

This is an Open Access document downloaded from ORCA, Cardiff University's institutional repository: <https://orca.cardiff.ac.uk/id/eprint/171561/>

This is the author's version of a work that was submitted to / accepted for publication.

Citation for final published version:

Fischer-Gödde, Mario, Tusch, Jonas, Goderis, Steven, Bragagni, Alessandro, Mohr-Westheide, Tanja, Messling, Nils, Elfers, Bo-Magnus, Schmitz, Birger, Reimold, Wolf U., Maier, Wolfgang D. , Claeys, Philippe, Koeberl, Christian, Tissot, François L. H., Bizzarro, Martin and Münker, Carsten 2024. Ruthenium isotopes show the Chicxulub impactor was a carbonaceous-type asteroid. *Science* 385 (6710) , pp. 752-756. 10.1126/science.adk4868

Publishers page: <http://dx.doi.org/10.1126/science.adk4868>

Please note:

Changes made as a result of publishing processes such as copy-editing, formatting and page numbers may not be reflected in this version. For the definitive version of this publication, please refer to the published source. You are advised to consult the publisher's version if you wish to cite this paper.

This version is being made available in accordance with publisher policies. See <http://orca.cf.ac.uk/policies.html> for usage policies. Copyright and moral rights for publications made available in ORCA are retained by the copyright holders.



1 **Ruthenium isotopes show the Chicxulub impactor was a carbonaceous-type**  
2 **asteroid**

3  
4  
5 Mario Fischer-Gödde<sup>1\*</sup>, Jonas Tusch<sup>1</sup>, Steven Goderis<sup>2</sup>, Alessandro Bragagni<sup>3,4</sup>, Tanja Mohr-  
6 Westheide<sup>5</sup>, Nils Messling<sup>6</sup>, Bo-Magnus Elfers<sup>7</sup>, Birger Schmitz<sup>8</sup>, Wolf U. Reimold<sup>9</sup>, Wolfgang  
7 D. Maier<sup>10</sup>, Philippe Claeys<sup>2</sup>, Christian Koeberl<sup>11</sup>, François L. H. Tissot<sup>12</sup>, Martin Bizzarro<sup>13</sup>,  
8 Carsten Münker<sup>1</sup>

9  
10 <sup>1</sup>Institut für Geologie und Mineralogie, University of Cologne, 50674 Cologne, Germany

11 <sup>2</sup>Archeology, Environmental Changes & Geo-Chemistry, Vrije Universiteit Brussel, 1050  
12 Brussels, Belgium

13 <sup>3</sup>Department of Earth Sciences, University of Florence, Firenze 50121, Italy

14 <sup>4</sup>Institute of Marine Sciences, National Research Council, Bologna 40129, Italy

15 <sup>5</sup>Museum für Naturkunde, Leibniz-Institut für Evolutions- und Biodiversitätsforschung, 10115  
16 Berlin, Germany

17 <sup>6</sup>Geochemistry and Isotope Geology Department, Geoscience Center, University of Göttingen,  
18 37073 Göttingen, Germany

19 <sup>7</sup>Zentrallabor, Technical University Hamburg, 21073 Hamburg, Germany

20 <sup>8</sup>Astrogeobiology Laboratory, Lund University, SE-22100 Lund, Sweden

21 <sup>9</sup>Laboratório de Geocronologia e Geoquímica Isotópica, Instituto de Geociências, Universidade  
22 de Brasília, Campus Darcy Ribeiro, Asa Norte, CEP 70910-900, Brasília, DF, Brazil

23 <sup>10</sup>School of Earth & Ocean Sciences, Cardiff University, Cardiff CF10 3 AT, UK

24 <sup>11</sup>Department of Lithospheric Research, University of Vienna, A-1090 Vienna, Austria

25 <sup>12</sup>The Isotoparium, Division of Geological and Planetary Sciences, California Institute of  
26 Technology, Pasadena CA 91125, USA

27 <sup>13</sup>StarPlan – Center for Star and Planet Formation, GLOBE Institute, University of Copenhagen,  
28 Copenhagen, DK-1350, Denmark

29  
30 \*Corresponding author. Email: mfisch48@uni-koeln.de  
31

32        **An impact at Chicxulub occurred 66 million years ago, producing a global**  
33 **stratigraphic layer that marks the boundary between the Cretaceous and Paleogene eras.**  
34 **That layer contains elevated concentrations of platinum-group elements, including**  
35 **ruthenium. We measure ruthenium isotopes in samples taken from three Cretaceous-**  
36 **Paleogene boundary sites, five other impacts that occurred between 36 to 470 million**  
37 **years ago, and ancient 3.5 to 3.2 billion-year-old impact spherule layers. Our data indicate**  
38 **that the Chicxulub impactor was a carbonaceous-type asteroid, which had formed beyond**  
39 **the orbit of Jupiter. The other younger impact structures have isotopic signatures more**  
40 **consistent with siliceous-type asteroids, which formed closer to the Sun. The ancient**  
41 **spherule layer samples are consistent with impacts of carbonaceous-type asteroids during**  
42 **Earth's final stages of accretion.**

43  
44  
45  
46        Several mass extinction events occurred on Earth during the last 500 million years of its  
47 history, all within the Phanerozoic era, a geologic time period from 539 million years ago to  
48 the present (1, 2). The most recent mass extinction occurred simultaneously with the  
49 Cretaceous-Paleogene (K-Pg) geologic boundary, 66 million years ago (Ma), during which  
50  $\geq 60\%$  of all species were extinguished (3). The geologic signature of the K-Pg boundary was  
51 produced by the impact on Earth of a  $>10$  km diameter asteroid at Chicxulub, Mexico (3, 4).  
52 Samples taken from the K-Pg boundary layers have elevated concentrations of platinum group  
53 elements (PGE): iridium, ruthenium, osmium, rhodium, platinum and palladium (5-7), which  
54 are rare in Earth's crustal rocks (8). Meteorites, which are fragments of asteroids, have orders  
55 of magnitude higher PGE contents (9). The PGE enrichment of K-Pg boundary layer samples,  
56 and other terrestrial impact-related rocks and deposits, is interpreted as being derived from the  
57 extraterrestrial impactors.

58        Elevated PGE concentrations have been identified in many samples from globally  
59 distributed K-Pg boundary sites (10-12), indicating the fallout produced by the impact extended  
60 worldwide. The PGE data have been interpreted as indicating the impactor was an asteroid with  
61 composition similar to the class of meteorites known as chondrites (13). Further evidence for  
62 extraterrestrial material in the K-Pg boundary layer includes chromium (Cr) isotope data (14,  
63 15) and the presence of a fossil meteorite fragment in a sample of the K-Pg boundary in the  
64 Pacific Ocean (16).

65        An alternative hypothesis for the origin of PGE in K-Pg boundary layer deposits is that  
66 they are derived from global ash fall originating from extensive volcanic eruptions in the  
67 Deccan Trap, India (17). However, the abundance ratios of PGEs in the K-Pg boundary differ  
68 from those in the Deccan Trap volcanic basalts (18); the K-Pg PGE relative abundances are  
69 more consistent with those of chondritic meteorites (13), not with Deccan basalts.

