interpreted as mixing between 215 216 matrix (volatile-rich) and chondrules (volatile-poor) (e.g., [17-19,24,26]). Such mixing between 217 distinct CC reservoirs is also observed in the relationships between  $\delta^{66}$ Zn and nucleosynthetic isotope anomalies, such as  $\varepsilon^{54}$ Cr (parts per ten thousand mass-independent variations of the 218 219 <sup>54</sup>Cr/<sup>52</sup>Cr ratio relative to a terrestrial standard) (Fig. 3) (e.g., [18]). Ryugu and the CIs have similar 220 Cu and Zn mass-dependent isotopic compositions and differ markedly from the CBs and CHs 221 (Figs. 1, 2 and 3). We can, therefore, exclude any genetic relationship to the CB or CH groups for 222 the Ryugu samples. A shared nucleosynthetic heritage between Ryugu and CI chondrites has been established based on their identical Ti and Cr nucleosynthetic isotope anomalies<sup>5,6</sup>. Our Zn and Cu 223 224 results show that this parentage extends to mass-dependent fractionation of moderately volatile 225 elements, strengthening the link between CI chondrites and Ryugu (Figs. 1, 2 and 3). The near 226 solar Zn and Cu relative abundances of the Ryugu samples, which are free of the potential 227 ambiguities of terrestrial alteration, suggests that the Zn and Cu isotopic compositions measured 228 for Ryugu and the CI chondrites most likely preserved the proto-Sun's composition<sup>1</sup> (Fig. 1c).

229

Our study also provides evidence for mass-independent Zn isotope variations ( $\epsilon^{66}$ Zn) in Ryugu samples (**Fig. 4 and Table 1**). These Zn isotopic anomalies are consistent with previous observations<sup>28,29</sup>. While non-carbonaceous chondrites (NCs) display negative  $\epsilon^{66}$ Zn (ordinary chondrites:  $-0.21 \pm 0.04$  ‱, 2SE, n = 12, [28,29]; enstatite chondrites:  $-0.19 \pm 0.08$  ‰, n = 8, [28,29]), the Ryugu samples and all CCs exhibit identical positive  $\epsilon^{66}$ Zn within error (+0.33 ± 0.04

235  $\infty$ , 2SE, with n = 7 for Ryugu (Table 1) and  $+0.39 \pm 0.07$   $\infty$ , n = 7 for CCs, respectively) with 236 the value previously reported for CC of  $+0.28 \pm 0.04$  ‰ (2SE, n = 11) [28,29]. It is worth noting that the first replicate of sample C0108 (measured at 100 ppb Zn) has an  $\epsilon^{66}$ Zn of  $-0.21 \pm 0.17$ 237 ‰, whereas the second C0108 replicate (measured at 250 ppb Zn) has an  $\varepsilon^{66}$ Zn of +0.35 ± 0.10 238 239 ‱ similar to all other Ryugu samples (see Methods section): the first replicate is thus considered 240 an outlier as it was analyzed at the lower concentration of 100 ppb and was excluded from the 241 mean value reported here. The reference geological material BHVO-2 and the Zn standard solution 242 IRMM 3702 measured during the first and second sessions have  $\epsilon^{66}$ Zn (-0.07 ± 0.15 ‰, 2SE, n 243 = 12;  $+0.02 \pm 0.11$  ‰, 2SE, n = 7, respectively), consistent within error with estimates for bulk 244 Earth (+0.015  $\pm$  0.075 ‰, 2SE, n = 4 [28] and -0.07  $\pm$  0.013 ‰, 2SE, n = 3 [29]). There are no 245 known terrestrial processes which can mass-independently fractionate Zn isotopes. The positive  $\varepsilon^{66}$ Zn values in the Ryugu samples, therefore, reinforce their genetic link with the CCs (Fig. 4). 246 247 Thus, the difference between the CCs and NCs, originally identified O and Cr isotope compositions<sup>30</sup>, and later with Ti, Ni and Mo anomalies<sup>31-36</sup>, appears to also hold for Zn isotopes. 248 249

Because meteorites show a large variability of isotope anomalies<sup>37</sup> and planetary accretion 250 is stochastic<sup>38-39</sup>, it is likely that Earth's composition does not reflect accretion from a single type 251 252 of material, both in terms of isotopic and elemental compositions. Although enstatite chondrites are isotopically closest to the Earth<sup>40</sup>, their chemical signatures are extreme and deviate 253 254 substantially from the bulk composition of Earth. Possible mixtures of primitive and thermally processed meteorites or their components (e.g., chondrules; [6, 41-43]) have been proposed to 255 explain the chemical and isotope composition of the Earth<sup>32,37,44-48</sup>. In particular, the mass-256 257 independent isotopic composition of Zn of the Earth appears intermediate between CCs and NCs.

