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Ru isotope vestige of Earth's pre-late veneer mantle preserved in

2 Archean rocks

4

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34

36 The accretion of volatile-rich material from the outer solar system represents a crucial
prerequisite for Earth developing oceans and becoming a habitable planet¹⁻⁴. However,
the timing of this accretion remains controversial⁵⁻⁸. It was proposed that volatile
38 elements were added to Earth by late accretion of a late veneer consisting of
carbonaceous chondrite-like material after core formation had ceased^{6,9,10}. This view,
40 however, could not be reconciled with the distinct ruthenium (Ru) isotope composition
of carbonaceous chondrites^{5,11} compared to the modern mantle¹², and in fact also not
42 with any known meteorite group⁵. As a possible solution, Earth's pre-late veneer mantle
could already have contained a significant amount of Ru that was not fully extracted by
44 core formation¹³. The presence of such pre-late veneer Ru could only be proven if its
isotope composition would be distinct from that of the modern mantle. Here we report
46 the first high-precision mass-independent Ru isotope compositions for Eoarchean
ultramafic rocks from SW Greenland, which display a relative ¹⁰⁰Ru excess of +22 parts
48 per million compared to the modern mantle value. This ¹⁰⁰Ru excess indicates that the
source of the Eoarchean rocks already contained a significant fraction of Ru prior to
50 the late veneer. By 3.7 Gyr the mantle beneath the SW Greenland rocks had not yet fully
equilibrated with late accreted material. Otherwise, no Ru isotopic difference relative to
52 the modern mantle would be observed. By considering constraints from other highly
siderophile elements beyond Ru¹⁴, the composition of the modern mantle can only be
54 reconciled if the late veneer contained significant portions of carbonaceous chondrite-
like materials with their characteristic ¹⁰⁰Ru deficits. These data therefore relax previous
56 constraints on the late veneer and now permit that volatile-rich material from the outer
solar system was delivered to Earth during late accretion.

58

Ruthenium is a highly siderophile element (HSE) and is therefore expected to be sequestered
60 into the metallic core during Earth's differentiation. Contrary to this prediction, the abundances
of Ru and other HSEs in the modern mantle are higher than expected compared to metal-
62 silicate equilibrium conditions^{15,16}. This observation is most commonly explained by HSE
replenishment of the mantle through addition of a 'late veneer' after core formation.
64 Approximately chondritic relative abundances of HSEs in the mantle suggest that the late
veneer must have consisted of primitive meteoritic material^{17,18}, amounting to ~0.5% of the
66 Earth's mass¹⁸. The chemical composition of the late veneer and its origin are a longstanding
matter of debate, especially in the context of how and when Earth accreted its water and
68 volatiles^{3,6,9,10}. In this regard, previous studies debated whether significant amounts of volatile-
rich carbonaceous chondrite-like material were added by the late veneer during the final stages
70 of Earth's accretion^{6,9,10} or had already been incorporated during earlier stages of Earth's
growth^{3,5,7,8,11}.

72
Mass-independent ruthenium isotopic variations among meteorites and the Earth have
74 provided evidence that the late veneer was derived from reduced and volatile-poor inner solar
system materials most similar to enstatite chondrites^{5,11,12,19}. This is in contrast to constraints
76 from relative abundances of volatile elements such as selenium (Se) – tellurium (Te) – sulphur
(S) and the Se isotope composition in the silicate Earth that were used to argue for a CM or CI
78 carbonaceous chondrite-like late veneer composition^{2,9,10}. Owing to its distinct Ru isotope
composition, volatile-rich carbonaceous chondrite-like material from the outer solar system
80 was excluded as possible late veneer source material^{5,11} and thus, the late veneer appeared
unlikely to be the primary source of water and volatiles on Earth^{5,11}. It should be noted,
82 however, that this conclusion depends on the premise that the Ru in the Earth's mantle
originates solely from the late accreted materials that were added after cessation of core
84 formation^{11,15,16,18}. If, however, the Earth's pre-late veneer mantle retained a significant fraction
of Ru during metal-silicate differentiation^{13,20}, as recently suggested, this conclusion would be
86 invalid. Thus, investigating Ru isotope signatures in the putative remnants of pre-late veneer

mantle would not only reveal new insights into the timescales and efficiencies of mixing the late veneer into the Earth's mantle, but also new constraints on the composition of the material that was added as a late veneer.

90

Until now, however, no unambiguous isotopic evidence for the preservation of pre-late veneer mantle on Earth exists. For instance, resolvable excesses in ^{182}W reported for 3.8 Gyr-old Archean rocks from Isua (Greenland) and Acasta (Canada) in conjunction with relatively low HSE abundances observed in 3.5–3.2 Gyr-old Archean komatiites from the Pilbara craton (Australia) and the Barberton greenstone belt (South Africa) were interpreted to reflect sluggish mixing of the late veneer into the early Archean mantle^{21,22}. However, it was later suggested that the mantle sources of the 3.8–3.7 Gyr-old Isua supracrustal belt (ISB) rocks, including 3.8 Gyr-old Eoarchean peridotites from Narssaq ultramafic body (NUB) and the south of the Isua supracrustal belt (SOISB), already had HSE abundances at about ~60-100% of the modern mantle value^{14,23}. This suggests that by ~3.8 Gyr the late veneer was to a large extent mixed into the ambient mantle. To reconcile ^{182}W excesses with the presence of modern mantle-like HSE abundances it was proposed that a small amount of core material could have been entrained into the proto-Earth's mantle as a consequence of the Moon-forming giant impact^{20,24}. Furthermore, ^{182}W anomalies could also be generated by early mantle differentiation processes during the first ~50 Myrs of the solar system²⁵⁻²⁹ or by core mantle interaction in the source of mantle plumes³⁰. In summary, ^{182}W and HSE concentration data alone fail to provide an unambiguous test as to whether pre-late veneer mantle domains were indeed preserved.

110 Here we explore the potential of mass-independent Ru isotope variations in terrestrial rocks as a new tool to investigate whether pre-late veneer isotope signatures can be found in the Archean mantle. While the Ru isotope composition of the modern mantle is well-constrained¹², this is not the case for the Archean mantle. To address this issue, we determined the Ru isotope composition for a set of ultramafic rocks from different Eoarchean and

Paleoproterozoic terranes (Extended data Table 1, see Methods for details). Herein, we focus
116 on the $^{100}\text{Ru}/^{101}\text{Ru}$ and $^{102}\text{Ru}/^{101}\text{Ru}$ ratios to constrain the Ru isotope compositions of the
mantle sources of these rocks because these are the isotope ratios measured at the highest
118 precision and they also show the largest variability among meteoritic materials^{5,19,31}. The
results are reported as ϵ -unit (0.01%) deviations of mass bias-corrected $^{100}\text{Ru}/^{101}\text{Ru}$ and
120 $^{102}\text{Ru}/^{101}\text{Ru}$ from a terrestrial standard.

