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1 **Pervasive aqueous alteration in the early Solar System revealed by**
2 **potassium isotopic variations in Ryugu samples and carbonaceous chondrites**

3
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99 **Abstract**

100 C-type asteroids are the presumed home to carbonaceous chondrites, some of which contain
101 abundant life-forging volatiles and organics. For the first time, samples from a C-type asteroid
102 (162173 Ryugu) were successfully returned to Earth by JAXA's Hayabusa2 mission. These
103 pristine samples, uncontaminated by the terrestrial environment, allow a direct comparison with
104 carbonaceous chondrites. This study reports the K isotopic compositions (expressed as $\delta^{41}\text{K}$) of
105 Ryugu samples and seven carbonaceous chondrites to constrain the origin of K isotopic variations
106 in the early Solar System. Three aliquots of Ryugu particles collected at two touchdown sites have
107 identical $\delta^{41}\text{K}$ values, averaged at $-0.194 \pm 0.038\%$ (2SD). The K isotopic composition of Ryugu
108 falls within the range of $\delta^{41}\text{K}$ values measured on representative CI chondrites, and together, they
109 define an average $\delta^{41}\text{K}$ value of $-0.178 \pm 0.075\%$ (95% c.i.), which provides the current best
110 estimate of the K isotopic composition of the bulk Solar System. Samples of CI chondrites with
111 $\delta^{41}\text{K}$ values that deviate from this range likely reflect terrestrial contaminations or compositional
112 heterogeneities at sampled sizes. In addition to CI chondrites, substantial K isotopic variability is
113 observed in other carbonaceous chondrites and within individual chondritic groups, with $\delta^{41}\text{K}$
114 values inversely correlated with K abundances in many cases. These observations indicate
115 widespread fluid activity in chondrite parent bodies, which significantly altered the original K
116 abundances and isotopic compositions of chondrules and matrices established at their accretion.

117

118 **Keywords:** Asteroid Ryugu; Hayabusa2 mission; Carbonaceous chondrites; Stable potassium
119 isotopes; Aqueous alteration

120 **1 Introduction**

121 Primitive asteroids accreted varying amounts of ice that melted to water-rich fluids due to heat
122 released from the radioactive decay of short-lived nuclides (e.g., ^{26}Al , McSween et al., 2002) and
123 possibly from impacts (Rubin, 2012). Consequently, fluid activity is believed to have been
124 pervasive in the early history of planetesimal and planet development (Brearley, 2006; Brearley,
125 2014; Clayton, 1993; Zolensky and McSween, 1988). Potassium (K) is a fluid-mobile, large-ion
126 lithophile element that resides primarily in the metastasis and fine-grained matrix in carbonaceous
127 asteroids. These components react readily with aqueous fluids, leading to redistribution of K^+ and
128 its isotopes. In addition, K is a moderately volatile metal that is variably depleted in carbonaceous
129 chondrites and terrestrial planets. Because both volatility-driven depletion and fluid-rock
130 interaction can lead to mass-dependent fractionations between the two stable K isotopes (i.e., ^{39}K
131 and ^{41}K), it is essential to understand how these processes affect $\delta^{41}\text{K}$ variations in meteorites to
132 facilitate the interpretation of K isotopic signatures of planetary materials.

133 Carbonaceous Ivuna-type (CI) chondrites are the chemically most primitive meteorites and
134 have been widely used for inferring the isotopic composition of the bulk Solar System (Palme et
135 al., 2014). Despite their primitive bulk composition, CI chondrites underwent near-complete
136 aqueous alteration of anhydrous precursors to secondary mineral assemblages dominated by
137 phyllosilicates (e.g., Tomeoka and Buseck, 1988) and display significant small-scale chemical
138 heterogeneities (e.g., Barrat et al., 2012; Morlok et al., 2006; Palme and Zipfel, 2022). Because CI
139 chondrites are limited in numbers and masses, and are susceptible to terrestrial modification,
140 previous K isotopic analyses on them yielded inconsistent results. Earlier analyses of Orgueil, the
141 largest CI witnessed fall (14 kg), returned a $\delta^{41}\text{K}$ value ($-0.534 \pm 0.097\%$, 2SE) that is similar to
142 the bulk Silicate Earth (Wang and Jacobsen, 2016). Later studies found that this terrestrial-like
143 $\delta^{41}\text{K}$ value of Orgueil reflects K contamination on Earth, and other Orgueil samples have $\delta^{41}\text{K}$
144 values varying between -0.290% and -0.039% (Hu et al., 2022; Hu et al., 2023; Koefoed et al.,
145 2023; Koefoed et al., 2022; Ku and Jacobsen, 2020; Nie et al., 2021). Two separate analyses on
146 Ivuna also yielded markedly different $\delta^{41}\text{K}$ values of $-0.460 \pm 0.046\%$ (Nie et al., 2021) and
147 $-0.180 \pm 0.060\%$ (Koefoed et al., 2023). The cause of this intra-group difference remains unclear.
148 It may reflect an unrepresentative sampling of the bulk composition due to sample heterogeneity
149 caused by aqueous alteration in the parent body(s) of the CI chondrites or remobilization of K in

150 terrestrial environments. A better-defined K isotopic composition of CI chondrites is critical for
151 constraining the bulk composition of the Solar System.

152 In December 2020, JAXA's Hayabusa2 mission returned the first samples from the
153 carbonaceous asteroid 162173 Ryugu, which had not been exposed to terrestrial environments
154 prior to laboratory analysis. These samples contain abundant organic material plausibly inherited
155 from the protosolar nebula and/or the interstellar medium, which attests to their primitive nature
156 (Nakamura et al., 2022; Pilorget et al., 2022). Furthermore, chemical and isotopic analyses suggest
157 that Ryugu has a similar bulk composition to CI chondrites (Hopp et al., 2022; Moynier et al.,
158 2022; Nakamura et al., 2022; Paquet et al., 2022; Yokoyama et al., 2022). In particular, the Ryugu
159 samples do not contain chondrules or refractory inclusions (Pilorget et al., 2022; Yokoyama et al.,
160 2022) and display no depletion of volatile metals relative to the solar photosphere (Yokoyama et
161 al., 2022), which are essential features of CI chondrites. Therefore, the Ryugu samples are a direct
162 asteroidal analogue to CI chondrites, providing unique insights into the pristine composition of CI
163 chondrites and the origin of K isotopic variability in the Solar System.