70        The abundance ratios of PGEs and osmium isotope compositions have been used to  
71 constrain the nature of the extraterrestrial impactors for Brent (19), Clearwater East (20),  
72 Morokweng (21, 22), Popigai (23) impact structures and ancient 3.5 to 3.2 Ga old impact  
73 spherule layers (24-26). This approach assumes that relative PGE abundances were not  
74 modified during the impact itself, during incorporation into the impact-generated host rocks, or  
75 by later processes affecting those rocks.

## 76 77        **Ruthenium isotope constraints on extraterrestrial impactors**

78        We investigate the nature of extraterrestrial impactors using the isotopic composition of  
79 ruthenium (Ru), a PGE. We chose Ru because it exhibits isotopic variations between different  
80 meteorite groups (27-30), which all differ from the terrestrial composition, so could serve as a  
81 genetic fingerprint for determining the source of the extraterrestrial component in impact rocks.  
82 For terrestrial impact rocks, the Ru isotopic signature of the impactor is expected to be

83 preserved, even if inter-element PGE abundance ratios are modified during the impact or  
84 subsequent geologic processes (13).

85 If Ru in the K-Pg boundary layer and other terrestrial impact structures originate from  
86 extraterrestrial bodies, their Ru isotopic compositions will differ from Earth's, but be similar to  
87 those of the associated classes of meteorites. The Ru isotope signatures among meteorites scale  
88 with the heliocentric distance (distance from the Sun) at which their parent asteroids formed in  
89 the early Solar System (30). Two major classes of meteorites can be distinguished based on  
90 systematic differences in isotopic compositions of various elements (31): 1.) the carbonaceous  
91 (CC) meteorites comprising chondrites of Ivuna- (CI), Mighei- (CM), Ornans- (CO), Vigarano-  
92 (CV), Karoonda- (CK), Renazzo- (CR), High-iron- (CH), and Bencubbinit-types (CB), as well  
93 as isotopically associated iron meteorite groups (CC irons: IIC, IID, IIF, IIIF, IVB); 2.) the non-  
94 carbonaceous (NC) meteorites comprising ordinary- (OC), enstatite- (EC), and Rumuruti-type  
95 (RC) chondrites, as well as associated iron meteorite groups (NC irons: IAB, IIAB, IIAB, IIIE,  
96 IVA).

97 OCs are by far the most common type of stony meteorites arriving at Earth. OCs, ECs  
98 and RCs are fragments of siliceous (S-type) asteroids that formed in the inner Solar System, in  
99 the same region as the rocky planets (31, 32). The Ru isotope signatures of NC meteorites (OC,  
100 EC, RC and most NC irons) are less distinct from the Ru isotope composition of Earth (Fig. 1).  
101 In contrast, carbonaceous chondrite (CC) meteorites and isotopically associated iron meteorites  
102 (CC irons) are derived from carbonaceous (C-type) asteroids which formed at greater  
103 heliocentric distances, beyond the orbit of Jupiter (31, 32). The average Ru isotope  
104 compositions of CCs and CC irons are more distinct from Earth than OCs and ECs (Fig. 1).  
105 However, unlike other meteorite groups the CCs have large variations in between individual  
106 meteorites (Fig. 1), and CIs appear to be distinct from other CC groups (30).

107 Almost all meteorites that impact Earth are delivered from the current asteroid belt,  
108 located between the orbits of Mars and Jupiter, with CCs having migrated there due to scattering  
109 by the giant planets (32). Nevertheless, the difference in Ru isotope compositions with Earth  
110 follows the sequence  $EC < OC < CC$ , so distinguishes between asteroid material with C-type or  
111 S-type composition. Therefore, Ru can potentially be used to determine if an impactor  
112 originally formed in the inner or outer Solar System (27-30).

113

#### 114 **Ruthenium isotope measurements**

115 We measured Ru isotopes to constrain the origins of the Chicxulub impactor, using  
116 samples taken from the K-Pg boundary (33). For comparison, we apply the same analysis to  
117 other Phanerozoic impact structures, ancient (3.5 to 3.2 Ga old) impact-related spherule layers,  
118 and two carbonaceous meteorites (CI and CV). Our samples were taken from widely separated  
119 K-Pg boundary sites from locations in Europe, to span a range of the Chicxulub ejecta layer.  
120 We used geologic sections collected from Denmark (Stevns Klint), Italy (Fonte D'Olio) and  
121 Spain (Caravaca). For the other Phanerozoic impacts, we used three drill core samples of impact  
122 melt rock from the Brent (Ontario, Canada), Clearwater East (Quebec, Canada) and  
123 Morokweng (South Africa) impact structures; surface impact melt rocks from Rochechouart  
124 (north-west Massif Central, France) and Popigai (Siberia, Russia) (34, 35). Three ancient  
125 impact spherule layer samples (BARB5\_SL2, CT3-1\_SL9, CT3-2\_SL13) of the Barberton  
126 greenstone belt (South Africa) were taken from drill cores (core names: BARB5 & CT3, Table  
127 S1) (33). These spherule layers are dated 3.5 to 3.2 Ga and represent the oldest records of large  
128 asteroid impacts in the early Earth's history during the Archean era (24-26), a geologic time  
129 period from 4.0 to 2.5 Ga. Table S1 lists the sample locations and other detailed information  
130 (33). We also measured terrestrial standard samples (PGE-rich chromitite layer (UG2) from the  
131 Bushveld intrusion in South Africa), the CV meteorite Allende and the CI meteorite Orgueil.

132 All isotopic measurements used multi-collector inductively coupled plasma mass  
133 spectrometry (MC-ICPMS) (33). The resulting Ru isotopic compositions are listed in Table 1.

134 The differences between the Ru isotope compositions of meteorites and Earth are very small,  
135 so are conventionally reported in  $\epsilon$  notation, which indicates the deviation in parts per 10,000  
136 (0.01 % from a terrestrial isotopic standard (Table 1) and ‘Materials and Methods’ for details)  
137 (33). The uncorrected raw data, interference corrected and internally normalized data, and  
138 calculated  $\epsilon$  values are provided in Data S1.

139 We find that all the impact-related samples have Ru isotopic compositions that are distinct  
140 from Earth and overlap those of meteorites (Fig. 1). A plot of  $\epsilon^{102}\text{Ru}$  as a function of  $\epsilon^{100}\text{Ru}$   
141 (Fig. 2) shows that these variations are the same as observed for meteorites. We interpret this  
142 plot as indicating variable incorporation into Solar System bodies of cosmic dust enriched in  
143 Ru nuclides, produced by the slow neutron capture process (s-process) of stellar  
144 nucleosynthesis (36).

145

### 146 **Origin of the Chicxulub impactor**

147 All our K-Pg boundary layer samples exhibit indistinguishable and uniform Ru isotope  
148 compositions. The  $\epsilon^{100}\text{Ru}$  values are distinct from the composition of Earth, ECs and OCs but  
149 consistent with the average composition of CCs (Fig. 1). This implies that the Chicxulub  
150 impactor was derived from the population of C-type asteroids that formed in the outer Solar  
151 System.