122 We report Ru isotope data for samples from four different cratons. The Ru isotope
compositions obtained for ultramafic samples from the Pilbara craton, the Superior Province
124 (Abitibi greenstone belt) and the Kaapvaal craton (Bushveld Complex) are indistinguishable
from the Ru solution standard (Fig. 1), indicating that their Ru isotope composition reflects that
126 of the modern terrestrial mantle. By contrast, Eoarchean 3.8–3.7 Gyr-old ultramafic rocks from
the North Atlantic craton, originating from various localities of the Itsaq gneiss complex (IGC)
128 in SW Greenland (NUB, SOISB, ISB, and the Ujaragssuit Nunât layered intrusion) exhibit a
uniform and well-resolved excess in $\epsilon^{100}\text{Ru}$ of $+0.22 \pm 0.04$ (95% confidence interval, Fig. 1)
130 combined with a smaller excess in $\epsilon^{102}\text{Ru}$ of $+0.09 \pm 0.02$ (95% confidence interval, Figure 2a).
Chromitites from the younger 3.0 Gyr-old Seqi ultramafic complex in SW Greenland show the
132 same excesses in $\epsilon^{100}\text{Ru}$ and $\epsilon^{102}\text{Ru}$. The combined $\epsilon^{100}\text{Ru}$ and $\epsilon^{102}\text{Ru}$ excesses in these rocks
represent mass-independent isotope anomalies of nucleosynthetic origin and indicate that
134 compared to the modern mantle the Ru in the SW Greenland mantle source is enriched in
nuclides produced by the slow neutron capture process (s-process) of nucleosynthesis (Fig.
136 2a). The isotope excesses cannot be explained by mass-independent fractionation effects or
by inherited fissiogenic Ru nuclides (see Methods and Extended Data items for details about
138 the accuracy of the Ru isotope data).

140 The s-process enriched composition inferred for the Archean SW Greenland mantle is an
unexpected finding because compared to the Earth's modern mantle the Ru isotope
142 compositions reported for all meteorites are deficient in s-process Ru and exhibit negative

$\epsilon^{100}\text{Ru}$ and $\epsilon^{102}\text{Ru}$ anomalies^{5,19,31}. Therefore, the SW Greenland data for the first time provide
144 unambiguous evidence for s-process enriched building material that contributed to the early
stages of Earth's growth. Owing to the observed heliocentric zoning of $\epsilon^{100}\text{Ru}$ anomalies
146 among meteorites⁵, we speculate that this reservoir was most likely located in the innermost
region of the solar system, within < 1 AU (Fig. 2b).

148

The ^{100}Ru excess provides the first unambiguous evidence that the mantle source of the
150 Greenland rocks did not receive the full complement of late veneer material²¹. Furthermore, it
also requires that Ru and possibly other HSEs were not completely stripped from the mantle
152 during the latest stages of core formation¹³. Otherwise, no Ru isotope anomaly could ever be
observed. The uniform and ubiquitous presence of the $\epsilon^{100}\text{Ru}$ anomaly in various 3.8–3.7 Gyr-
154 old ultramafic rock types from different Eoarchean terranes in Greenland (Isuakasia,
Færingehaven) suggests that a larger mantle domain is lacking a full late veneer
156 component^{20,21}. The presence of the $\epsilon^{100}\text{Ru}$ anomaly in the younger >3.0 Gyr-old chromitites
from Seqi (Akia terrane) also indicates that even 700 Myrs later, the SW Greenland mantle
158 had not fully equilibrated with the late veneer. Such a prolonged timescale for mixing-in of the
late veneer component is consistent with significant HSE depletions observed in Archean mafic
160 rocks from the Pilbara and Kaapvaal cratons²², which previously had been explained by
sluggish inmixing of late veneer material.

162

As outlined above, the $\epsilon^{100}\text{Ru}$ excess identified in Eoarchean ultramafic rocks from SW
164 Greenland indicates that Ru was not completely sequestered into the core, most likely because
some late accretionary component was already delivered during the waning stages of core
166 formation^{14,23,32}. Depending on the composition of this early late-veneer material, the ^{100}Ru
excess measured in the Greenland rocks would then represent a minimum estimate for the
168 $\epsilon^{100}\text{Ru}$ excess of the pure pre-late veneer mantle. The nature of the early component that
supplied the ^{100}Ru excess and was already mixed into the Greenland mantle before 3.8 Gyr,
170 likely inner solar system material (Fig. 2b), can be further constrained by osmium (Os) isotope

systematics. This is because the initial osmium isotopic compositions of chromitite and
172 peridotite samples from the IGC overlap the $^{187}\text{Os}/^{188}\text{Os}$ composition of chondrites at 3.8
Gyr^{14,23,32,33} (Extended Data Table 2). Assuming that the positive $\epsilon^{100}\text{Ru}$ anomaly and the
174 chondritic Os signature were both imparted by this component, it is unlikely that it is
represented by any of the presently known chondritic meteorites because these all exhibit
176 negative $\epsilon^{100}\text{Ru}$ values at chondritic Os isotope composition. Importantly, owing to its positive
 $\epsilon^{100}\text{Ru}$ value, this material cannot derive from a carbonaceous chondrite-like Moon-forming
178 impactor⁸ because carbonaceous chondrites also exhibit the most negative $\epsilon^{100}\text{Ru}$ values
among all known chondrite groups⁵ (Fig. 2).

180

Regardless of the detailed nature and origin of the early accreted component, the ^{100}Ru excess
182 inferred for the Eoarchean SW Greenland mantle source could only be balanced by addition
of chondritic materials with negative $\epsilon^{100}\text{Ru}$ to yield the composition of the modern mantle
184 ($\epsilon^{100}\text{Ru} = 0$). This mixing relationship is further illustrated in Figure 3, where possible $\epsilon^{100}\text{Ru}$
compositions for the pre-late veneer mantle are calculated by subtracting enstatite, ordinary
186 or carbonaceous chondrite-like materials from the Ru isotopic composition of the modern
mantle. The model is based on a recently proposed inefficient core formation scenario where
188 about ~20% of the Ru ($\sim 1.4 \text{ ng g}^{-1}$) in the modern mantle derives from pre-late veneer stage¹³.
Assuming a minimum late accretion contribution of $\geq 60\%$ for the ≥ 3.8 Gyr Itsaq mantle
190 source¹⁴, only the addition of a late veneer consisting of carbonaceous chondrites could
account for $\epsilon^{100}\text{Ru} \approx 0$, as observed for the modern mantle¹² (Figure 3). The required proportion
192 of late accreted material would amount to a maximum estimate of ~0.3% of the Earth's mass
of average carbonaceous chondrite or CM carbonaceous chondrite material, consistent with a
194 recent estimate based on Se isotopes¹⁰. A late veneer consisting of CM-like material is also
supported by the abundance pattern of volatile elements in the silicate Earth^{2,9,10}. This
196 conclusion remains robust, even if a larger fraction of Ru would have been present in the pre-
late veneer mantle or if the late accretion component in the mantle by 3.8 Gyr was $>60\%$, but
198 in these cases a lower carbonaceous chondrite mass fraction would be sufficient. Ordinary

chondrites would only become viable late veneer materials if the Greenland mantle by 3.8 Gyr
200 contained a significantly lower late veneer contribution (<50%). Moreover, while a late veneer
consisting of carbonaceous chondrites is in accord with the relative abundances of S-Se-Te
202 and the Se isotopic composition of the modern mantle^{2,9,10}, the addition of a late veneer
composed of ordinary chondrites cannot be reconciled with these constraints, because the
204 relative abundances of S-Se-Te and the Se isotope composition of ordinary chondrites are
markedly distinct from those of the Earth's mantle^{9,10}. If a major part of the late veneer would
206 have consisted of core fragments from differentiated impactors²⁴, one potential caveat would
be that this material cannot readily account for chondritic S-Se-Te and broadly chondritic HSE
208 relative abundances in the Earth's mantle^{2,9,16,18}.