164 Here, we report the K isotopic compositions of three aliquots of Ryugu particles collected from
165 two touchdown sites and seven carbonaceous chondrites measured with the Nu Sapphire collision-
166 cell multi-collector inductively coupled plasma mass spectrometer (CC-MC-ICP-MS). We found
167 that the Ryugu samples and CI chondrites have similar $\delta^{41}\text{K}$ values, except for a significantly lower
168 value previously reported for Ivuna. This finding further strengthens the isotopic links between
169 Ryugu and CI chondrites. The large discrepancy in the $\delta^{41}\text{K}$ values reported for Ivuna may reflect
170 an unrepresentative bulk composition acquired on this sample. Fluid-rock interactions were likely
171 widespread and heterogeneous in the parent bodies of the carbonaceous chondrites, which also
172 resulted in considerable K isotopic variability in the CM (Mighei-type), CO (Ornans-type), CV
173 (Vigarano-type), and CK (Karoonda-type) chondrites.

174

175 **2 Samples and methods**

176 **2.1 Sample description and pre-chemistry preparation**

177 Ryugu formed as a rubble-pile asteroid (approximately 1 km in diameter) reaccumulated from
178 the shattered debris of a larger parent body (Sugita et al., 2019); therefore, Ryugu likely sampled
179 rock fragments from all depths of its parent body. The Hayabusa2 mission retrieved 5.4 g of

180 pebbles and sands at two locations on Ryugu (Tachibana et al., 2022; Yada et al., 2022). Around
181 3 g of surface material was collected from the touchdown site 1 and stored in Chamber A (Morota
182 et al., 2020). The second landing targeted at collecting impact ejecta from a ~ 15-m diameter crater
183 artificially made by the onboard Small Carry-on Impactor (SCI) (Arakawa et al., 2020). Around 2
184 g of samples containing subsurface material was collected from the touchdown site 2 and stored
185 in Chamber C. Samples collected from these two sites are considered representative of the
186 compositionally homogeneous Ryugu surface based on their consistent spectral features and
187 physical properties (color, shape, surface morphology, and structure) with onboard measurements
188 made by the spacecraft (Kitazato et al., 2019; Nakamura et al., 2022; Pilonget et al., 2022;
189 Tachibana et al., 2022).

190 Three aliquots of Ryugu particles were analyzed for K isotopes. Sample A0106 is from
191 Chamber A, while samples C0107 and C0108 are from Chamber C. Preliminary sample treatment
192 has been performed at the Tokyo Institute of Technology (Tokyo Tech). Samples A0106 and
193 C0107 were first treated to extract soluble organic matter (Naraoka et al., 2023). Then, together
194 with C0108, they were dissolved in precleaned perfluoroalkoxy (PFA) vials in a mixture of
195 concentrated HF and HNO₃, as described in Yokoyama et al. (2022). All three Ryugu samples
196 were first processed to separate the Zn fractions from other constituent elements in the samples
197 (Paquet et al., 2022). This was followed by a three-step sequential chemical separation procedure
198 for the isotopic measurements of Fe (Hopp et al., 2022), Ti, and Cr (Yokoyama et al., 2022), after
199 which we obtained a fraction containing K, Mg, and Ni. Aliquots of the K-Mg-Ni fraction for the
200 Ryugu samples were transferred to the Institut de Physique du Globe de Paris (IPGP) for K isotopic
201 analyses. The amounts of K finally obtained from the three Ryugu samples ranged from 1365 to
202 2867 ng. To verify whether the multi-stage chemical separation fractionated the K isotopes, the K-
203 Mg-Ni fractions of three carbonaceous chondrites, including Tarda (C2-ungrouped), Tagish Lake
204 (C2-ungrouped), and Allende (CV3), which were subjected to the same processing as the Ryugu
205 samples at Tokyo Tech, were chemically purified for K isotopic analyses at IPGP.

206 We also analyzed four geostandards (BIR, BCR-2, AGV-2, and seawater) and seven in-house
207 carbonaceous chondrites at IPGP to examine possible sample heterogeneity and to compare with
208 the K isotopic compositions of the Ryugu samples. The additional chondrite samples were: Orgueil
209 (CI1), Tagish Lake (C2-ungrouped), Tarda (C2-ungrouped), Cold Bokkeveld (CM2), Murchison
210 (CM2), Lance (CO3.5), and Allende (CV3). At IPGP, approximately 8-15 mg of the sample

211 powders were dissolved in Savillex screw-top PFA beakers using sequential addition of
212 concentrated HF-HNO₃ (3:1), HCl-HNO₃ (3:1), and HNO₃. The dissolved sample solutions were
213 refluxed with and redissolved in 0.5 mol/L HNO₃.

214 2.2 Potassium purification and isotope measurement

215 Potassium was isolated from other elements by cation-exchange chromatography described in
216 Xu et al. (2019). Two mL of Bio-Rad AG 50W-X8 cation exchange resin (200-400 mesh) was
217 filled into pre-cleaned Bio-Rad Poly-Prep columns. The resin was cleaned by three passes with 6
218 mol/L HCl, one pass with 6 mol/L HNO₃, and one pass with 1 mol/L HNO₃. Each acid pass was
219 rinsed with 10 mL of Milli-Q deionized water. The resin was then conditioned with 10 mL of 0.5
220 mol/L HNO₃. Dissolved sample solutions were loaded onto the resin in 1 mL of 0.5 mol/L HNO₃.
221 A volume of 13 mL of 0.5 mol/L HNO₃ was passed through the column, and the K fraction was
222 collected in the subsequent 22 mL of the same acid. The sample solutions were passed through the
223 column four times.

224 Potassium isotopic analyses followed the protocol described by Moynier et al. (2021). Purified
225 K fractions were diluted in 0.5 mol/L HNO₃ to have K concentrations between 60 ppb and 70 ppb
226 K. They were introduced into the mass spectrometer using an Apex Omega desolvation nebulizer
227 system fitted with a 100 µL/min nebulizer. The ion beam was first decelerated to enter a hexapole
228 collision cell to remove interfering species (e.g., ⁴⁰ArH⁺ on ⁴¹K⁺), and the ⁴¹K⁺ and ³⁹K⁺ ion beams
229 were accelerated and directed through the magnet to the Faraday collector. Each analysis consisted
230 of a 90-second transfer time, a 60-second zero measurement in a blank solution, and 50 cycles of
231 sample measurement with 5-second integration. A 150-second wash was performed between
232 analyses. Each sample solution was paired with a standard solution diluted to the same K
233 concentration (to within 2%). Standard and sample solutions were analyzed alternatively during a
234 sequence to correct for instrumental mass bias. Potassium isotopic data are reported as the average
235 of repeated analyses (4 to 8 times) relative to NIST SRM 3141a in delta notation:

$$236 \quad \delta^{41}\text{K} (\text{‰}) = \left\{ \frac{\left(\frac{{}^{41}\text{K}}{{}^{39}\text{K}} \right)_{\text{sample}}}{\left(\frac{{}^{41}\text{K}}{{}^{39}\text{K}} \right)_{\text{NIST SRM 3141a}}} - 1 \right\} \times 1000$$

237 Analytical uncertainties are reported as 2SD (standard deviation) and 95% c.i. (confidence
238 interval) in Table 1 and Table S1. In the following sections, analytical uncertainty used for
239 individual sample is 95% c.i. and that used for group average is 2SD unless stated otherwise.