152 Although the  $\epsilon^{100}\text{Ru}$  values of the K-Pg boundary layer samples are consistent with the  
153 average CC value ( $-0.88 \pm 0.12$ , 95 % conf., Table S3), they are well resolved different from  
154 those of the CI group ( $-0.31 \pm 0.13$ , 2 s.d., Table S4) (33). CI carbonaceous chondrites were  
155 interpreted to have similar composition to comets (37); if CI chondrites are a proxy for cometary  
156 matter, our Ru measurements exclude a previously proposed cometary origin of the Chicxulub  
157 impactor (38). A CI-like composition of the Chicxulub impactor has previously been excluded  
158 by Cr isotope data (15), inter-element PGE ratios (13), and the fossil meteorite in a K-Pg  
159 boundary drill core section (16).

160 We computed (33) the  $\epsilon^{100}\text{Ru}$  values that would be measured for various mixtures  
161 between an average carbonaceous chondrite composition and the continental crust. The results  
162 (Fig. 3A) show that Ru isotope signatures are almost insensitive to contamination by terrestrial  
163 target rocks, because the Ru abundance in continental crust (0.34 ppb) (8) is orders of  
164 magnitude lower than the average for CCs (838 ppb) (9). Even minute amounts of  
165 extraterrestrial impactor material (<0.5 %) are sufficient to produce a  $\epsilon^{100}\text{Ru}$  value that is  
166 indistinguishable from that of the impactor. This is consistent with our measurement of all K-  
167 Pg boundary samples having uniform Ru isotope signatures (Figs. 1 & 2). If the Chicxulub  
168 impactor had an average carbonaceous chondrite Ru composition, we calculate the average  
169 amount of extraterrestrial material in our K-Pg boundary layer samples is between 0.8 % at  
170 Fonte D’Olio (Italy) and 6.6 % at Stevns Klint (Denmark). This is lower than previous estimates  
171 but falls within the range determined from Cr isotopes (0.1 % to 20 %) (15) and PGE  
172 abundances (1.6 % to 21 %) (5).

173 The CC-like Ru isotope compositions we measure in the K-Pg boundary layer samples  
174 are consistent with evidence from Cr isotopes (14, 15) and chondritic PGE ratios (13), which  
175 were also interpreted as indicating a C-type asteroid as the Chicxulub impactor. Additionally,  
176 our Ru data exclude Deccan Trap volcanic eruptions as the origin of the elevated PGE  
177 concentrations within the K-Pg boundary (17), because any Ru derived from the eruptions  
178 would have terrestrial Ru isotope composition so would not match the Ru isotope signatures of  
179 CCs.

180

### 181 **Phanerozoic and Archean impactor compositions**

182 Unlike the Chicxulub impact, our samples from other terrestrial impact structures and  
183 Archean spherule layers have Ru isotope signatures distinct from average CCs (Fig. 1). The  
184 investigated Phanerozoic impact structures have ages of 36 to 470 Ma (34, 35) (Table S1), but

185 exhibit uniform Ru isotope signatures that are consistent with OCs, CIs, COs, RCs and IVA  
186 iron meteorites. The OC-like  $\epsilon^{100}\text{Ru}$  values of Popigai, Brent, Clearwater East, and Morokweng  
187 impact melt rocks are consistent with previous interpretation of their PGE ratios as indicating  
188 OC impactor compositions (19-23). OC meteorites are derived from S-type asteroids that  
189 formed in the inner Solar System (31, 32). The Clearwater East (460 to 470 Ma) and Brent  
190 (453 Ma) impacts occurred during a period (the Ordovician era) that had a higher flux of OC  
191 material to Earth than at present, due to the breakup of an S-type parent asteroid at 466 Ma (39,  
192 40). We computed the same mixing model as above but assuming an OC-like impactor. The  
193 results (Fig. 3A) show the relative proportions of extraterrestrial material in each of these  
194 samples is 0.18 % for Popigai, 2.6 % for Brent, 3.1 % for Clearwater East, 4.3 % for  
195 Morokweng, and 0.57 % for Rochechouart.

196 The three Archean spherule layer samples from Barberton also have uniform Ru isotope  
197 compositions which overlap those of CIs, COs, OCs, RCs and IVA iron meteorites. However,  
198 Previous Cr isotope measurements of other Barberton spherule layers with similar ages (3.5 to  
199 3.2 Ga) were consistent with a CC-like (CI, CM, CO, CV) impactor composition (41). The Cr  
200 constraints (41) in conjunction with the general isotopic distinctions between CC and NC  
201 meteorites (31) exclude NC meteorite-like impactor compositions like OCs, RCs and IVA  
202 irons. However, the Cr isotope data used different samples than our study, because BARB5 and  
203 CT3 drill core samples were not available at that time. Our Ru isotope measurements of impact  
204 spherule layer samples from the BARB5 and CT3 drill cores exclude the compositions of most  
205 carbonaceous meteorite groups, with only CIs and COs remaining viable impactor  
206 compositions (Fig. 1). The Barberton spherule layer samples have very high Ru concentrations  
207 (529 to 2737 ppb, Table S1) (33), with the CT3 samples (CT3-1\_SL9, CT3-2\_SL13) exceeding  
208 the average Ru concentration of carbonaceous chondrites (838 ppb, Table S4) (33). We  
209 calculated another mixing model for CI or CO impactors (Fig 3B) (33), which reproduces the  
210 high Ru concentrations in the Barberton spherule layers only for very high impactor  
211 contributions (>83 % for CI and >54 % for CO). Similarly high impactor contributions (>90 %)  
212 to other Barberton spherule samples were previously inferred from Cr isotopes and PGE  
213 abundances (41, 42). The very high impactor contents in these spherule layers have been  
214 interpreted as due to accumulation or reworking processes of the primary impact deposits and  
215 their inherent extraterrestrial components, e.g., by hydraulic fractionation of components of  
216 different sizes and densities during fall, and after deposition by waves and currents (43), or by  
217 condensation of PGE-rich alloys from the impact vapor plume (26, 43).

218

## 219 **Summary and conclusions**

220 Our Ru isotope measurements constrain the origin of the Chicxulub impactor, five  
221 Phanerozoic impactors and Archean spherule layers which lack an identifiable impact structure.  
222 For five of the six investigated Phanerozoic impact structures, we conclude that most of the  
223 impactors were derived from S-type asteroids that formed in the inner Solar System, with Ru  
224 isotope compositions and PGE inter-element ratios most similar to OCs. In contrast, the  
225 Chicxulub impactor which produced the K-Pg boundary (66 Ma) and the much older Archean  
226 spherule layers (3.5 to 3.2 Ga) were both derived from objects with CC-like composition,  
227 indicating an origin in the outer Solar System (33, 31). The Ru data for Chicxulub are  
228 inconsistent with a previous proposal that the impactor was a comet (38). For the Archean  
229 spherule layers, the CC-like composition could arise from C-type asteroid material that  
230 impacted during the final stages of Earth's accretion (44).