210 Collectively, our new data imply that the distinct ¹⁰⁰Ru isotope excess in the Eoarchean SW
Greenland mantle source is best explained by late mixing of a carbonaceous chondrite-like
212 late veneer fraction into the Earth's mantle. Thus, contrary to previous Ru isotope constraints
on the late veneer^{5,18}, these data imply that significant amounts of volatile-rich outer solar
214 system materials including water and volatiles were indeed added with the late veneer. This
revised view is also in accord with other constraints such as those independently obtained
216 from relative abundances and isotope compositions of Earth's volatile elements^{1,2,9,10}, which
also indicate that the major share of Earth's volatiles was inherited from a carbonaceous
218 chondrite source¹⁻⁴. Finally, our new data demonstrate that investigating the Ru isotope
composition of terrestrial rocks represents a powerful and distinctive tool to identify primordial
220 mantle heterogeneities arising from incomplete equilibration of the ambient mantle with Earth's
late stage building blocks.

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318

Author contributions

320 M.F.-G. and C.M. designed the project. M.F.-G., B.-M. E. and N.M. developed the analytical
method and obtained the Ru isotope data. M.F.-G. wrote the manuscript. All authors
322 contributed to the discussion of the results and editing of the manuscript.

Competing interests

The authors declare no competing interests.

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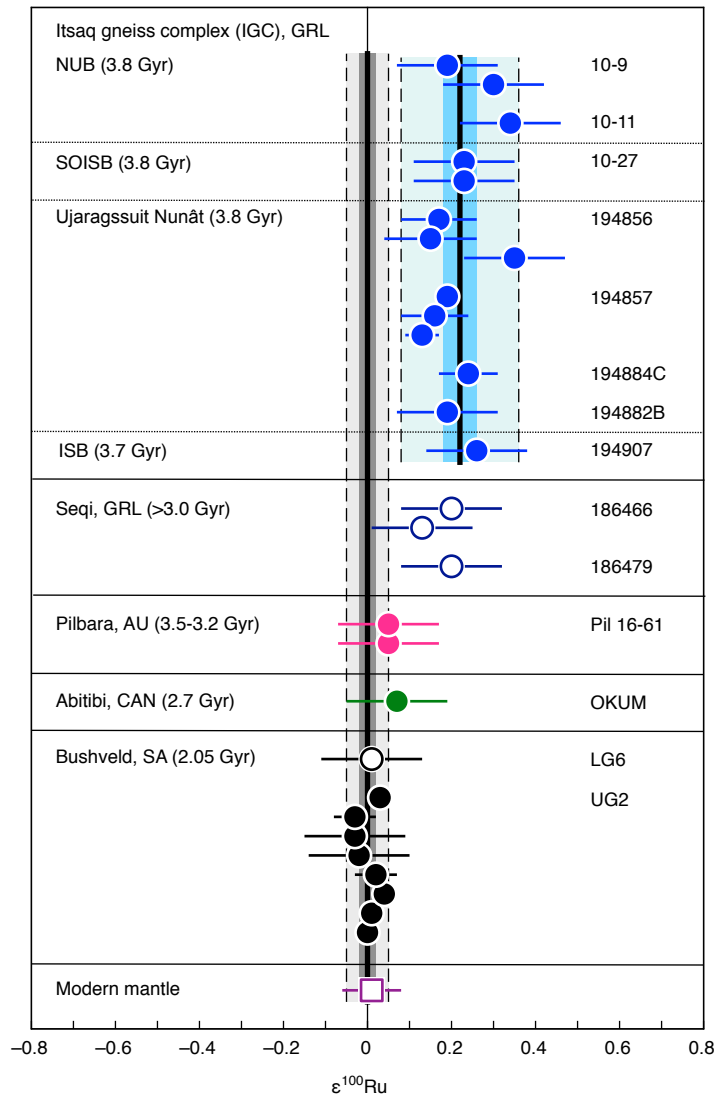
Additional information

328 Correspondence and requests for materials should be addressed to M.F.-G. (mfisch48@uni-
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Data availability

332 The data that support the findings of this study are available from the EarthChem library.



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Figure 1. | $\epsilon^{100}\text{Ru}$ data for Archean and Paleoproterozoic rocks, the modern mantle and

336

chondrites. Shown are the individual results for all analyzed samples (Extended data Table 1) in comparison to the composition of the modern mantle¹². The uncertainties for individual

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data points reflect the external uncertainty of the method (2 s.d. for samples measured $n < 4$ times) or 95% confidence intervals of replicate analyses of a given sample (if $n \geq 4$).

340

The mean values for 3.8–3.7 Gyr-old Eoarchean samples from the Itsaq gneiss complex (IGC) in SW Greenland (NUB: Narssaq ultramafic body; SOISB: south of Isua supracrustal belt; ISB: Isua supracrustal belt; Ujaragssuit Nunât layered intrusion) and chromitite samples from the

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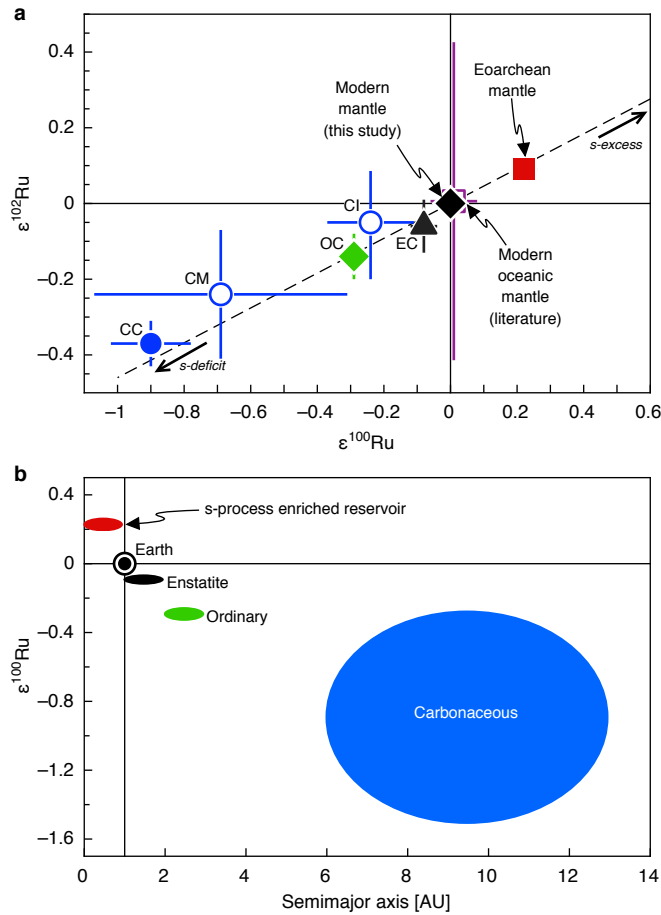
Bushveld complex are shown as a solid vertical line. The darker grey and blue areas represent the respective 95% confidence interval uncertainties. Light grey and blue areas limited by

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dashed lines indicate the 2 s.d. uncertainty of the mean values. The uncertainty for the modern mantle composition is 2 s.d.¹².