240

241 **3 Results and discussions**

242 **3.1 Analytical accuracy**

243 We first evaluate the accuracy of our analyses by comparing the $\delta^{41}\text{K}$ values of representative
244 terrestrial standards and chondrites from analyses in this study to previous results. The $\delta^{41}\text{K}$ values
245 of basalt BIR ($-0.418 \pm 0.031\text{‰}$) and BCR-2 ($-0.426 \pm 0.030\text{‰}$), andesite AGV-2 ($-0.455 \pm$
246 0.030‰), and Pacific seawater ($0.126 \pm 0.028\text{‰}$) analyzed during the course of this study agree
247 well with published results (Chen et al., 2019; Hille et al., 2019; Hu et al., 2018; Moynier et al.,
248 2021; Xu et al., 2019). In addition, Orgueil ($-0.081 \pm 0.066\text{‰}$), Murchison ($-0.250 \pm 0.043\text{‰}$),
249 Allende ($-0.169 \pm 0.030\text{‰}$), Cold Bokkeveld ($-0.267 \pm 0.035\text{‰}$), and Lancé ($-0.382 \pm 0.040\text{‰}$)
250 processed and analyzed in this study yielded consistent values with our previous analyses (Hu et
251 al., 2022; Hu et al., 2023). This consistency confirms the accuracy of our analyses.

252 We then evaluate whether the multi-stage chemical separation procedures performed at Tokyo
253 Tech affected the isotopic compositions of K in the samples. For Tagish Lake, the K extracted
254 from the K-Mg-Ni fraction has a $\delta^{41}\text{K}$ value of $-0.180 \pm 0.049\text{‰}$, which is indistinguishable from
255 the values obtained from two new dissolutions of separate pieces of this meteorite from Tokyo
256 Tech ($-0.215 \pm 0.043\text{‰}$) and IPGP ($-0.215 \pm 0.032\text{‰}$). Likewise, the K purified from the K-Mg-
257 Ni fraction of Tarda ($-0.223 \pm 0.037\text{‰}$) is isotopically identical to that purified from a separate
258 piece of this meteorite at IPGP ($-0.205 \pm 0.024\text{‰}$). This similarity in $\delta^{41}\text{K}$ values suggests that the
259 preliminary chemical processing performed at Tokyo Tech affects K negligibly. In support of this
260 inference, the anion resin used to separate Zn from other constituent elements in the samples should
261 not retain any K^+ , which would be eluted from the resin. Therefore, it is reasonable to assume that
262 the $\delta^{41}\text{K}$ values of K extracted from the K-Mg-Ni fraction of the three Ryugu samples are
263 representative of these samples.

264

265 **3.2 K isotopic compositions of CI chondrites and the bulk Solar System**

266 The three Ryugu samples have K abundances that are comparable to those of the CI chondrites
267 (Fig. 1A). In addition, they display consistent $\delta^{41}\text{K}$ values (Fig. 1B), with no significant differences
268 between the samples collected from the touchdown site 1 (Chamber A sample A0106 = $-0.172 \pm$

269 0.039‰) and the touchdown site 2 (Chamber C samples C0107 = $-0.204 \pm 0.048\text{‰}$ and C0108 =
270 $-0.207 \pm 0.055\text{‰}$). Furthermore, the two samples from Chamber C have essentially identical $\delta^{41}\text{K}$
271 values, indicating that the extraction of soluble organic matter from samples C0107 and A0106
272 prior to K separation did not affect their K isotopic compositions. The three Ryugu samples yield
273 an average $\delta^{41}\text{K}$ value of $-0.194 \pm 0.038\text{‰}$ (2SD), which falls within the range of CI chondrites
274 (Fig. 1B). This result is consistent with previous observations of CI-like isotopic compositions of
275 Ryugu for the moderately volatile elements Zn and Cu (Paquet et al., 2022) and the more refractory
276 elements Fe, Cr, Ti, and Ca (Hopp et al., 2022; Moynier et al., 2022; Yokoyama et al., 2022).
277 Potassium isotopes thus further strengthens the compositional links between Ryugu and CI
278 chondrites.

279 The new data from Ryugu samples provide critical constraints on the K isotopic composition
280 of the bulk Solar System, which can otherwise only be inferred from CI chondrites. Previous
281 analyses of CI chondrites show highly variable $\delta^{41}\text{K}$ values from -0.534‰ to -0.039‰ , covering
282 almost the entire variation measured in carbonaceous chondrites (Hu et al., 2022; Hu et al., 2023;
283 Koefoed et al., 2023; Koefoed et al., 2022; Ku and Jacobsen, 2020; Nie et al., 2021; Wang and
284 Jacobsen, 2016). Ku and Jacobsen (2020) found that the lowest $\delta^{41}\text{K}$ values were measured for a
285 piece of Orgueil contaminated with 8% of continental crust material, resulting in its substantially
286 higher K abundance and lower $\delta^{41}\text{K}$ value than other Orgueil samples (Fig. 1). In comparison, the
287 majority of K isotopic analyses on Orgueil show a limited variation from -0.220‰ to -0.039‰ ,
288 except for two specimens with relatively higher K concentrations (~ 700 ppm) that might also be
289 affected by crustal contamination (Fig. 1B). Excluding these two lower $\delta^{41}\text{K}$ values, the analyses
290 on nine separate samples of Orgueil give an average $\delta^{41}\text{K}$ value of $-0.159 \pm 0.118\text{‰}$ (2SD),
291 suggesting a largely homogeneous K isotopic composition in Orgueil.

292 Unlike Orgueil, however, there is a large discrepancy in the $\delta^{41}\text{K}$ values reported for two
293 separate analyses of the CI-type specimen Ivuna. The lower value of $-0.460 \pm 0.046\text{‰}$ does not
294 appear to reflect terrestrial contamination because this Ivuna sample has a normal K abundance
295 (458 ppm, Nie et al., 2021) as the uncontaminated Orgueil samples and the other Ivuna sample,
296 which has a $\delta^{41}\text{K}$ value ($-0.180 \pm 0.060\text{‰}$) similar to the Orgueil (Fig. 1B). The lower Ivuna value
297 is thus likely an unrepresentative sampling of the bulk Ivuna composition. This inference is
298 supported by the heterogenous distribution of soluble elements in CI chondrites, in particular for
299 Ivuna (Barrat et al., 2012; Brearley, 2006; Morlok et al., 2006; Palme and Zipfel, 2022) (Fig. 1A).