231

232 **References**

- 233 1. W. J. Foster, B. J. Allen, N. H. Kitzmann, J. Münchmeyer, T. Rettelbach, J. D. Witts,  
234 R. J. Whittle, E. Larina, M. E. Clapham, A. M. Dunhill, How predictable are mass  
235 extinction events? *Royal Society Open Science* **10**, 221507 (2023).
- 236 2. D. M. Raup, J. J. Sepkoski, Mass Extinctions in the Marine Fossil Record. *Science*  
237 **215**, 1501-1503 (1982).
- 238 3. P. Schulte, L. Alegret, I. Arenillas, J. A. Arz, P. J. Barton, P. R. Bown, T. J. Bralower,  
239 G. L. Christeson, P. Claeys, C. S. Cockell, G. S. Collins, A. Deutsch, T. J. Goldin, K.  
240 Goto, J. M. Grajales-Nishimura, R. A. F. Grieve, S. P. S. Gulick, K. R. Johnson, W.  
241 Kiessling, C. Koeberl, D. A. Kring, K. G. MacLeod, T. Matsui, J. Melosh, A.  
242 Montanari, J. V. Morgan, C. R. Neal, D. J. Nichols, R. D. Norris, E. Pierazzo, G.  
243 Ravizza, M. Rebolledo-Vieyra, W. U. Reimold, E. Robin, T. Salge, R. P. Speijer, A.  
244 R. Sweet, J. Urrutia-Fucuguchi, V. Vajda, M. T. Whalen, P. S. Willumsen, The  
245 Chicxulub Asteroid Impact and Mass Extinction at the Cretaceous-Paleogene  
246 Boundary. *Science* **327**, 1214-1218 (2010).
- 247 4. S. L. Lyons, A. T. Karp, T. J. Bralower, K. Grice, B. Schaefer, S. P. S. Gulick, J. V.  
248 Morgan, K. H. Freeman, Organic matter from the Chicxulub crater exacerbated the K–  
249 Pg impact winter. *Proceedings of the National Academy of Sciences* **117**, 25327-25334  
250 (2020).
- 251 5. F. T. Kyte, Z. Zhou, J. T. Wasson, Siderophile-enriched sediments from the  
252 Cretaceous–Tertiary boundary. *Nature* **288**, 651-656 (1980).
- 253 6. L. W. Alvarez, W. Alvarez, F. Asaro, H. V. Michel, Extraterrestrial Cause for the  
254 Cretaceous-Tertiary Extinction. *Science* **208**, 1095-1108 (1980).
- 255 7. J. Smit, J. Hertogen, An extraterrestrial event at the Cretaceous–Tertiary boundary.  
256 *Nature* **285**, 198-200 (1980).
- 257 8. R. L. Rudnick, S. Gao, in *Treatise on Geochemistry*, H. D. Holland, K. K. Turekian,  
258 Eds. (Pergamon, Oxford, 2003), pp. 1-64.
- 259 9. J. M. D. Day, A. D. Brandon, R. J. Walker, Highly Siderophile Elements in Earth,  
260 Mars, the Moon, and Asteroids. *Reviews in Mineralogy and Geochemistry* **81**, 161-238  
261 (2016).
- 262 10. S. Goderis, H. Sato, L. Ferrière, B. Schmitz, D. Burney, P. Kaskes, J. Vellekoop, A.  
263 Wittmann, T. Schulz, S. M. Chernonozhkin, P. Claeys, S. J. de Graaff, T. Déhais, N. J.  
264 de Winter, M. Elfman, J.-G. Feignon, A. Ishikawa, C. Koeberl, P. Kristiansson, C. R.  
265 Neal, J. D. Owens, M. Schmieder, M. Sinnesael, F. Vanhaecke, S. J. M. Van  
266 Malderen, T. J. Bralower, S. P. S. Gulick, D. A. Kring, C. M. Lowery, J. V. Morgan, J.  
267 Smit, M. T. Whalen, I.-I. E. Scientists, Globally distributed iridium layer preserved  
268 within the Chicxulub impact structure. *Science Advances* **7**, eabe3647 (2021).
- 269 11. B. Schmitz, Origin of microlayering in worldwide distributed Ir-rich marine  
270 Cretaceous/Tertiary boundary clays. *Geology* **16**, 1068-1072 (1988).
- 271 12. P. Claeys, W. Kiessling, W. Alvarez, in *Catastrophic events and mass extinctions:*  
272 *impacts and beyond*, C. Koeberl, K. G. MacLeod, Eds. (Geological Society of  
273 America, 2002), vol. 356, pp. 55-68.



274

- 275 13. S. Goderis, R. Tagle, J. Belza, J. Smit, A. Montanari, F. Vanhaecke, J. Erzinger, P.  
276 Claeys, Reevaluation of siderophile element abundances and ratios across the  
277 Cretaceous–Paleogene (K–Pg) boundary: Implications for the nature of the projectile.  
278 *Geochimica et Cosmochimica Acta* **120**, 417-446 (2013).
- 279 14. A. Shukolyukov, G. W. Lugmair, Isotopic Evidence for the Cretaceous-Tertiary  
280 Impactor and Its Type. *Science* **282**, 927-930 (1998).
- 281 15. A. Trinquier, J.-L. Birck, C. Jean Allègre, The nature of the KT impactor. A 54Cr  
282 reappraisal. *Earth and Planetary Science Letters* **241**, 780-788 (2006).
- 283 16. F. T. Kyte, A meteorite from the Cretaceous/Tertiary boundary. *Nature* **396**, 237-239  
284 (1998).
- 285 17. C. B. Officer, C. L. Drake, The Cretaceous-Tertiary Transition. *Science* **219**, 1383-  
286 1390 (1983).
- 287 18. B. J. Peters, J. M. D. Day, A geochemical link between plume head and tail volcanism.  
288 *Geochemical Perspectives Letters* **5**, 29-34 (2017).
- 289 19. H. Palme, R. A. F. Grieve, R. Wolf, Identification of the projectile at the Brent crater,  
290 and further considerations of projectile types at terrestrial craters. *Geochimica et*  
291 *Cosmochimica Acta* **45**, 2417-2424 (1981).
- 292 20. I. McDonald, Clearwater East impact structure: A re-interpretation of the projectile  
293 type using new platinum-group element data from meteorites. *Meteoritics & Planetary*  
294 *Science* **37**, 459-464 (2002).
- 295 21. I. McDonald, M. A. G. Andreoli, R. J. Hart, M. Tredoux, Platinum-group elements in  
296 the Morokweng impact structure, South Africa: Evidence for the impact of a large  
297 ordinary chondrite projectile at the Jurassic-Cretaceous boundary | Associate editor:  
298 C. Koeberl. *Geochimica et Cosmochimica Acta* **65**, 299-309 (2001).
- 299 22. W. D. Maier, M. A. G. Andreoli, I. McDonald, M. D. Higgins, A. J. Boyce, A.  
300 Shukolyukov, G. W. Lugmair, L. D. Ashwal, P. Gräser, E. M. Ripley, R. J. Hart,  
301 Discovery of a 25-cm asteroid clast in the giant Morokweng impact crater, South  
302 Africa. *Nature* **441**, 203-206 (2006).
- 303 23. R. Tagle, P. Claeys, Comet or Asteroid Shower in the Late Eocene? *Science* **305**, 492  
304 (2004).
- 305 24. S. Ozdemir, T. Schulz, D. van Acken, A. Luguët, W. U. Reimold, C. Koeberl,  
306 Meteoritic highly siderophile element and Re-Os isotope signatures of Archean  
307 spherule layers from the CT3 drill core, Barberton Greenstone Belt, South Africa.  
308 *Meteoritics & Planetary Science* **54**, 2203-2216 (2019).
- 309 25. T. Schulz, C. Koeberl, A. Luguët, D. van Acken, T. Mohr-Westheide, S. Ozdemir, W.  
310 U. Reimold, New constraints on the Paleoproterozoic meteorite bombardment of the Earth  
311 – Geochemistry and Re-Os isotope signatures of spherule layers in the BARB5 ICDP  
312 drill core from the Barberton Greenstone Belt, South Africa. *Geochimica et*  
313 *Cosmochimica Acta* **211**, 322-340 (2017).