258	Thus, our new data show that CC-like materials, potentially akin to Ryugu, have likely contributed
259	to the delivery of Zn and more generally the volatile elements to the Earth. Thus, following the
260	same approach as in [28,29], and using the average $\epsilon^{66}Zn$ = +0.33 $\pm$ 0.04 ‰ for Ryugu, +0.35 $\pm$
261	0.13 ‰ for CI [this study, 28, 29], $-0.20 \pm 0.04$ ‰ (2SE, n = 20) for NC (ordinary, enstatite from
262	[28,29]) and $-0.02 \pm 0.04$ ‱ for the BSE (2SE, n = 7, [28,29]), the mass fraction of Ryugu- or
263	CI-derived Zn in the BSE is estimated 33.5% or 32.2%, respectively. Thus, we find that $\sim$ 30% of
264	the terrestrial Zn derives from outer Solar System material, while the NC reservoir contributes to
265	$\sim$ 70% to the terrestrial Zn. Then, to account for the Zn abundances of the accreting materials by
266	Earth, we estimate the mass fractions of NC and Ryugu-like or CI-like bodies accreted by Earth
267	using the Zn abundance of the BSE of $53.5 \pm 2.7$ ppm [49], and the [Zn] <sub>Ryugu</sub> of $361 \pm 40$ ppm [this
268	study] and [Zn] <sub>CI</sub> of $309 \pm 43.8$ ppm [this study, 17,18,21]. Thus, up to ~5% of Ryugu-like material
269	(or ~6% of CI-like material) might be needed to account for Earth's Zn isotopic composition,
270	consistent with estimations from previous studies on Zn isotopic anomalies <sup>28,29</sup> and representing a
271	substantial contribution to the terrestrial budget of moderately volatile elements <sup>11,28,29</sup> .

272

#### 273 Methods

274 Major and trace elements. Zinc and copper isotopic compositions were measured in four 275 samples from the asteroid (162173) Ryugu [C0108, C0107, A0106-A0107 and A0106]. Fragments 276 A0106-A0107 and A0106 are coming from the first touchdown site, and C0108 and C0107 from the second touchdown site<sup>4-6</sup>. Samples A0106-A0107 and C0108 were pristine samples, whereas 277 278 A0106 and C0107 were treated for Soluble Organic Matter (SOM) extraction before chemical 279 purification (see Supplementary Table 1). In addition, six CCs [Alais, Allende A, Allende B, 280 Murchison, Orgueil, Tagish Lake and Tarda] were processed following the exact same protocol as 281 the Ryugu samples and were analyzed as controls. For each sample, ~25 mg of powder of all the

samples were dissolved at Tokyo Institute of Technology. Elemental abundances were determined
using Inductively-Coupled-Plasma Mass-Spectrometry (ICP-MS): major and trace elements for
A0106-A0107 and C0108 samples are from [5]. After chemical analysis, the same sample
solutions were used to determine Zn and Cu isotopic compositions: Zn fractions were preseparated, as well as 3% of the bulk rock dissolution for Cu purification which represent about 80100 ng of Cu.

288

289 Zinc and copper purification. All the CC meteorites (except Tarda) have previously been 290 measured for Cu and Zn isotopic compositions and were analyzed as controls. Further chemical 291 purifications of Zn and Cu on the same sample aliquots were conducted at the Institut de Physique 292 du Globe de Paris, using the procedure described by [50] for Zn, and by [51,52] for Cu. For Zn, samples were loaded in 1.5 mol.L<sup>-1</sup> HBr on 50 µL of AG1-X8 (200-400 mesh) anion exchange 293 294 resin in home-made PTFE columns. Matrix elements were washed by further addition of 2 mL of 1.5 mol.L<sup>-1</sup> HBr, and Zn was eluted using 2 mL of 0.5 mol.L<sup>-1</sup> HNO<sub>3</sub>. The collected samples were 295 then evaporated to dryness. For Cu, samples were loaded in 1 mL of 7 mol.L<sup>-1</sup> HCl on home-made 296 297 PTFE columns filled with 1.6 mL of AG-MP1 resin. After washing the resin with 8 mL of 7 mol.L<sup>-</sup> 298 <sup>1</sup> HCl, the Cu was collected with 16 mL of 7 mol.L<sup>-1</sup> HCl. Both procedures were repeated twice 299 to ensure clean Zn and Cu fraction. Procedural blank is < 0.3 ng of Zn, and 0.6 ng of Cu which is 300 negligible relative to the amount of Zn and Cu in the sample mass analyzed for the Ryugu samples 301 and the CCs.