300 Excluding the anomalous Ivuna value, representative analyses of Ryugu and CI chondrites define
301 an average $\delta^{41}\text{K}$ value of $-0.178 \pm 0.075\%$ (95% c.i.), which is currently the best estimate of the
302 K isotopic composition of the bulk Solar System.

303

304 **3.3 Origin of K isotopic variations in carbonaceous chondrites**

305 A well-established average $\delta^{41}\text{K}$ value of CI chondrites is an important reference for
306 understanding the origin of K isotopic variations among different carbonaceous chondritic groups.
307 This is because CI chondrites are generally used to approximate the isotopic composition of the
308 matrix component in carbonaceous chondrites (e.g., Alexander, 2005; Braukmüller et al., 2018).
309 Due to the lack of a robust $\delta^{41}\text{K}$ value for CI chondrites in previous studies, a wide range of $\delta^{41}\text{K}$
310 values (-0.28 to 2.1%) was invoked for chondrules to explain K isotopic variations in
311 carbonaceous chondrites (Bloom et al., 2020). The average $\delta^{41}\text{K}$ values established for CI
312 chondrites and Ryugu samples in this study agree with each other within uncertainty (Fig. 2). Their
313 $\delta^{41}\text{K}$ values also overlap within uncertainty with those of the two ungrouped C2 chondrites (Tagish
314 Lake and Tarda), which contain the second-highest matrix volume among carbonaceous chondrites
315 (Fig. 2). These observations indicate that the CI-like matrix in carbonaceous chondrites is largely
316 homogeneous in $\delta^{41}\text{K}$.

317 Compared with CI chondrites and Ryugu samples, carbonaceous chondrites from the CM
318 (Murchison), CO (Lance), and CV (Allende) groups are variably depleted in the heavier K isotope,
319 and their $\delta^{41}\text{K}$ values correlate positively with the $\delta^{66}\text{Zn}$ and $\delta^{65}\text{Cu}$ values (Fig. 2). Positive
320 correlations are also evident between $\delta^{41}\text{K}$ with isotopes of other MVEs, including Rb, Sn, and Te,
321 in a larger dataset of carbonaceous chondrites (Hu et al., 2023; Koefoed et al., 2023; Nie et al.,
322 2021). These systematic correlations reflect the early formation of two nebular reservoirs, with a
323 volatile-depleted refractory component such as chondrules or Ca-Al-rich inclusions (CAIs)
324 carrying the light isotopic signatures, and a CI-like reservoir with the heaviest isotopic
325 compositions, as initially proposed by Luck et al. (2005; 2003). This interpretation is consistent
326 with a broad negative correlation between $\delta^{41}\text{K}$ and $1/[\text{K}]$ reported by Nie et al. (2021) for seven
327 carbonaceous chondrites, from which they extrapolated a $\delta^{41}\text{K}$ value of $-0.33 \pm 0.12\%$ for the
328 chondrule component and of $0.04 \pm 0.08\%$ for the matrix component. When all available data are
329 considered, there is a coinciding increase in $\delta^{41}\text{K}$ with water content (as a proxy for matrix content)

330 and a decrease in $\delta^{41}\text{K}$ with chondrule content in chondrites, further substantiating the role of
331 chondrules as the carriers of K depletion and low- $\delta^{41}\text{K}$ signature in chondrites (Hu et al., 2023).
332 Therefore, the inter-group K isotopic variations in carbonaceous chondrites primarily reflect
333 variable mixing between the two main K hosts, i.e., chondrules and the matrix, accreted by the
334 parent bodies of carbonaceous chondrites.

335

336 **3.4 K isotopic evidence for widespread aqueous alteration on chondrite parent bodies**

337 Although chondrule-matrix mixing could explain the inter-group $\delta^{41}\text{K}$ variation among
338 carbonaceous chondrites, the significant variability within individual chondrites remains
339 perplexing. In addition to the anomalously low $\delta^{41}\text{K}$ value reported for Ivuna, substantial
340 variability has also been documented for Allende and Murchison. Our in-house Allende sample
341 has a higher $\delta^{41}\text{K}$ value ($-0.169 \pm 0.030\text{‰}$) than the sample provided by the Smithsonian Museum
342 ($-0.292 \pm 0.044\text{‰}$), while they both fall within the previously reported range of -0.620‰ to
343 -0.080‰ for Allende (Bloom et al., 2020; Jiang et al., 2021a; Koefoed et al., 2023; Ku and
344 Jacobsen, 2020; Nie et al., 2021). Furthermore, the Allende sample provided by the Smithsonian
345 Museum is an aliquot from a large batch of homogenized powder, and its $\delta^{41}\text{K}$ value is in the
346 middle of the reported range. Our Murchison sample also has a $\delta^{41}\text{K}$ value ($-0.250 \pm 0.043\text{‰}$) that
347 is in the middle of the previously reported range for Murchison (-0.410‰ to -0.101‰ , Jiang et
348 al., 2021b; Koefoed et al., 2023; Ku and Jacobsen, 2020; Nie et al., 2021).

349 To identify the cause of intra-chondrite isotopic variability, we compare the two sets of $\delta^{41}\text{K}$
350 vs. $\delta^{87}\text{Rb}$ data obtained from IPGP and those reported in Nie et al. (2021), respectively, for four
351 carbonaceous chondrites. While the two datasets differ by varying extents for individual
352 chondrites, the $\delta^{41}\text{K}$ and $\delta^{87}\text{Rb}$ values correlate in both datasets (Fig. 3A). For example, the
353 Murchison specimen analyzed at IPGP has both lower $\delta^{41}\text{K}$ and $\delta^{87}\text{Rb}$ values than the specimen
354 reported by Nie et al. (2021). The correlation between $\delta^{41}\text{K}$ and $\delta^{87}\text{Rb}$ values suggests that the
355 variability reflects isotopic heterogeneity at the analyzed sample scale. This isotopic heterogeneity
356 could reflect different proportions of chondrules present in the two different specimens of a given
357 chondrite. In this case, the specimen containing more chondrules should have a lower K abundance
358 and a lower $\delta^{41}\text{K}$ value because chondrules are inferred to be depleted in K and its lighter isotope
359 compared with the matrix, as indicated by the mixing curve in Fig. 3B. However, the specimen

360 with the lower K abundance is often found to have a higher $\delta^{41}\text{K}$ value than that with the higher K
361 abundance of the same chondrite (Fig. 3B), which is opposite to the expectation of mixing between
362 varying proportions of chondrules with the matrix. Therefore, the observed sample heterogeneity
363 cannot be due to the chondrule nugget effect alone but, to a greater extent, reflects the redistribution
364 of K and its isotopes during aqueous alteration in chondrite parent bodies, which significantly
365 altered the original K abundances and isotopic compositions in chondrules and matrix.