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Figure 2. | Ruthenium isotope plot illustrating compositional differences between enstatite (EC), ordinary (OC), average carbonaceous (CC), CI and CM carbonaceous chondrites, modern mantle and Eoarchean mantle.

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a: Dashed line represents a mixing line between the modern mantle composition ($\epsilon^{100}\text{Ru} = 0$) and an s-process component as defined by Ru isotope data for pre-solar silicon carbide (SiC) grains³⁴. The compositions of enstatite chondrites (EC, $\epsilon^{100}\text{Ru} = -0.08 \pm 0.04$, 95% confidence interval); ordinary chondrites (OC, $\epsilon^{100}\text{Ru} = -0.29 \pm 0.03$, 95% confidence)⁵, CI chondrites (CI,

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$\epsilon^{100}\text{Ru} = -0.24 \pm 0.13$, 2 s.d.)⁵; CM chondrites (CM, $\epsilon^{100}\text{Ru} = -0.69 \pm 0.38$, 95% confidence)⁵, and average carbonaceous chondrites (average CC, $\epsilon^{100}\text{Ru} = -0.90 \pm 0.12$, 95% confidence interval)⁵ are shown for comparison. The uncertainties for CI chondrites reflect a single measurement and are thus shown with the external uncertainty of the method (2 s.d. as stated

360

in ref. 5). Uncertainties for the modern and the Eoarchean mantle composition are the same as stated in Fig. 1. Note that the uncertainty of the modern oceanic mantle composition from the literature is shown as 2 s.d.¹².

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b: Plot illustrating the heliocentric zoning of $\epsilon^{100}\text{Ru}$ anomalies⁵. The presence of an s-process

366

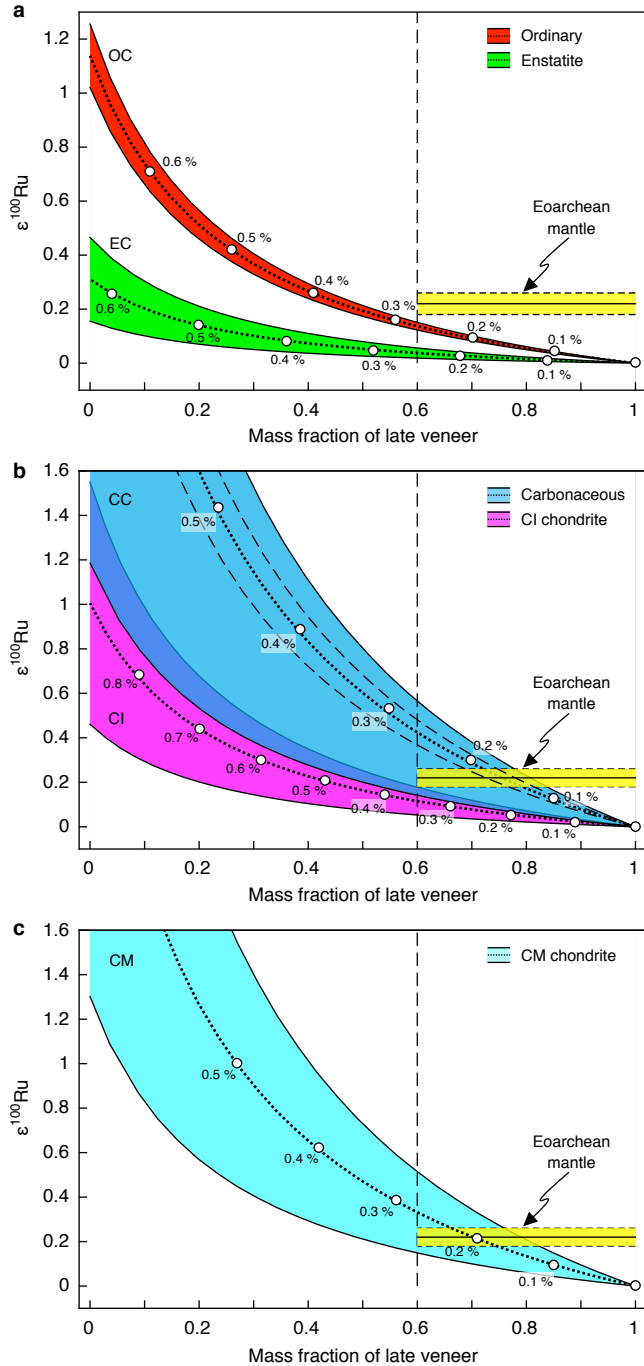
enriched reservoir that contributed to the Earth's growth is inferred from the Ru isotope composition obtained for the Eoarchean mantle of SW Greenland (Fig. 1). Chondrite groups

368

formed at increasing heliocentric distances exhibit more negative $\epsilon^{100}\text{Ru}$ because they are

370 more depleted in s-process Ru relative to Earth's modern mantle⁵. The $\epsilon^{100}\text{Ru}$ uncertainty for
 carbonaceous chondrites in **b** is shown as 2 s.d. to account for significant within-group
 variation of their $\epsilon^{100}\text{Ru}$ values (Figure modified from ref. 5).

372



374 **Figure 3. | Model estimates for the amount of late veneer added to the Eoarchean mantle**
 based on Ru isotope compositions.