- 314 26. T. Mohr-Westheide, W. U. Reimold, J. Fritz, C. Koeberl, T. Salge, A. Hofmann, R. T.  
315 Schmitt, Discovery of extraterrestrial component carrier phases in Archean spherule  
316 layers: Implications for estimation of Archean bolide sizes. *Geology* **43**, 299-302  
317 (2015).
- 318 27. E. A. Worsham, C. Burkhardt, G. Budde, M. Fischer-Gödde, T. S. Kruijjer, T. Kleine,  
319 Distinct evolution of the carbonaceous and non-carbonaceous reservoirs: Insights from  
320 Ru, Mo, and W isotopes. *Earth and Planetary Science Letters* **521**, 103-112 (2019).
- 321 28. K. R. Bermingham, E. A. Worsham, R. J. Walker, New insights into Mo and Ru  
322 isotope variation in the nebula and terrestrial planet accretionary genetics. *Earth and*  
323 *Planetary Science Letters* **487**, 221-229 (2018).
- 324 29. M. Fischer-Gödde, C. Burkhardt, T. S. Kruijjer, T. Kleine, Ru isotope heterogeneity in  
325 the solar protoplanetary disk. *Geochimica et Cosmochimica Acta* **168**, 151-171 (2015).
- 326 30. M. Fischer-Gödde, T. Kleine, Ruthenium isotopic evidence for an inner Solar System  
327 origin of the late veneer. *Nature* **541**, 525-527 (2017).
- 328 31. T. S. Kruijjer, C. Burkhardt, G. Budde, T. Kleine, Age of Jupiter inferred from the  
329 distinct genetics and formation times of meteorites. *Proceedings of the National*  
330 *Academy of Sciences* **114**, 6712-6716 (2017).
- 331 32. K. J. Walsh, A. Morbidelli, S. N. Raymond, D. P. O'Brien, A. M. Mandell, A low  
332 mass for Mars from Jupiter's early gas-driven migration. *Nature* **475**, 206-209 (2011).
- 333 33. Materials and methods are available as supplementary materials.
- 334 34. T. Kenkmann, The terrestrial impact crater record: A statistical analysis of  
335 morphologies, structures, ages, lithologies, and more. *Meteoritics & Planetary Science*  
336 **56**, 1024-1070 (2021).
- 337 35. M. Gottwald, T. Kenkmann, W. U. Reimold, *Terrestrial impact structures: the*  
338 *TanDEM-X atlas*. (Verlag Dr. Friedrich Pfeil, 2020).
- 339 36. M. R. Savina, A. M. Davis, C. E. Tripa, M. J. Pellin, R. Gallino, R. S. Lewis, S.  
340 Amari, Extinct technetium in silicon carbide stardust grains: implications for stellar  
341 nucleosynthesis. *Science* **303**, 649-652 (2004).
- 342 37. H. Campins, T. D. Swindle, Expected characteristics of cometary meteorites.  
343 *Meteoritics & Planetary Science* **33**, 1201-1211 (1998).
- 344 38. A. Siraj, A. Loeb, Breakup of a long-period comet as the origin of the dinosaur  
345 extinction. *Scientific Reports* **11**, 3803 (2021).
- 346 39. F. Terfelt, B. Schmitz, Asteroid break-ups and meteorite delivery to Earth the past 500  
347 million years. *Proceedings of the National Academy of Sciences* **118**, e2020977118  
348 (2021).
- 349 40. P. R. Heck, B. Schmitz, W. F. Bottke, S. S. Rout, N. T. Kita, A. Cronholm, C.  
350 Defouilloy, A. Dronov, F. Terfelt, Rare meteorites common in the Ordovician period.  
351 *Nature Astronomy* **1**, 0035 (2017).

- 352 41. F. T. Kyte, A. Shukolyukov, G. n. W. Lugmair, D. R. Lowe, G. R. Byerly, Early  
353 Archean spherule beds: Chromium isotopes confirm origin through multiple impacts  
354 of projectiles of carbonaceous chondrite type. *Geology* **31**, 283-286 (2003).
- 355 42. W. U. Reimold, C. Koeberl, S. Johnson, I. McDonald, in *Impacts and the Early Earth*,  
356 I. Gilmour, C. Koeberl, Eds. (Springer Berlin Heidelberg, Berlin, Heidelberg, 2000),  
357 pp. 117-180.
- 358 43. D. R. Lowe, G. Byerly, F. T. Kyte, A. Shukolyukov, F. Asaro, A. Krull, Spherule Beds  
359 3.47–3.24 Billion Years Old in the Barberton Greenstone Belt, South Africa: A Record  
360 of Large Meteorite Impacts and Their Influence on Early Crustal and Biological  
361 Evolution. *Astrobiology* **3**, 7-48 (2003).
- 362 44. M. Fischer-Gödde, B.-M. Elfers, C. Münker, K. Szilas, W. D. Maier, N. Messling, T.  
363 Morishita, M. Van Kranendonk, H. Smithies, Ruthenium isotope vestige of Earth's  
364 pre-late-veener mantle preserved in Archaean rocks. *Nature* **579**, 240-244 (2020).
- 365 45. J. H. Chen, D. A. Papanastassiou, G. J. Wasserburg, Ruthenium endemic isotope  
366 effects in chondrites and differentiated meteorites. *Geochimica et Cosmochimica Acta*  
367 **74**, 3851-3862 (2010).
- 368 46. N. Dauphas, A. M. Davis, B. Marty, L. Reisberg, The cosmic molybdenum-ruthenium  
369 isotope correlation. *Earth and Planetary Science Letters* **226**, 465-475 (2004).
- 370 47. M. McGregor, M. R. Dence, C. R. M. McFarlane, J. G. Spray, U–Pb geochronology of  
371 apatite and zircon from the Brent impact structure, Canada: a Late Ordovician  
372 Sandbian–Katian boundary event associated with L-Chondrite parent body disruption.  
373 *Contributions to Mineralogy and Petrology* **175**, 63 (2020).
- 374 48. G. Schmidt, Clues to the nature of the impacting bodies from platinum-group elements  
375 (rhenium and gold) in borehole samples from the Clearwater East crater (Canada) and  
376 the Boltysh impact crater (Ukraine). *Meteoritics & Planetary Science* **32**, 761-767  
377 (1997).
- 378 49. R. Tagle, P. Claeys, An ordinary chondrite impactor for the Popigai crater, Siberia.  
379 *Geochimica et Cosmochimica Acta* **69**, 2877-2889 (2005).
- 380 50. R. Tagle, R. T. Schmitt, J. Erzinger, Identification of the projectile component in the  
381 impact structures Rochechouart, France and Sääksjärvi, Finland: Implications for the  
382 impactor population for the earth. *Geochimica et Cosmochimica Acta* **73**, 4891-4906  
383 (2009).
- 384 51. H. A. Tornabene, C. D. Hilton, K. R. Bermingham, R. D. Ash, R. J. Walker, Genetics,  
385 age and crystallization history of group IIC iron meteorites. *Geochimica et*  
386 *Cosmochimica Acta* **288**, 36-50 (2020).
- 387 52. M. F. Horan, R. J. Walker, J. W. Morgan, J. N. Grossman, A. E. Rubin, Highly  
388 siderophile elements in chondrites. *Chemical Geology* **196**, 5-20 (2003).
- 389 53. M. Fischer-Gödde, H. Becker, F. Wombacher, Rhodium, gold and other highly  
390 siderophile element abundances in chondritic meteorites. *Geochimica et*  
391 *Cosmochimica Acta* **74**, 356-379 (2010).