366 The effects of asteroidal aqueous alteration on the redistribution of alkalis in carbonaceous
367 chondrites have been well documented, including the formation of diverse K-bearing phyllosilicate
368 phases at $< 100^\circ\text{C}$ and/or anhydrous phases (e.g., nepheline and sodalite) due to Fe-alkali-halogen
369 metasomatism at $\sim 200^\circ\text{-}300^\circ\text{C}$ (e.g., Brearley, 2014; Ikeda and Kimura, 1996; Kimura and Ikeda,
370 1998; Krot et al., 1998; Krot et al., 1995). Ordinary chondrites also show signs, albeit more subtle,
371 of interaction with aqueous fluids at varying temperatures, ranging from low-temperature
372 alteration ($< 200^\circ\text{C}$, in the least-equilibrated petrologic type 3) to fluid-assisted metamorphism
373 ($200\text{-}400^\circ\text{C}$, in petrologic types of 4-6). Before or during the earliest stage of thermal
374 metamorphism, aqueous fluids were suggested to have flowed through the fine-grained matrix,
375 dissolving the mesostasis near the edge of chondrules and migrating alkalis into chondrule cores
376 (e.g., Grossman et al., 2000; Grossman and Brearley, 2005). The presence of fluids is evidenced
377 by the brine-bearing salt crystals found in the Monahans and Zag ordinary chondrites, which are
378 argued to represent fluid samples from the early Solar System (Rubin et al., 2002; Zolensky et al.,
379 1999). More recently, fluid activity on S-type asteroids is further supported by nanometer-sized
380 halite crystals detected in particles returned from the asteroid Itokawa by JAXA's Hayabusa
381 mission (Che and Zega, 2023). These observations collectively suggest the widespread action of
382 fluids on primitive asteroids in the early Solar System.

383 Fluid-rock interactions have also been invoked to explain K isotopic variations in chondritic
384 components of the Allende and Hamlet (LL4) chondrites (Jiang et al., 2021a; Koefoed et al., 2020).
385 While inter-group variations in $\delta^{41}\text{K}$ are attributable to mixing between a CI-like matrix and K-
386 poor, isotopically light chondrules, direct measurements on Allende and Hamlet show highly
387 variable $\delta^{41}\text{K}$ in chondrules with values both higher and lower than those of the matrices (Fig. 3C
388 and D). Furthermore, CAIs formed well above the condensation temperature of K contain
389 anomalously high K concentrations and $\delta^{41}\text{K}$ values. These observations are inconsistent with the
390 low $\delta^{66}\text{Zn}$ and $\delta^{71}\text{Ga}$ values measured in CAIs interpreted as reflecting incomplete condensation

391 (Kato et al., 2017; Luck et al., 2005). Instead of pristine nebular signatures, Jiang et al. (2021a)
392 considered the high $\delta^{41}\text{K}$ values of CAIs as a secondary feature inherited from aqueous fluids
393 assuming that most K in the CAIs was secondary in origin (Fig. 3C). Furthermore, they proposed
394 that as the fluids interact with the porous matrix, the heavier K isotope was preferentially leached
395 from the matrix and entered chondrules or CAIs, overprinting the original K abundances and
396 isotopic signatures of the chondritic components.

397 The preference for the heavier K isotope by aqueous fluids is supported by the direction of K
398 isotope fractionation during chemical weathering on Earth. Global rivers (-0.59‰ to 0.12‰) and
399 oceans ($0.12 \pm 0.07\text{‰}$, 2SD) have heavier K isotopic compositions (Hille et al., 2019; Li et al.,
400 2019; Wang et al., 2020; Wang et al., 2021) than fresh basaltic rocks averaging at $-0.42 \pm 0.08\text{‰}$
401 (2SD) (Hu et al., 2021; Tuller-Ross et al., 2019a; Tuller-Ross et al., 2019b). In addition, studies of
402 weathering profiles and riverine sediments indicate that aqueous fluids preferentially leach the
403 heavy K isotope from the bedrock with apparent isotope fractionation factors of 0.08‰ to 0.55‰ ,
404 leaving behind isotopically light weathered residues (down to -0.94‰ , Chen et al., 2020; Li et al.,
405 2019; Teng et al., 2020). Consistent with field analyses, theoretical calculations based on K-O
406 bond strengths also suggest an enrichment of the heavier K isotope in aqueous solutions relative
407 to typical silicate minerals and a fractionation factor of 0.24‰ between aqueous fluids and illite
408 (Zeng et al., 2019).

409 At the onset of aqueous alteration, the K abundance and $\delta^{41}\text{K}$ value of matrix would have
410 decreased, while the chondrules or CAIs would have increased K abundances and $\delta^{41}\text{K}$ values.
411 With increasing degrees of alteration, chondrules, CAIs, and matrix would tend to approach
412 equilibrium. The significant $\delta^{41}\text{K}$ variability in Allende and Murchison (Fig. 2) and the fact that
413 the specimen with a lower K abundance typically has a higher $\delta^{41}\text{K}$ value (Fig. 3B) suggest that
414 these chondrites record early stages of aqueous alteration. A broad negative correlation between
415 $\delta^{41}\text{K}$ values and K abundances is also observed in major groups of carbonaceous chondrites (Fig.
416 S1), suggesting that aqueous alteration and associated redistribution of K isotopes occurred
417 pervasively in the parent bodies of carbonaceous chondrites. Therefore, K isotopic variations in
418 carbonaceous chondrites record volatility-driven isotope fractionations during chondrule
419 formation, variable chondrule-matrix mixing at the accretion of chondrite parent bodies, and post-
420 accretionary redistribution of K in chondrite parent bodies assisted by aqueous fluids.

421

422 **4 Conclusions**

423 Previous estimates of the K isotopic composition of the bulk Solar System were based solely
424 on CI chondrites, which yielded inconsistent results that made it challenging to interpret $\delta^{41}\text{K}$
425 variability in planetary materials. This study reports the K isotopic composition of the first samples
426 returned from a carbonaceous asteroid (Ryugu) by JAXA's Hayabusa2 mission. The Ryugu
427 samples are free of terrestrial contamination, thereby, represent a pristine analogue of CI
428 chondrites. Three aliquots of Ryugu particles were analyzed, yielding similar $\delta^{41}\text{K}$ values between
429 -0.207‰ and -0.172‰ . This range is consistent with the K isotopic compositions of most CI
430 chondrites except for lower $\delta^{41}\text{K}$ values found in contaminated Orgueil samples and an
431 anomalously low value previously reported for Ivuna. The lack of K enrichment in this Ivuna
432 sample suggests that its anomalously low $\delta^{41}\text{K}$ value does not reflect terrestrial contamination but
433 is more likely an unrepresentative sampling of its bulk composition due to compositional
434 heterogeneity at the sampled size. Considerable K isotopic heterogeneity is also observed in other
435 carbonaceous chondrites and within individual chondritic groups, whereby $\delta^{41}\text{K}$ values are broadly
436 negatively correlated with K abundances. These observations suggest the widespread
437 redistribution of K and its isotopes during aqueous alteration in chondrite parent bodies.