376 The model illustrates the effect of subtracting variable mass fractions of late veneer from the
 Ru isotope composition of the modern mantle. The composition of the modern mantle was
 378 fixed at $\epsilon^{100}\text{Ru} = 0$, as indicated by the composition obtained for samples from the Bushveld

380 complex (Extended data Table 1), which is indistinguishable from previously reported data for
the modern oceanic mantle composition¹². Dotted lines indicate the respective mass fractions
of different chondritic late veneer compositions subtracted from the modern mantle
382 composition. Solid black lines show the minimum and maximum $\epsilon^{100}\text{Ru}$ values for different
chondrite classes in **a**: enstatite chondrites (EC, $\epsilon^{100}\text{Ru} = -0.08 \pm 0.04$, 95% confidence
384 interval); ordinary chondrites (OC, $\epsilon^{100}\text{Ru} = -0.29 \pm 0.03$, 95% confidence)⁵; **b**: carbonaceous
chondrites (CC, $\epsilon^{100}\text{Ru} = -0.90 \pm 0.61$, 2 s.d.; ± 0.12 , 95% confidence)⁵; CI chondrites (CI,
386 $\epsilon^{100}\text{Ru} = -0.24. \pm 0.13$, 2 s.d.)⁵; and **c**: CM chondrites (CM, $\epsilon^{100}\text{Ru} = -0.69. \pm 0.38$, 95%
confidence)⁵. The uncertainties for carbonaceous chondrites in **b** are given as 2 s.d. to account
388 for significant within-group variation of their $\epsilon^{100}\text{Ru}$ values (dashed line indicates 95 %
confidence interval uncertainty). The 2 s.d. uncertainty for CI chondrites reflects the external
390 uncertainty of the method (as stated in ref. 5). The amount of subtracted late veneer material
for each respective chondrite composition was adjusted to match a presumed Ru
392 concentration in the pre-late veneer mantle of $\sim 1.4 \text{ ng g}^{-1}$, corresponding to $\sim 20\%$ of the Ru
contained in the modern mantle. The yellow box in **a**, **b** and **c** indicates the composition of the
394 Eoarchean mantle inferred from the mean value of all analyzed 3.8–3.7 Gyr-old samples
originating from various localities of the Itsaq gneiss complex ($\epsilon^{100}\text{Ru} = +0.22 \pm 0.04$, average
396 value shown as solid black line, dashed lines indicate 95% confidence interval uncertainty,
Extended data Table 1). The solid vertical dashed line indicates the minimum late veneer
398 contribution inferred for the mantle source of peridotite samples from the Narssaq ultramafic
body (NUB) and the south of Isua supracrustal belt (SOISB), based on previously reported
400 $^{187}\text{Os}/^{188}\text{Os}$ data and HSE concentrations¹⁴. The parameters used for the mixing model are
given in Extended Data Table 3.

402 **Methods**

Samples. The samples analyzed in this study comprise ultramafic rocks from four different
404 cratons. The North Atlantic craton is represented by peridotite and chromitite samples of from
various localities of the Eoarchean Itsaq gneiss complex (IGC) and the Mesoarchean Seqi
406 ultramafic complex in southern W Greenland. The sample set is complemented by chromitites
from the Kaapvaal craton (Bushveld Complex, South Africa) and the Pilbara craton (Australia),
408 and a komatiite reference sample from the Superior Province (Abitibi greenstone belt,
Canada). Where available, the Ru concentration and osmium isotope data of the samples
410 analyzed in this study are given in Extended Data Table 2. For samples where no data were
reported previously, Ru and Os data obtained for similar samples from the same location are
412 listed.

The Itsaq gneiss complex (IGC) in SW Greenland represents one of the few worldwide
414 localities where remnants of Eoarchean mantle are preserved. The IGC comprises two
Eoarchean crustal terranes (Isuakasia and Færingehavn), where possible mantle rocks are
416 exposed as ultramafic lenses in the 3.8-3.7 Gyr-old Isua supracrustal belt and ultramafic
bodies in the 3.8 Gyr-old South of the Isua supracrustal belt (SOISB), both located in the
418 Isuakasia terrane^{35,36}. In the Færingehavn terrane such rocks are exposed in the 3.8 Gyr-old
Narssaq ultramafic body³⁷ (NUB). The peridotite and chromitite samples investigated in this
420 study were selected to cover all of these different localities.

Samples 10-9 and 10-11 from NUB are massive, coarse-grained peridotites. Olivine is the
422 dominant phase in these rocks. They also contain orthopyroxene, amphibole, spinel and
magnetite¹⁴. The chemical composition of these samples including concentration data for
424 highly siderophile elements and ¹⁸⁷Os/¹⁸⁸Os data were reported in a previous study¹⁴. Sample
10-27 is a harzburgite from the South of the Isua supracrustal belt (SOISB). The mineral
426 assemblage of this rock is comparable to other harzburgites collected from the same locality¹⁴.
These rocks are typically spinel-peridotites with harzburgitic mineral assemblages composed
428 of mainly olivine and variable amounts of orthopyroxene, amphibole and opaque phases¹⁴. A
minimum age of 3.8 Gyr for the analyzed SOISB and NUB peridotites was estimated based

430 on field relationships to surrounding 3.8 Gyr old tonalitic gneisses and crosscutting
dykes^{14,36,37}.

432 Two of the investigated chromitites (194856, 194857) were collected from the Ujargssuit Nunât
layered intrusion³⁸. For chromitites from this locality Pt-Os model ages as old as 4.36 Gyr were
434 reported³⁹. Samples 194882B and 19488C are chromitites from a locality close to the inland
ice that most likely belongs to the same sequence as the chromitites from the Ujargssuit Nunât
436 layered intrusion.

The dunite sample 194907 was collected from an antigorite lens located within the
438 northeastern part of the 3.7 Gyr-old Isua supracrustal belt, which has previously been referred
to as Dunite Lens B^{40,41}. The ISB dunites also contain orthopyroxene and spinel, and very
440 minor amounts of mostly altered clinopyroxene⁴⁰.

Two of the analyzed chromitites (186466, 186479) derive from the Seqi ultramafic complex.
442 The major and trace element composition including concentration data for platinum-group
elements of these samples were reported in a previous study⁴². The Seqi ultramafic complex
444 represents a peridotite enclave hosted by tonalitic orthogneiss within the 3.0 Gyr-old Akia
terrane. A minimum age for the ultramafic body is constrained by 2.98 Gyr-old crosscutting
446 granitoid sheets⁴², although unpublished Re-Os isotope data show a consistent 3.1 Gyr mantle
depletion age for the Seqi ultramafic complex. The highly refractory peridotites and chromitites
448 are interpreted to represent the remnant of a fragmented layered complex or a magma conduit.
The ultramafic rocks formed from a magnesian-rich near-anhydrous magma as olivine
450 dominated cumulates with high modal contents of chromite⁴². Their parental magma was
generated by high degrees of partial melting of a mantle source that likely represents the
452 precursor of the regional sub-continental lithospheric mantle.

The chromitite sample Pil 16-61 was collected from the Warawoona Group located within the
454 Pilbara craton. The chromitite may be as old as the associated Mount Ada basalt unit (3.5 Gyr)
or it may be part of the younger 3.2 Gyr-old Dalton Suite sill complex⁴³.

456 The investigated komatiite rock (OKUM) from the 2.7 Gyr-old Abitibi greenstone belt (Canada)
is a commercially available rock reference sample provided by the International Association of
458 Geoanalysts.

Two chromitites (UG2, LG6) from the 2.05 Gyr-old Bushveld complex (South Africa) were used
460 as a reference sample to validate the analytical method and to assess the precision and the
accuracy of the Ru isotope measurements. The Ru isotope composition of UG-2 was
462 previously determined employing a different digestion method (alkaline fusion)⁵.