392  
393  
394  
395  
396  
397  
398  
399  
400  
401  
402  
403  
404  
405  
406  
407  
408  
409  
410  
411  
412  
413  
414  
415  
416  
417  
418  
419  
420

**Acknowledgments:** We thank Frank Wombacher, Ralf Schmitt and Almut Katzemich for their help and support. We thank James Day, Honami Sato and another anonymous reviewer for constructive comments that improved the manuscript. **Funding:** M.F.-G. was supported by DFG grant number FI 1704/5-1 within the priority program SPP 1833 ‘Building a Habitable Earth’. C.M. was supported by the European Commission through ERC grant number 669666 ‘Infant Earth’. P.C. and S.G. were supported by the Research Foundation Flanders (FWO), BELSPO-Desire and VUB Strategic Research Program. A.B. was supported by the research infrastructure ECORD participating in the ITINERIS project, EU – Next Generation EU Mission 4 “Education and Research” CUP B53C22002150006. W.U.R. was supported by the Brazilian Coordination for the Improvement of Higher Education Personnel, Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brazil (CAPES) - Finance Code 001. **Author contributions:** Conceptualization: M.F.-G, S.G., A.B., T.M.-W., C.M. Data acquisition and analysis: M.F.-G., J.T., N.M., B.-M.E. Interpretation, modelling and visualization: M.F.-G. Writing: M.F.-G. with contributions from all co-authors. **Competing interests:** The authors declare no competing interests. **Data and materials availability:** Samples were obtained from the locations and sources listed in table S1 and are archived for further study; details are given in the supplementary material. All data shown in figures or used for modelling are listed in tables S1-S4. Our Ru isotope measurements (raw, corrected and normalized) are provided in Data S1.

**Supplementary Materials**  
Materials and Methods  
Tables S1 to S4  
References (45-53)  
Data S1

421 **Figure 1:  $\epsilon^{100}\text{Ru}$  measurements terrestrial samples and meteorites.** From top to bottom, the  
 422 data are for K-Pg boundary sites, Phanerozoic impact structures, Archean spherule layers, CC  
 423 meteorites (divided into types), EC meteorites, OC meteorites, Rumuruti-type meteorites, CC-  
 424 like and NC-like iron meteorites (divided into groups). Vertical colored lines indicate the  
 425 average values of ECs (green,  $\epsilon^{100}\text{Ru} = -0.08 \pm 0.04$ , 95 % conf.), OCs (red,  $\epsilon^{100}\text{Ru} = -$   
 426  $0.29 \pm 0.03$ , 95 % conf.), CCs (blue,  $\epsilon^{100}\text{Ru} = -0.88 \pm 0.12$ , 95 % conf.), and Earth's mantle (44)  
 427 (black,  $\epsilon^{100}\text{Ru} = 0.00 \pm 0.02$ , 95 % conf.), with shaded regions indicating their 95 % confidence  
 428 intervals. For CC iron meteorites the calculated average composition is shown including groups  
 429 IIC, IID, IIF, IIIF, IVB and Chinga (see Table S3 for details) (33). For ECs and OCs, white  
 430 open symbols indicate individual meteorites and black solid symbols are their averages. All  
 431 plotted terrestrial and meteorite data are listed in Tables 1 and S3 respectively; error bars reflect  
 432 either 95 % confidence interval or 2 s.d. uncertainties as indicated in Tables 1 and S3 (33).  
 433  
 434

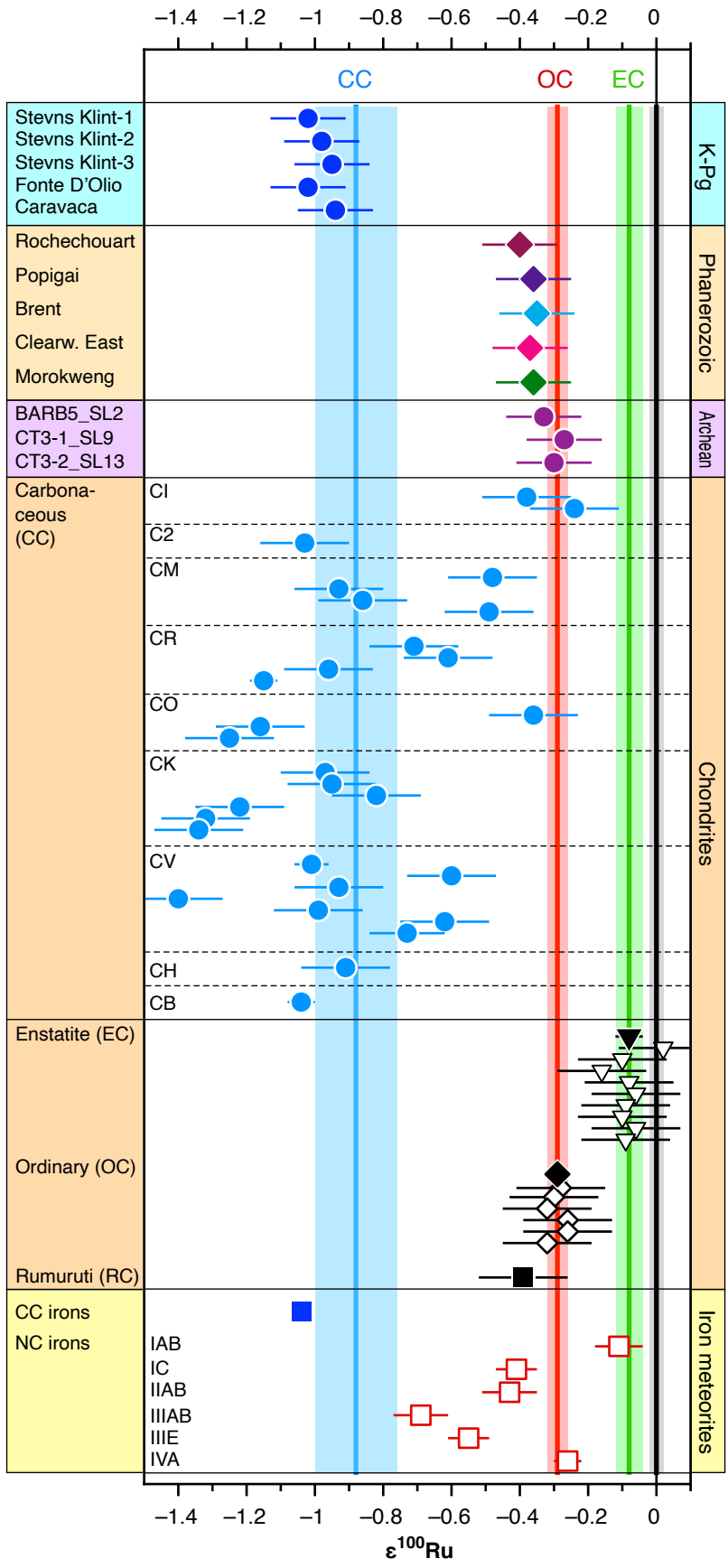
435 **Figure 2:  $\epsilon^{102}\text{Ru}$  as a function of  $\epsilon^{100}\text{Ru}$ .** Data for the same terrestrial samples as in Fig. 1 (see  
 436 legend) are compared to averages of each of the meteorite classes (solid symbols) except CIs,  
 437 which are plotted individually (open circles) because they are distinct from other CCs in Fig. 1.  
 438 The solid black lines indicate the Ru isotope composition of Earth's crust,  $\epsilon^{102}\text{Ru} \equiv 0$  and  
 439  $\epsilon^{100}\text{Ru} \equiv 0$ . The dashed line is our mixing model (33) between Earth's composition and a  
 440 nucleosynthetic component (s-process) (see 'Materials and Methods' for details) (33). Solid  
 441 black arrows indicate directions of excess and deficit in s-process component. Data are listed  
 442 in Tables 1 and S3. Error bars reflect 95 % confidence interval or 2 s.d. uncertainties as  
 443 indicated in Tables 1 and S3.  
 444  
 445