302

303 Zinc and Cu measurements. Zinc and Cu isotope compositions were determined using a
 304 Neptune Plus Multi-Collector Inductively-Coupled-Plasma Mass-Spectrometer (MC-ICP-MS) at

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305	IPGP, using sample-standard bracketing for instrumental mass bias correction as in [50] for Zn
306	and [51,52] for Cu. Each replicate was analyzed 6–8 times for Zn and 1–5 times for Cu depending
307	on the amount of Cu available for each sample, and the reported errors are the two standard
308	deviations (2SD) of these repeated measurements. For the Zn measurements, the samples were
309	analyzed in two sessions with different sample solution concentrations: one at 100 ppb of Zn and
310	a second one at 250 ppb of Zn, with an uptake of 100 $\mu$ L.min <sup>-1</sup> . For the Cu measurements, the
311	samples were analyzed in one session at the concentration of 30 ppb of Cu, with the same uptake.
312	The high purity of the final Zn fraction is needed to remove isobaric and non-isobaric interferences
313	from the signal. Interference on <sup>64</sup> Zn by <sup>64</sup> Ni is corrected by measuring the intensity of the <sup>62</sup> Ni,
314	assuming natural abundances of Ni isotopes ( $^{62}$ Ni = 3.63%; $^{64}$ Ni = 0.93%). No N <sub>2</sub> was used during
315	the measurements, as this results in high background on mass 68 from ArN <sub>2</sub> . No interference on
316	mass 68.5 from Ba <sup>2+</sup> was detected during the sessions. The reference geological material BHVO-
317	2 and the Zn standard solution IRMM 3702 measured during the first and second sessions give
318	values consistent with the literature (e.g., [18,20]). However, during the first session, the Zn
319	fractions were measured at 100 ppb of Zn. All the Ryugu and CC samples had similar positive
320	$\epsilon^{66}$ Zn, except for the first replicate of sample C0108 which had a negative value. In other words,
321	all the samples plot below the mass-dependent equilibrium fractionation line in a $\delta^{68} Zn$ against
322	$\delta^{66}$ Zn plot, whereas the C0108 replicate falls above it ( <b>Supplementary Figure 1a</b> ). This motivated
323	our second session of measurements on replicates at higher concentrations (250 ppb of Zn) to
324	ensure that the observed $\epsilon^{66}$ Zn were not analytical artifacts. The second replicate of sample C0108,
325	analyzed at 250 ppb of Zn, shows the same isotopic signature as the rest of the Ryugu sample set
326	and plots below the mass-dependent fractionation line with a positive $\epsilon^{66} Zn$ (Supplementary

- 327 Figure 1b). In the discussion and associated figures, only the second replicate of sample C0108 is
- 328 considered and represented.
- 329

#### 330 Data availability

- All data referred to in this article can be found in the tables or source data.
- 332

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- 340

### 341 Author Contributions

- 342 F.M., M.P. and T.Y. designed the project. H.Y. and T.Y coordinated the isotopic analyses of the
- 343 samples among members of the Hayabusa2-initial-analysis chemistry team. M.P. and T.Y.
- 344 processed the samples and separated the Zn and Cu from the matrix. M.P. measured the Zn and
- 345 Cu isotopic compositions. M.P. and F.M. wrote the first draft of the manuscript, with contributions
- 346 from T.Y., W. D., Y. H., Y. A., J. A., C. M. O'D. A., S. A., Y. A., K. B., M. B., A. B., R. W. C.,
- 347 M. C., B.-G. C., N. D., A. M. D., T. D. R., W. F., R. F., I. G., M. K. H., Y. H., H. Hi., H. Ho., P.
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- 353