464 **Ruthenium separation and purification.** The required amount of sample material to yield
sufficient Ru for a high-precision measurement was estimated based on previously reported
466 Ru concentrations (10-9, 10-11, UG-2, LG-6, OKUM, 186466, 186479)^{42,44,45} or Ru
concentrations reported for samples of similar composition from the same locality (10-27,
468 194907)^{23,46}. For samples where such information was not available (e.g. 194856, 194857,
Pil16-61) the Ru concentrations were determined on a 1 g powder test portion digested in a
470 high pressure asher in reverse aqua regia (5 ml conc. HNO₃ + 2.5 ml conc. HCl). Before
quantification of Ru for these samples, the digestion solution was dried down, converted twice
472 with 5 ml of 6M HCl, taken up in 0.2 M HCl and loaded on a cation column to remove matrix
elements as described below. Ruthenium concentrations were determined in the eluted Ru
474 fractions by external calibration using a quadrupole inductively coupled plasma mass-
spectrometer (ThermoScientific iCap). We note that the concentrations determined by this
476 procedure may underestimate the actual concentration of samples because some Ru may
have been lost as a volatile tetroxide (RuO₄) when the aqua regia solutions were dried down.
478 Therefore, these concentrations are considered only as informal values. In a similar manner,
the Ru contents of two chromitites (194882B, 194884C) were estimated based on a 1% sample
480 aliquot taken after NiS digestion and cation column chemistry as described below. However,
we note that these estimates represent only informational values too because as described
482 below the Ru yield of the NiS procedure is <100%.

For the NiS procedure powder aliquots of 5-10 g were digested using a NiS fire assay
484 technique⁴⁷. For chromitite samples with high Ru concentrations (UG-2, LG-6, 194856,
194857, Pil16-61) one NiS digestion with 5 g of sample powder was needed to yield sufficient
486 amounts of Ru. For ultramafic samples with lower Ru concentrations (harzburgites, dunites,
komatiites, and some chromitites) multiple NiS digestions with 10 g of sample powder had to
488 be prepared. The total number of NiS digestions and the amount of sample material used for
each respective NiS bead are given in Extended Data Table 2. To each 5-10 g sample portion
490 appropriate amounts of Ni, S, Borax and Na₂CO₃ were added and thoroughly mixed. The
mixture was fluxed in a muffle furnace for 75 minutes at 1000°C. After cooling, the NiS beads
492 were physically removed from the quenched silicate melt.

For the majority of samples, the NiS procedure resulted in about one to three cm-sized beads
494 that could readily be recovered from the quenched silicate. The Ru yield of the NiS procedure
was determined based on sample powders with well-known Ru concentrations (UG-2, OKUM,
496 10-9, 10-11, 186466, 186479). For these samples the Ru yield usually varied from 60-95%.
However, in case of three replicate UG-2 digestions the Ru yields were only on the order of
498 10-20%. The lower yields resulted from incomplete homogenization and subsequent inefficient
extraction of NiS beads from the quenched silicate. For these samples the NiS digestions
500 produced finely dispersed mm- to µm-sized spherules within the quenched silicate. Careful
homogenization of the NiS sample-flux mixtures before digestion helped to avoid this problem.
502 The NiS beads were crushed in an agate mortar, transferred into 60 ml Savillex beakers
followed by the addition of 30 ml concentrated HCl. The solutions were evaporated to near
504 dryness on a hotplate at 100°C. This step was repeated with another 30 ml of concentrated
HCl and 20 ml 1 M HCl.

506 Ruthenium was separated from the dissolved NiS beads using cation exchange
chromatography⁴⁸. Each dissolved NiS bead from a single fire assay digestion was split over
508 three cation columns filled with 10 ml AG50 X8 resin, respectively. The resin was equilibrated
with 20 ml 0.2 M HCl. Ruthenium and other platinum-group elements were loaded and eluted
510 in 14 ml 0.2 M HCl. The eluted Ru fractions from each sample were recombined and a small

aliquot (1%) was taken to determine the amount of Ru and remaining matrix elements (mainly
512 Ni). If significant amounts of matrix elements passed through the column (if Ni/Ru > 1), the
combined fractions of samples were passed for a second time over a single 10 ml cation
514 column. The Ru yields from the cation column are usually >95%. The eluted sample solutions
were dried down on a hotplate, recombined and Ru was further purified using a macro-
516 distillation unit as described elsewhere⁴⁸. After the distillation the purified Ru fractions were
dried down on a hotplate and dissolved in 0.5 ml 0.28 M HNO₃ from which a small aliquot was
518 prepared as a predilution to determine the Ru yield and to check for potential interfering
elements. The distillation yields were usually between ~40-80%. The total Ru yield of the
520 analytical procedure including NiS digestion, column chemistry and distillation is typically 30–
70%, estimated based on samples with known Ru concentrations (UG-2, OKUM, 10-9, 10-11,
522 186466, 186479). In case of three UG-2 digestions the total yield was only 6-21%. Even though
for these samples the yields of the distillation were 50-80%, the low total Ru yields are caused
524 by inefficient extraction of NiS beads, as described above. However, neither the total Ru yield
of the entire analytical procedure nor the respective yields from the NiS digestion or the Ru
526 distillation have any effect on the accuracy of the Ru isotope data (Extended Data Figure 1).
The procedural blank for a single NiS digestion, including column chemistry and distillation
528 varied between 185 and 435 pg (n=3). The blank contribution was <<1% for the majority of
samples and <2% for OKUM and 194907 given that per each respective NiS digestion ≥30 ng
530 of Ru were processed.

532 **Mass spectrometry.** The Ru isotope measurements were performed using a ThermoScientific
Neptune Plus multicollector inductively coupled plasma mass spectrometer (MC-ICPMS) in
534 the Institut für Geologie und Mineralogie at the University of Cologne. For the measurements,
the Ru fractions were further diluted in 0.28 M HNO₃ to yield Ru solutions of 100 ng ml⁻¹. The
536 diluted solutions were checked for the presence of interfering elements (Zr, Ni) that could affect
the accuracy of the isotope data and cannot be monitored online during the measurements.
538 The sample solutions were introduced into the mass spectrometer at an uptake rate of ~50 ul