438

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445

446 The authors declare no conflicts of interest.

447

448 All data referred to in this article can be found in the tables or cited references.

449

450 **Tables**

451 **Table 1.** Potassium abundance (ppm) and isotopic composition (‰) of Ryugu samples and
 452 carbonaceous chondrites analyzed in this study.

Sample	Group	$\delta^{41}\text{K}$ (‰)	2SD (‰)	95%c.i. (‰)	N	[K] (ppm)
Ryugu particles						
A0106		-0.150	0.065	0.060	4	436
duplicate		-0.172	0.085	0.056	5	
repeat		-0.191	0.059	0.048	5	
Wtd average		-0.172	0.040	0.039		
C0107		-0.192	0.070	0.040	6	457
duplicate		-0.214	0.066	0.056	5	
Wtd average		-0.204	0.030	0.048		
C0108		-0.188	0.086	0.059	5	604
repeat		-0.220	0.072	0.069	4	
Wtd average		-0.207	0.045	0.055		
Ryugu average		-0.194	0.038			
Carbonaceous chondrites						
Orgueil	C11	-0.081	0.070	0.066	5	568
Tagish lake-1	C2-ung	-0.178	0.097	0.050	5	358
duplicate		-0.181	0.057	0.048	5	
replicate		-0.215	0.057	0.043	6	
Wtd average		-0.195	0.042	0.037		
Tagish lake-2		-0.201	0.042	0.023	8	360
repeat		-0.236	0.051	0.03	7	
Wtd average		-0.215	0.049	0.032		
Tagish lake average		-0.205	0.029			
Tarda-1	C2-ung	-0.217	0.067	0.054	6	416
duplicate		-0.230	0.076	0.037	4	
repeat		-0.224	0.056	0.045	5	
Wtd average		-0.223	0.013	0.037		
Tarda-2		-0.166	0.063	0.050	5	416
repeat		-0.222	0.054	0.047	5	
repeat		-0.218	0.058	0.039	4	
replicate		-0.204	0.056	0.038	7	
duplicate		-0.189	0.060	0.047	6	
repeat		-0.222	0.060	0.050	5	
Wtd average		-0.205	0.044	0.024		
Tarda average		-0.214	0.026			
Murchison	CM2	-0.250	0.049	0.043	7	411
Cold Bokkeveld	CM2	-0.267	0.064	0.035	7	476
Lancé	CO3.5	-0.382	0.087	0.040	7	429.9
Allende (A)-1	CV3	-0.293	0.056	0.052	5	296
repeat		-0.292	0.072	0.048	5	
Wtd average		-0.292	0.001	0.044		
Allende-2		-0.151	0.062	0.059	5	267
repeat		-0.181	0.062	0.055	4	
repeat		-0.168	0.052	0.045	6	
replicate		-0.178	0.065	0.031	4	
Wtd average		-0.169	0.027	0.030		

453 Note: 'repeat' indicates repeat instrumental analysis. 'duplicate' indicate repeat column chemistry and instrumental
 454 analysis. 'replicate' indicates repeat sample dissolution, column chemistry, and instrumental analysis. The number '-1'
 455 and '-2' attached to the same names indicate different pieces of a given chondrite.

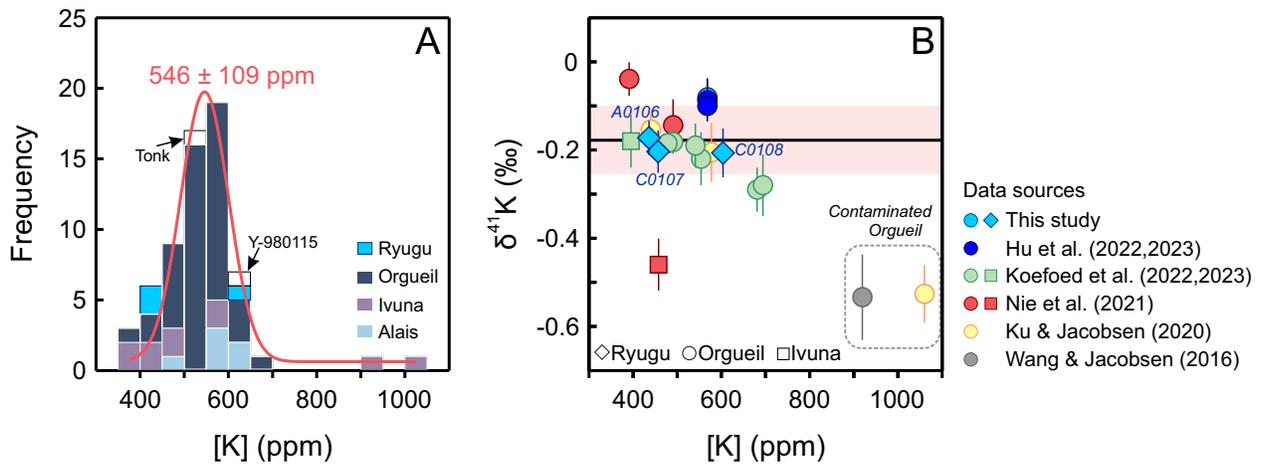
456 **Table S1.** Potassium isotopic compositions (‰) of terrestrial samples analyzed in this study.

Geostandard	Description	$\delta^{41}\text{K}$ (‰)	2SD (‰)	95%c.i. (‰)	N
BIR	Basalt	-0.448	0.059	0.036	7
	replicate	-0.400	0.052	0.076	4
	repeat	-0.414	0.050	0.062	4
	Wtd average	-0.418	0.050	0.031	
BCR-2	Basalt	-0.404	0.051	0.019	8
	repeat	-0.443	0.044	0.024	7
	replicate	-0.425	0.066	0.034	5
	Wtd average	-0.426	0.039	0.030	
AGV-2	Andesite	-0.455	0.042	0.030	7
Pacific seawater		0.152	0.060	0.054	4
	repeat	0.128	0.078	0.050	6
	repeat	0.113	0.039	0.037	7
	repeat	0.133	0.084	0.056	5
	Wtd average	0.126	0.032	0.028	