## 354 Competing Interests Statement

355 The authors declare no conflicts of interest.

Zn and Cu isotopes in Ryugu

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# 356 Tables

# 357 Table 1. Zinc and copper stable isotope of Ryugu samples and carbonaceous chondrites.

Sample	Туре	n <sup>a</sup> (Zn)	δ <sup>66</sup> Zn (‰)	2SD <sup>b</sup>	δ <sup>67</sup> Zn (‰)	2SD <sup>b</sup>	δ <sup>68</sup> Zn (‰)	2SD <sup>b</sup>	ε <sup>66</sup> Zn	2SE <sup>b</sup>	n <sup>a</sup> (Cu)	δ <sup>65</sup> Cu (‰)	2SD <sup>I</sup>
Ryugu													
C0108°		<u>8</u>	0.44	<u>0.05</u>	<u>0.70</u>	<u>0.10</u>	<u>0.91</u>	<u>0.09</u>	-0.21	0.17	5	0.00	0.08
Rpt		6	0.44	0.05	0.60	0.05	0.79	0.09	0.35	0.10			
C0107		8	0.42	0.06	0.57	0.10	0.75	0.09	0.37	0.11			
Rpt		6	0.41	0.05	0.60	0.10	0.76	0.13	0.29	0.11			
Average site C		20	0.43	0.05	0.62	0.13	0.81	0.17	0.34	0.06	5	0.00	0.08
A0106-A107		8	0.45	0.02	0.62	0.06	0.80	0.05	0.42	0.10	3	0.09	0.05
Rpt		6	0.41	0.06	0.59	0.08	0.75	0.11	0.33	0.03			
A0106		8	0.43	0.03	0.63	0.07	0.80	0.06	0.25	0.14			
Rpt		6	0.41	0.06	0.58	0.07	0.76	0.11	0.31	0.05			
Average site A		28	0.43	0.04	0.61	0.08	0.78	0.08	0.33	0.05	3	0.09	0.05
Average Ryugu		48	0.43	0.05	0.61	0.11	0.79	0.14	0.33	0.04	8	0.04	0.11
Carbonaceous chondrites													
Orgueil	CI1	8	0.52	0.06	0.67	0.11	0.91	0.06	0.62	0.15			
Rpt		8	0.52	0.09	0.71	0.09	0.96	0.17	0.33	0.14			
Average Orgueil		16	0.52	0.08	0.69	0.11	0.94	0.14	0.52	0.12	2	0.06	0.11
Alais	CI1	8	0.45	0.07	0.62	0.11	0.82	0.08	0.35	0.19			
Rpt		6	0.44	0.07	0.62	0.10	0.80	0.12	0.35	0.09			
Average Alais		14	0.45	0.07	0.62	0.10	0.80	0.10	0.35	0.11	2	0.17	0.00.

Paquet et al		Zn and Cu isotopes in Ryugu Nature Astronomy											
	C2-												
Tagish Lake	ung	8	0.43	0.02	0.55	0.12	0.74	0.06	0.53	0.08			
Rpt Average Tagish	C	6	0.41	0.08	0.54	0.08	0.73	0.15	0.41	0.07			
Lake	14	0.42	0.06	0.55	0.10	0.73	0.11	0.48	0.06				
	C2-												
Tarda	ung	8	0.46	0.06	0.58	0.09	0.80	0.06	0.50	0.12			
Rpt		6	0.46	0.09	0.64	0.14	0.83	0.15	0.41	0.08			
Average Tarda		14	0.46	0.07	0.60	0.13	0.81	0.11	0.46	0.08	1	-0.40	
Murchison	CM2	8	0.38	0.03	0.52	0.09	0.70	0.06	0.25	0.13			
Rpt Average		6	0.37	0.08	0.52	0.09	0.67	0.15	0.35	0.16			
Murchison		14	0.38	0.05	0.52	0.09	0.69	0.10	0.29	0.10	2	-0.58	0.12
Allende A	CV3	5	0.21	0.03	0.26	0.09	0.37	0.08	0.28	0.17			
Rpt		6	0.22	0.10	0.28	0.16	0.35	0.20	0.47	0.15			
Average Allende A		11	0.22	0.07	0.27	0.13	0.36	0.15	0.38	0.12	2	-0.80	0.08
Allende B	CV3	8	0.24	0.07	0.30	0.14	0.43	0.09	0.23	0.12			
Rpt	0.15	6	0.23	0.06	0.31	0.12	0.38	0.18	0.32	0.12			
Average Allende B		14	0.24	0.06	0.31	0.13	0.41	0.14	0.27	0.09			
Reference materials													
IRMM3702		7	0.22	0.04	0.26	0.05	0.43	0.06	0.02	0.11			
BHVO2		12	0.30	0.07	0.46	0.08	0.58	0.10	-0.07	0.15			

<sup>a</sup>n is the number of measurements

\_\_\_\_\_

<sup>b</sup>2SD is 2 x standard deviation; 2SE is 2 x standard error <sup>c</sup>Value excluded from the averages for Ryugu *Numbers in italic represent averages for Ryugu and the carbonaceous*.