min⁻¹ using an ESI microflow PFA nebulizer attached to a Cetac Aridus II desolvator. The
540 isotope measurements were conducted with total ion beam intensities between 8×10^{-11} and
 2×10^{-10} A, obtained for 100 ng ml⁻¹ Ru sample and standard solutions using conventional Ni
542 H-cones. The setup was optimized to yield oxide production rates <<1% (CeO/Ce). The
measurements were conducted in static mode and the seven stable Ru isotopes ⁹⁶Ru, ⁹⁸Ru,
544 ⁹⁹Ru, ¹⁰⁰Ru, ¹⁰¹Ru, ¹⁰²Ru and ¹⁰⁴Ru as well as ⁹⁷Mo and ¹⁰⁵Pd were monitored simultaneously.
Each Ru isotope analysis consisted of an on-peak baseline on a solution blank (40 integrations
546 of 4.2 s) followed by 100 integrations of 8.4 s for each sample or standard solution and typically
consumed about ~90 ng Ru. Each sample analysis was bracketed by measurements of an in-
548 house Ru standard solution (Alfa Aesar Ru). The data were internally normalized to ⁹⁹Ru/¹⁰¹Ru
= 0.7450754³¹ using the exponential law to corrected for mass-dependent isotope
550 fractionation. The isotope data are reported as $\epsilon^i\text{Ru} = ({}^i\text{Ru}/{}^{101}\text{Ru}_{\text{Sample}}/{}^i\text{Ru}/{}^{101}\text{Ru}_{\text{Standard}} - 1) \times$
 10^4 , calculated relative to the bracketing standard of each analytical session. The accuracy
552 and precision of the Ru isotopic measurements were evaluated by replicate digestions and
multiple analyses of the UG-2 chromitite (Bushveld, South Africa), which was used as
554 reference sample. The Ru isotope data obtained for UG-2 in this study agrees well with
previously reported data⁵, where a different digestion method (alkaline fusion) was used for
556 sample decomposition. This demonstrates that the isotope data obtained by the NiS method
yields accurate results. The external reproducibility (2 s.d.) obtained for a total number of 103
558 individual measurements from 8 replicate UG-2 digestions is $\pm 0.43 \epsilon^{96}\text{Ru}$, $\pm 0.49 \epsilon^{98}\text{Ru}$, ± 0.12
 $\epsilon^{100}\text{Ru}$, $\pm 0.16 \epsilon^{102}\text{Ru}$ and $\pm 0.30 \epsilon^{104}\text{Ru}$.

560

Correction for mass-dependent isotope fractionation. The exponential law is one of the
562 most commonly used methods to correct for natural and instrumental mass-dependent isotope
fractionation. For the Ru isotope measurements, one potential caveat could be that the
564 distillation technique used to purify the Ru could induce an isotope fraction that would not
follow the exponential law. This could cause apparent isotopic anomalies for a given sample
566 as a consequence of inaccurate mass fractionation correction. The exponential law assumes

that the logarithmic fractionation $\beta = \ln(r/R)$ of a given isotopic ratio is expressed as a function
568 of the mass log-difference $\Delta(\ln M) = \ln(M_2/M_1)$. Considering two isotopic ratios ($r =$
 $^{99}\text{Ru}/^{101}\text{Ru}$ and $r' = ^{100}\text{Ru}/^{101}\text{Ru}$) the exponential law predicts that mass fractionation produces
570 a linear array in a $\ln(r/r')$ plot⁴⁹. This is illustrated in Extended Data Figure 2 for the measured
raw ratios of $^{99}\text{Ru}/^{101}\text{Ru}$ and $^{100}\text{Ru}/^{101}\text{Ru}$. The ratios in this figure are not corrected for mass-
572 fractionation and are normalized to a reference ratio (R and R' , respectively)³¹. If the mass
fractionation experienced by the samples is accurately described by the exponential law, the
574 ratios should fall on a linear array with a slope of ~ 0.5 . In the plot two distinct mass fractionation
lines can be observed for different sessions. Importantly, the slopes for both groups of sessions
576 are indistinguishable within error and are in very good agreement with the slope predicted by
the exponential law. Most importantly, the samples purified by distillation fall on the same
578 respective mass fractionation line as their associated Alfa Aesar bracketing standards. This
clearly demonstrates that the Ru distillation does not induce any non-exponential mass-
580 fractionation effects for the samples in comparison to the bracketing standard. This observation
is also independent from the Ru yield of the samples and does not change if other Ru isotope
582 ratios are considered. Therefore, the Ru isotope anomalies obtained for the SW Greenland
samples cannot reflect inaccurate mass fractionation correction. The shift observed for
584 samples and associated standards plotting on a distinct mass fractionation array was caused
by a maintenance in May 2019 during which a Faraday cup was replaced. However, because
586 the data are reported as relative deviations in parts per 10^4 from the Alfa Aesar bracketing
standard, and because samples and bracketing standards are shifted by the same magnitude,
588 this does not affect the accuracy of the data. This is also confirmed by replicate digestions of
sample 10-9 that were analyzed in both groups of sessions. The $\epsilon^{100}\text{Ru}$ values for this sample
590 is indistinguishable within analytical uncertainty.

An additional argument against non-exponential mass fractionation effects is that
592 nucleosynthetic Ru isotope anomalies caused by variable contributions of s-process Ru
nuclides would not cause any $\epsilon^{104}\text{Ru}$ anomalies in the $^{99}\text{Ru}/^{101}\text{Ru}$ normalization scheme.
594 Because the $\epsilon^{104}\text{Ru}$ values for all analyzed samples fall within the external reproducibility of

the method (± 0.30 for $\epsilon^{104}\text{Ru}$), this further demonstrates that sample distillation does not cause
596 non-exponential mass fractionation effects.

598 **Isobaric interferences.** The accuracy of the Ru isotopic measurements could be
compromised by isobaric interferences from Mo, Pd, Zr and Ni argide species, or potential
600 effects related to remaining S in the analyzed sample solutions. While interferences from Mo
and Pd are simultaneously monitored and corrected for during the measurements⁴⁸, this is not
602 the case for isobars from Zr and Ni argides. Due to the design of the collector block and limited
availability of collectors, Zr and Ni could not be simultaneously monitored during the
604 measurements. However, Zr is very effectively separated from Ru by cation exchange
chemistry. Hence, all analyzed sample solutions (except for one digestion of sample 10-27)
606 had Zr intensities indistinguishable from the background of the 0.28 M HNO_3 and the Ru
standard solution. Only one analyzed sample (10-27) had slightly elevated Zr/Ru of 0.0008
608 and, hence, its $\epsilon^{96}\text{Ru}$ value is slightly elevated due to an isobaric interference from ^{96}Zr that
could not be corrected. The Zr contained in the one analyzed sample solution most likely
610 reflects a random contamination from the lab-ware used during sample preparation which was
not observed for other samples.

612 In case of Ni, during the initial stage of the project, we noticed that a few processed reference
samples after the cation chemistry still contained considerable amounts of Ni. For these
614 samples, even after further purification of Ru by distillation, smaller amounts of Ni (between 1
and 10 ng ml^{-1}) were observed in the sample solutions to be analyzed. During the isotopic
616 measurements Ni readily forms argide species in the plasma that interfere with Ru isobars⁵⁰.
In order to assess potential effects from Ni argide species on the measured Ru isotope data,
618 a 100 ng ml^{-1} Ru standard solution was doped with varying amounts of Ni to yield
concentrations between 0.2 pg ml^{-1} and 50 ng ml^{-1} . The results of this test show that the
620 measured Ru isotope compositions for 100 ppb Ru solutions are not affected for samples with
Ni/Ru ratios < 0.01 (Extended Data Figure 3a,b). For sample solutions with higher amounts of
622 Ni, positive anomalies are observed, which are most pronounced for ^{98}Ru and to a lesser extent

for ^{100}Ru . Other Ru isotope masses (^{102}Ru and ^{104}Ru), owing to the lower abundance of the
624 higher mass Ni isotopes, are not significantly affected by Ni argide species. In order to avoid
any interferences from Ni argides during the isotopic measurements, the final dilutions of all
626 samples analyzed in this study were carefully checked for their Ni contents before the analysis.
The intensity of Ni, monitored with a scan on mass ^{58}Ni , in the finally diluted sample solutions
628 was indistinguishable from the background intensity observed for the Ru solution standard and
for 0.28 M HNO_3 (10–30 mV on ^{58}Ni). These negligible amounts of Ni are insignificant and
630 have no effect on the measured data. The minimal Ni background originates from the Ni cones
of the instrumental setup.