457

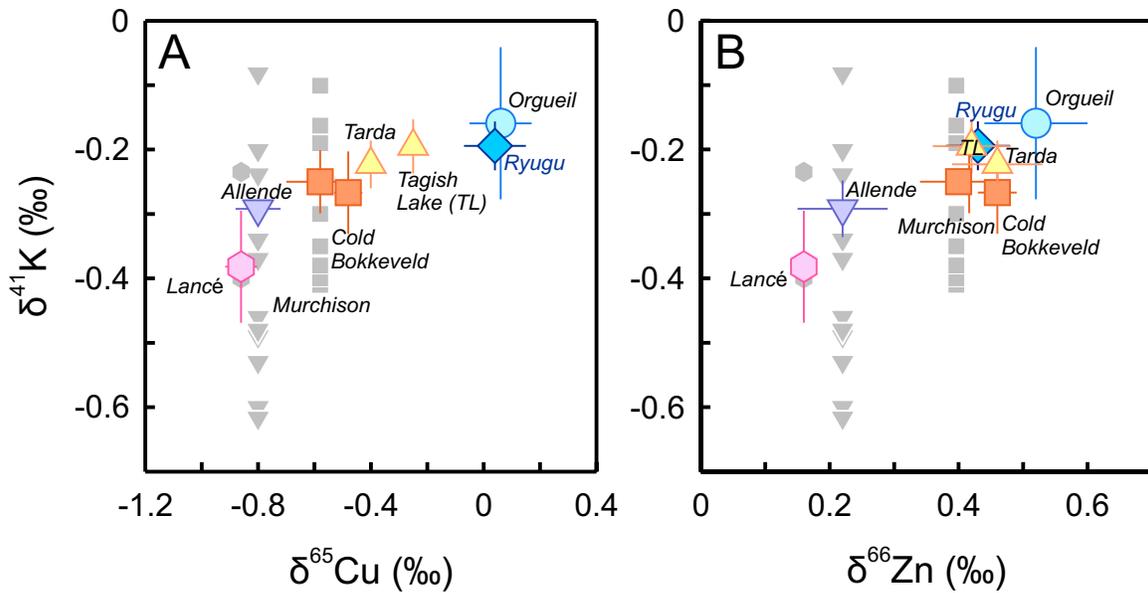
458 **Figures**

459



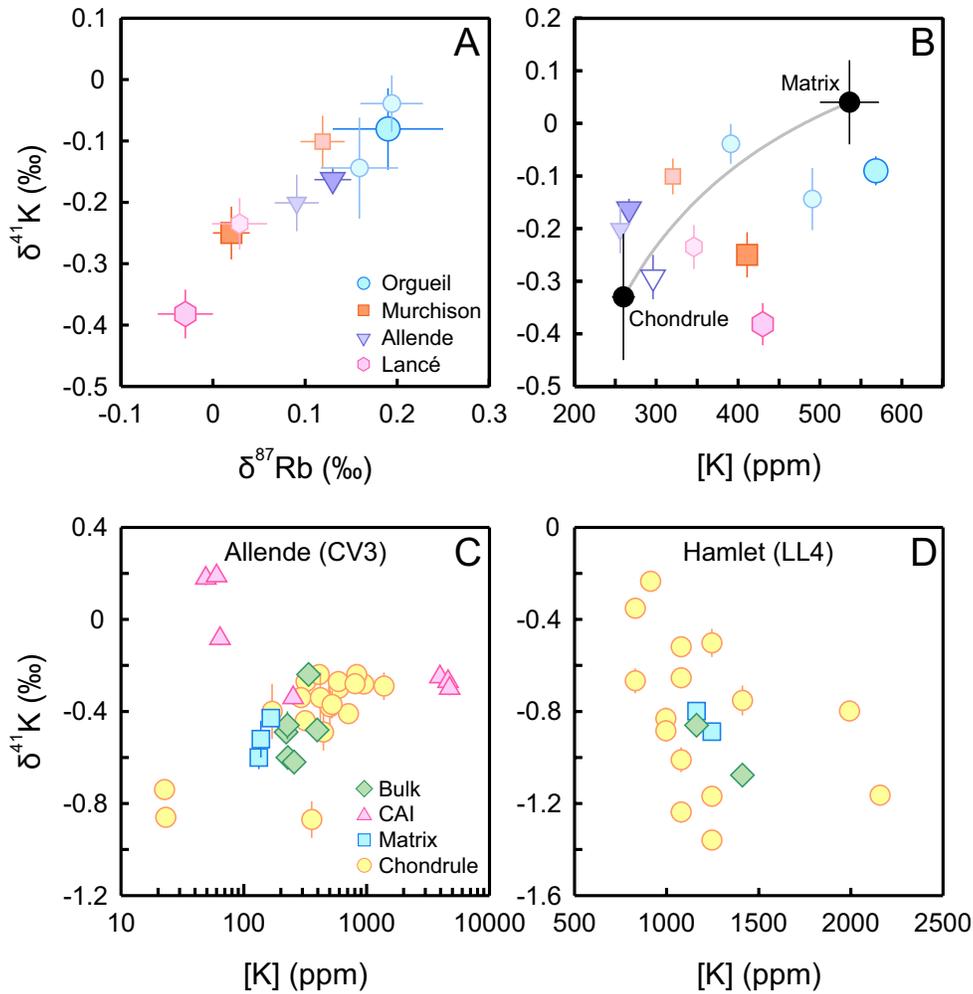
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461 **Figure 1.** Potassium abundances ([K], ppm) and isotope compositions ($\delta^{41}\text{K}$, ‰) of CI chondrites
 462 and Ryugu samples. (A) A histogram of K abundances in CI chondrites reported in the literature
 463 (Ahrens et al., 1969; Anders and Grevesse, 1989; Barrat et al., 2012; Beer et al., 1984; Braukmüller
 464 et al., 2018; Edwards and Urey, 1955; Jarosewich, 1990; Kallemeyn and Wasson, 1981; Kaushal
 465 and Wetherill, 1970; Makishima and Nakamura, 2006; Mittlefehldt, 2002; Nakamura, 1974;
 466 Nichiporuk and Moore, 1974; Palme and Zipfel, 2022; Von Michaelis et al., 1969; Wiik, 1956).
 467 (B) The three aliquots of Ryugu particles have indistinguishable $\delta^{41}\text{K}$ values and fall within the
 468 range of CI chondrites except for an anomalously lower $\delta^{41}\text{K}$ value previously reported for Ivuna.
 469 The horizontal black line and pink field indicate the average $\delta^{41}\text{K}$ value of Ryugu samples and CI
 470 chondrites (-0.178 ± 0.075 ‰), representing the current best estimate of the bulk K isotopic
 471 composition of the Solar System. Crustal contamination results in elevated K abundances and
 472 crust-like, lower $\delta^{41}\text{K}$ compared with pristine CI chondrite values (Ku and Jacobsen, 2020; Wang
 473 and Jacobsen, 2016). The K abundance of Ryugu C0108 is from Yokoyama et al. (2022), while
 474 those of A0106 and C0107 are new data reported in this study (Table 1).