Numbers in italic represent averages for Ryugu and the carbonaceous chondrites for the Zn data

358

359 Table 2. Major and trace element compositions of Ryugu samples and carbonaceous chondrites.

Sample	Туре	Zn (ppm)	2SD	Cu (ppm)	2SD	Mg (ppm)	2SD	Mg/Zn	Mg/Cu
Ryugu									
C0108*		352	4	156	2	104222	1153	296	668
C0103		383	6	168	1	98823	2890	258	589
Average site C		368	45	162	17	101523	7635	277	628
A0106-A107*		338	4	133	2	106866	1250	316	804
A0106		369	5	130	2	112899	3191	306	870
Average site A		354	45	132	5	109883	8533	311	837
Average Ryugu		361	40	147	37	101509	11700	294	733
Carbonaceous cl	ondrites								
Orgueil	CI1	288	4	131	1	91158	2706	3.0	696
Alais	CI1	298	3	127	1	84683	2489	2.9	667
Tagish Lake	C2-ung	204	5	105	3	107210	1275	1.2	1021
Tarda	C2-ung	201	3	110	2	111296	2388	2.1	1012
Murchison	CM2	174	2	117	1	111130	1257	1.1	950
Allende A	CV3	110	2	97	2	141784	2461	1.7	1459
Allende B	CV3	121	1	105	1	157609	4882	3.1	1501

\*Abundances from [5]

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Numbers in italic represent averages for Ryugu, and each of Ryugu sample site

360

#### 362 Figures captions

363 Figure 1. Zinc and copper elemental and isotopic compositions for Ryugu and carbonaceous 364 chondrites samples. (a)  $\delta^{66}$ Zn vs Mg/Zn, (b)  $\delta^{65}$ Cu vs Mg/Cu and (c) Zn/Mg vs Cu/Mg that we measured for the Ryugu samples (diamonds) and carbonaceous chondrites (large circles with 365 abbreviations: Or=Orgueil, Als=Alais, Tag=Tagish Lake, Tar=Tarda, Mur=Murchison, 366 367 All=Allende). Small circles are from the literature [17-21] for Zn and Cu isotope compositions 368 (and references therein for major and trace element compositions). The color identifies the type of 369 chondrite as described in the legend. The purple star in panel c represents the CI chondrite 370 composition from [1]. Data are presented as mean values with 2SD error bars, reported in Table 371 1.

372

**Figure 2.**  $\delta^{66}Zn$  vs  $\delta^{65}Cu$  for Ryugu samples and carbonaceous chondrites. Literature data are from [17,19]. Same symbols as in Figure 1 for the samples analyzed in this study. Other chondrite groups from the literature are reported directly on the figure. Data are presented as mean values with 2SD error bars, reported in Table 1. For clarity, only the error bars of our measurements are displayed. Error bars for literature data are not shown.

378

Figure 3.  $\delta^{66}Zn$  (this study) vs  $\varepsilon^{54}Cr$  [5,30,53-55] for Ryugu samples and carbonaceous chondrites. Literature data are from [17,18,20] for Zn isotope compositions, and from [56] for Cr isotope compositions. The dark and light blue shaded areas correspond to the  $\varepsilon^{54}Cr$  ranges for site A and site C, respectively, from [6]. Same symbols as in Figure 1 for the samples analyzed in this study. Other chondrite groups from the literature are reported directly on the figure. Data are presented as mean values with 2SD error bars, reported in Table 1.

385

Figure 4. Variations of ε<sup>66</sup>Zn among different groups of meteorites. For comparison purposes,
only Ryugu (diamond) and CI (purple circles) samples measured in this study are represented
here. Literature data for carbonaceous chondrites ([28] (large symbols), [29] (small symbols)),
ordinary chondrites [28,29], enstatite chondrites [28,29], NC and CC iron chondrites [29],
ureilites [29] are shown with gray symbols. Bulk Silicate Earth: +0.015 ± 0.075 ‰o, 2SE, n = 4
[28] and -0.07 ± 0.013 ‰o, 2SE, n = 3 [29]). Data are presented as mean values with 2SE error
bars, reported in Table 1.

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