446 **Figure 3: Ruthenium mixing models.** Dashed lines indicate the calculated  $\epsilon^{100}\text{Ru}$ , as a  
 447 function of Ru abundance, for model compositions consisting of a mixture between Earth's  
 448 continental crust (black square) and potential meteorite impactor compositions, in various  
 449 proportions (labeled crosses). Color shaded regions indicate minimum and maximum calculated  
 450  $\epsilon^{100}\text{Ru}$  (curved solid black lines) based on the uncertainties of the meteorite impactor  
 451 compositions as detailed below. Horizontal solid black lines indicate the Ru isotope  
 452 composition of Earth's crust,  $\epsilon^{100}\text{Ru} \equiv 0$  (0.34 ppb Ru). (A) Models assuming the impactor  
 453 composition was (blue) the average CCs ( $\epsilon^{100}\text{Ru} = -0.88 \pm 0.12$  (95 % conf.) and 838 ppb Ru,  
 454 black circle) or (red) average OCs ( $\epsilon^{100}\text{Ru} = -0.29 \pm 0.03$  (95 % conf.) and 818 ppb Ru, black  
 455 diamond). Data for the K-Pg boundary samples (blue circles) are consistent with the CC mixture  
 456 model in proportions of 1 to 10%. The other Phanerozoic impact samples (colored diamonds,  
 457 see legend) are closer to the OC mixture model. (B) Models assuming impactor compositions  
 458 matching (cyan) CIs ( $\epsilon^{100}\text{Ru} = -0.31 \pm 0.13$  (2 s.d.) and 637.4 ppb Ru, empty blue circle) or  
 459 (purple) COs ( $\epsilon^{100}\text{Ru} = -0.36 \pm 0.13$  (2 s.d.) and 981 ppb Ru, empty purple circle). Plotted  
 460 measurements are listed in Tables 1 and S4 and the parameters of each model are given in Table  
 461 S4. Uncertainties on the Ru abundances are negligible (see 'Materials and Methods' for details  
 462 about the mixing calculations) (33). In all cases, we find that even a small contribution (> 0.5%)  
 463 of impactor material causes the measured  $\epsilon^{100}\text{Ru}$  to be close to the meteorite value.  
 464  
 465

466 **Table 1: Ruthenium isotope measurements.** Isotope data are listed for five ruthenium  
467 isotopes, measured from the samples of the K-Pg boundary layer, other Phanerozoic impact  
468 structures, Archean spherule layers, two meteorites, and a terrestrial reference sample UG2  
469 chromitite. n is the number of analyses of the same sample solution. Ruthenium isotope data  
470 have been internally normalized to  $^{99}\text{Ru}/^{101}\text{Ru}$  and are expressed in  $\epsilon$  notation as deviations  
471 from the Alfa Aesar Ru standard solution (33). Uncertainties for all samples are expressed as  
472 twice the standard deviation (2 s.d.) of repeated measurements calculated for the average for  
473 reference sample UG2 (UG2\_average), from 11 individual analyses of 2 replicate digestions  
474 ('Materials and Methods', Table S2) (33).  
475  
476