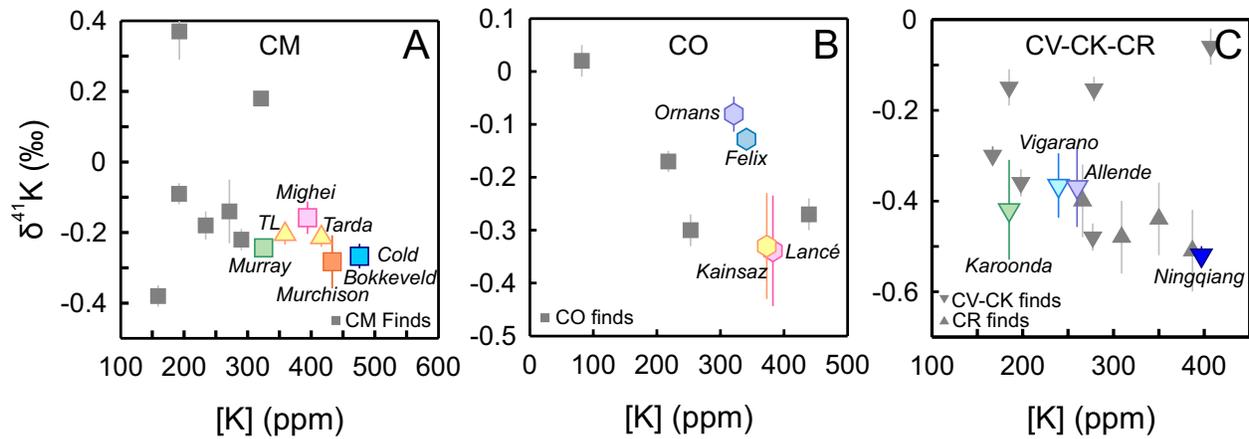
475

476 **Figure 2.** Positive correlations of $\delta^{41}\text{K}$ values with (A) $\delta^{65}\text{Cu}$ values and (B) $\delta^{66}\text{Zn}$ values in Ryugu
 477 samples and different groups of carbonaceous chondrites. These correlations suggest inter-group
 478 variations in $\delta^{41}\text{K}$ primarily reflect mixing of a CI-, or Ryugu-like matrix component with the
 479 heaviest isotopic compositions and a volatile-depleted refractory component such as chondrules
 480 carrying the light isotopic signatures. The colored symbols are data from this study and the grey
 481 symbols are literature values. In (A), $\delta^{41}\text{K}$ and $\delta^{65}\text{Cu}$ values (Paquet et al., 2022) for Ryugu, Tarda,
 482 Allende were measured from the same specimens. $\delta^{65}\text{Cu}$ values for Orgueil and Murchison are
 483 from Paquet et al. (2022), for Tagish Lake, Cold Bokkeveld, and Lancé are from Luck et al. (2003).
 484 In (B), $\delta^{41}\text{K}$ and $\delta^{66}\text{Zn}$ values (Paquet et al., 2022; Pringle et al., 2017) for Ryugu, Tagish Lake,
 485 Tarda, Murchison, Cold Bokkeveld, Lancé, and Allende were measured from the same specimens.
 486 $\delta^{66}\text{Zn}$ value for Orgueil is from Paquet et al. (2022). Literature $\delta^{41}\text{K}$ values are from Bloom et al.
 487 (2020); Jiang et al. (2021a); Jiang et al. (2021b); Koefoed et al. (2023); Koefoed et al. (2022); Ku
 488 and Jacobsen (2020); Nie et al. (2021). Although literature $\delta^{41}\text{K}$ values were plotted with $\delta^{65}\text{Cu}$
 489 and $\delta^{66}\text{Zn}$ values measured from different specimens of a given chondrite, $\delta^{65}\text{Cu}$ and $\delta^{66}\text{Zn}$ values
 490 reported for different specimens of Orgueil, Murchison, and Allende generally agree well (Barrat
 491 et al., 2012; Luck et al., 2005; Luck et al., 2003; Paquet et al., 2022; Pringle et al., 2017).



492

493 **Figure 3.** K isotopic evidence of aqueous alteration of chondrites on their parent bodies. (A)
 494 Positively correlated $\delta^{41}\text{K}$ and $\delta^{87}\text{Rb}$ values indicate sample heterogeneity for a given chondrite.
 495 The larger symbols are data from this study and the smaller symbols are from Nie et al. (2021).
 496 (B) The broad positive correlation between $\delta^{41}\text{K}$ values and K abundances across different
 497 carbonaceous chondrite groups indicates mixing of the CI-like, isotopically heavy matrix with K-
 498 depleted, isotopically light chondrules, as indicated by the mixing curve using endmember
 499 compositions extrapolated in Nie et al. (2021). However, for a given chondrite (coded with the
 500 same color), the specimen with the higher K abundance often has a lower $\delta^{41}\text{K}$ value than that with
 501 the lower K abundance. The large solid triangle down is an Allende specimen from IPGP, and the
 502 open triangle down is an aliquot of pulverized Allende provided by the Smithsonian Museum. (C)
 503 and (D) $\delta^{41}\text{K}$ values measured in chondrules, calcium-aluminum-rich inclusions (CAIs), and
 504 matrices in Allende and Hamlet chondrites show significant alteration of the original K abundances
 505 and $\delta^{41}\text{K}$ values of all chondritic components. Data source: Data presented in (A) and (B) are from
 506 this study and the literature (Nie et al., 2021; Pringle and Moynier, 2017), whereas those presented
 507 in (C) and (D) are from Jiang et al. (2021a); Ku et al. (2022), and Koefoed et al. (2020).



508

509 **Figure S1.** $\delta^{41}\text{K}$ values of bulk carbonaceous chondrites from the CM, CO, CV-CK, and CR
 510 groups as a function of K abundances. There is a broad negative correlation between $\delta^{41}\text{K}$ values
 511 and K abundances. These correlations are opposite to the positive correlations reflective of binary
 512 mixing of varying proportions of K-depleted, isotopically light chondrules with the CI-like matrix
 513 (also see the grey curve in Fig. 3B). Instead, the correlations suggest mixing between aqueously
 514 altered chondrules (with elevated $\delta^{41}\text{K}$ values) and matrix (with lowered $\delta^{41}\text{K}$ values). The colored
 515 symbols are witnessed falls and the grey symbols are chondrite finds. Data sources: this study and
 516 literature values (Bloom et al., 2020; Hu et al., 2022; Hu et al., 2023; Jiang et al., 2021a; Jiang et
 517 al., 2021b; Koefoed et al., 2023; Nie et al., 2021).

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