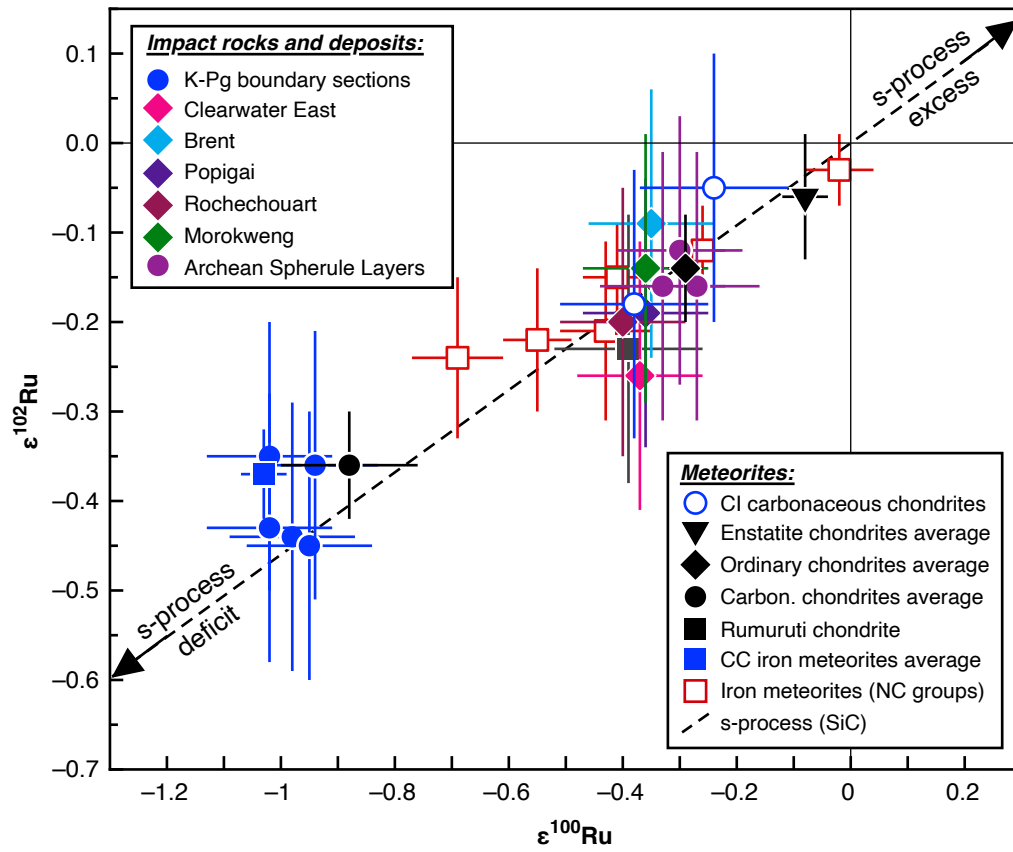
Sample	n	$\epsilon^{96}\text{Ru}$	$\epsilon^{98}\text{Ru}$	$\epsilon^{100}\text{Ru}$	$\epsilon^{102}\text{Ru}$	$\epsilon^{104}\text{Ru}$
K-Pg boundary layer:						
Caravaca	1	-0.0 ± 0.27	2.29 ± 0.46	-0.94 ± 0.11	-0.36 ± 0.15	0.18 ± 0.25
Fonte D'Olio	13	0.25 ± 0.27	0.07 ± 0.46	-1.02 ± 0.11	-0.43 ± 0.15	-0.01 ± 0.25
Stevns Klint-1	2	0.68 ± 0.27	0.58 ± 0.46	-1.02 ± 0.11	-0.35 ± 0.15	0.17 ± 0.25
Stevns Klint-2	1	0.07 ± 0.27	0.92 ± 0.46	-0.98 ± 0.11	-0.44 ± 0.15	0.09 ± 0.25
Stevns Klint-3	1	0.38 ± 0.27	1.41 ± 0.46	-0.95 ± 0.11	-0.45 ± 0.15	-0.12 ± 0.25
Phanerozoic impact structures:						
Popigai	1	0.52 ± 0.27	1.01 ± 0.46	-0.36 ± 0.11	-0.19 ± 0.15	-0.06 ± 0.25
Morokweng	5	0.14 ± 0.27	0.66 ± 0.46	-0.36 ± 0.11	-0.14 ± 0.15	0.04 ± 0.25
Rochechouart	3	0.20 ± 0.27	0.43 ± 0.46	-0.40 ± 0.11	-0.20 ± 0.15	-0.07 ± 0.25
Brent	2	0.15 ± 0.27	1.43 ± 0.46	-0.35 ± 0.11	-0.09 ± 0.15	-0.08 ± 0.25
Clearwater East	2	0.26 ± 0.27	0.29 ± 0.46	-0.37 ± 0.11	-0.26 ± 0.15	-0.08 ± 0.25
Archean impact spherule layers:						
BARB5_SL2	1	0.40 ± 0.27	0.03 ± 0.46	-0.33 ± 0.11	-0.16 ± 0.15	-0.01 ± 0.25
CT3-1_SL9	7	0.12 ± 0.27	0.27 ± 0.46	-0.27 ± 0.11	-0.16 ± 0.15	-0.04 ± 0.25
CT3-2_SL13	8	0.09 ± 0.27	0.10 ± 0.46	-0.30 ± 0.11	-0.12 ± 0.15	0.05 ± 0.25
Terrestrial reference samples:						
UG2_1	7	-0.09 ± 0.27	0.11 ± 0.46	0.01 ± 0.11	-0.06 ± 0.15	-0.11 ± 0.25
UG2_2	4	-0.12 ± 0.27	-0.12 ± 0.46	0.01 ± 0.11	0.03 ± 0.15	-0.11 ± 0.25
UG2_average	11	-0.10 ± 0.27	0.03 ± 0.46	0.01 ± 0.11	-0.02 ± 0.15	-0.11 ± 0.25
Meteorites:						
Allende (CV3)	1	0.52 ± 0.27	0.53 ± 0.46	-0.73 ± 0.11	-0.25 ± 0.15	0.21 ± 0.25
Orgueil (CI1)	1	1.52 ± 0.27	0.99 ± 0.46	-0.38 ± 0.11	-0.18 ± 0.15	0.01 ± 0.25

477  
478  
479  
480  
481  
482  
483  
484  
485  
486  
487  
488



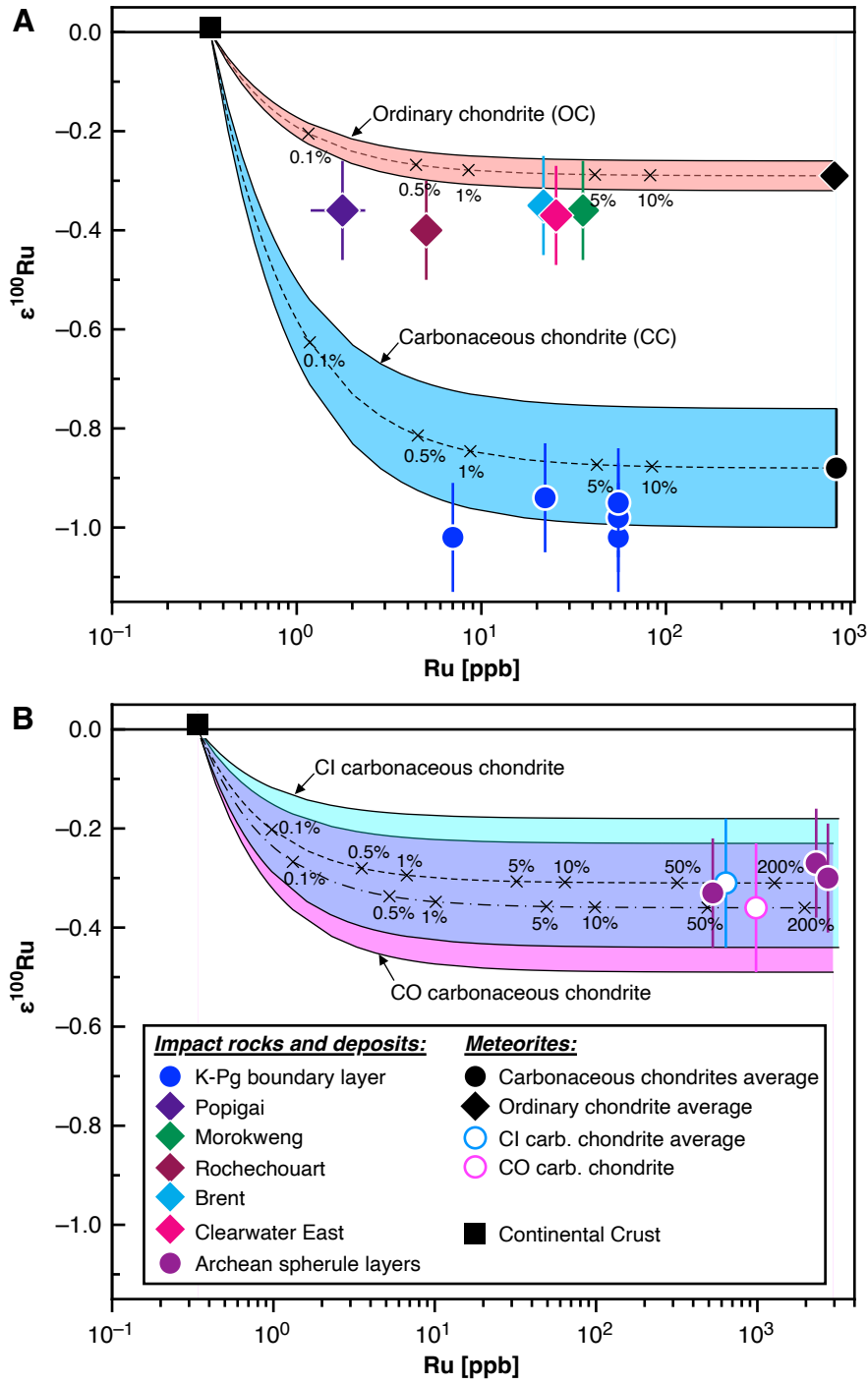
489  
490

**Figure 1**



491  
 492 **Figure 2**  
 493





494  
495  
496  
497

Figure 3