632 In order to eliminate any potential effects on the isotopic measurements caused by sulfur (S)
in the analyzed sample solutions, the S from the crushed NiS beads was nearly quantitatively
634 removed by evaporation as H_2S gas during dissolution of the beads with concentrated HCl.
After further purification of Ru by column chemistry and distillation, the S contents in the final
636 sample solutions were $<25 \text{ ng ml}^{-1}$ for all analyzed samples. Tests with S-doped Alfa Aesar Ru
standard solutions showed that, even if a 100 ng ml^{-1} Ru standard solution contains large
638 excesses of S (S/Ru = 5), the accuracy of the Ru isotope measurements is not compromised
(Extended Data Figure 3c,d).

640

Nuclear field shift. Previous studies have shown that mass-independent Ru isotope
642 anomalies could be caused by nuclear field shift-induced fractionation effects⁵¹. In case of
meteorites and their components such effects could be a primary feature resulting from
644 evaporation/condensation processes in nature. However, experimental studies have shown
that mass-independent effects could also be generated in the laboratory during sample
646 preparation⁵¹. In this section we explore the potential effects from nuclear field shift-induced
fractionation of Ru isotopes. These fractionations can be predicted based on differences in the
648 mean-squared nuclear charge radii between nuclides of a given element. The resulting effects
on the measured Ru isotopic composition can be calculated in ϵ -units using the following
650 equation⁵¹:

$$\varepsilon_{m_i} = \left(\delta\langle r^2 \rangle_{m_1, m_i} - \frac{m_2(m_i - m_1)}{m_i(m_2 - m_1)} \delta\langle r^2 \rangle_{m_1, m_2} \right) \times \alpha$$

652

where m_1 and m_2 are the atomic masses of the two isotopes of an element chosen for internal
 654 normalization, m_i refers to the atomic mass of another isotope indexed with variable i ,
 $\delta\langle r^2 \rangle$ denotes the difference in mean-squared nuclear charge radii of the respective isotope
 656 pair and α is an adjustable parameter that determines the magnitude of mass-independent
 fractionation, which is a function of temperature T as $1/T$. In plots of $\varepsilon^{102}\text{Ru}$ and $\varepsilon^{96}\text{Ru}$ vs. $\varepsilon^{100}\text{Ru}$
 658 (Extended Data Figure 4) the slopes calculated for the nuclear field shift fractionation are
 clearly distinct from the slope predicted by a variation in s -process Ru nuclides. The Ru isotopic
 660 compositions obtained for Eoarchean SW Greenland rocks does not plot on the calculated
 slope for nuclear field shift but instead plots on the s -process mixing line. As such the
 662 anomalies identified in the SW Greenland rocks cannot be explained by nuclear field shift-
 induced fractionation and therefore reflect isotope anomalies of nucleosynthetic origin.

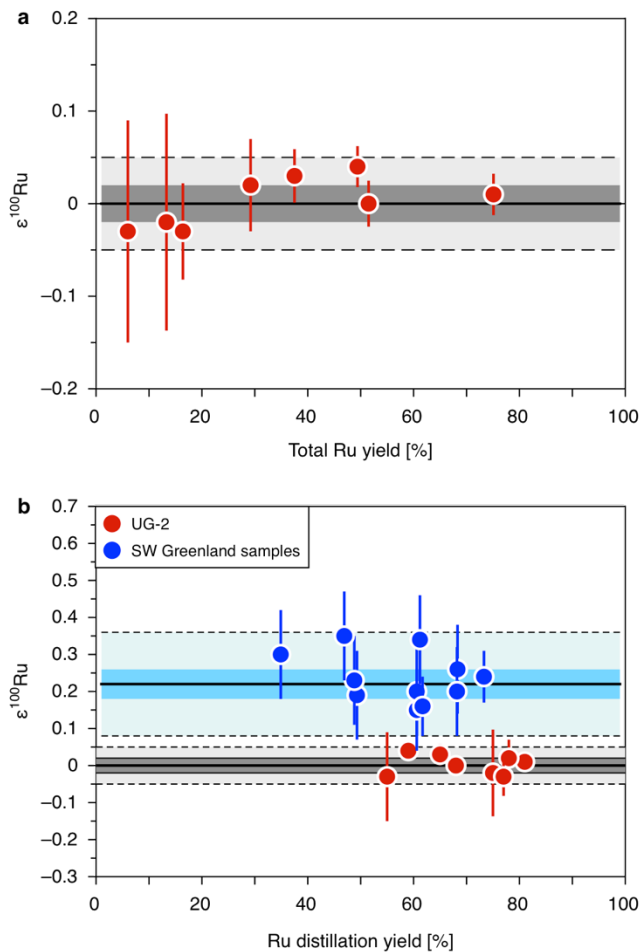
664

Fissiogenic Ru. Spontaneous fission of uranium has been shown to produce Ru nuclides with
 666 relative abundances that are distinct from naturally occurring Ru⁵². Fissiogenic Ru primarily
 consists of ⁹⁹Ru (33.4 %), ¹⁰¹Ru (28.9 %), ¹⁰²Ru (24.7 %) and ¹⁰⁴Ru (12.4 %)⁵³. The presence
 668 of an inherited fission-produced fraction of Ru in a rock sample would induce a characteristic
 isotope anomaly pattern that would be distinct from anomalies of nucleosynthetic or nuclear
 670 field shift origin. Because ⁹⁶Ru and ¹⁰⁰Ru are not a significant fission product⁵³, the presence
 of an inherited fraction of fissiogenic Ru in a rock sample would cause negative $\varepsilon^{96}\text{Ru}$ and
 672 $\varepsilon^{100}\text{Ru}$ anomalies, which are not observed for any of the analyzed samples. On the other hand,
 a deficit of such an inherited fissiogenic Ru component would yield positive $\varepsilon^{96}\text{Ru}$ and $\varepsilon^{100}\text{Ru}$
 674 anomalies, which are also not observed. This is shown in Extended Data Figure 4b where
 samples with an excess or a deficit of such a fissiogenic Ru component would fall on a mixing
 676 line with a distinct slope. Hence, the isotopic composition of the samples with positive $\varepsilon^{100}\text{Ru}$
 anomaly cannot be explained by either an excess or a deficit of fissiogenic Ru nuclides.

678 **Additional references cited in methods section and Extended Data**
680 **Figures/Tables**

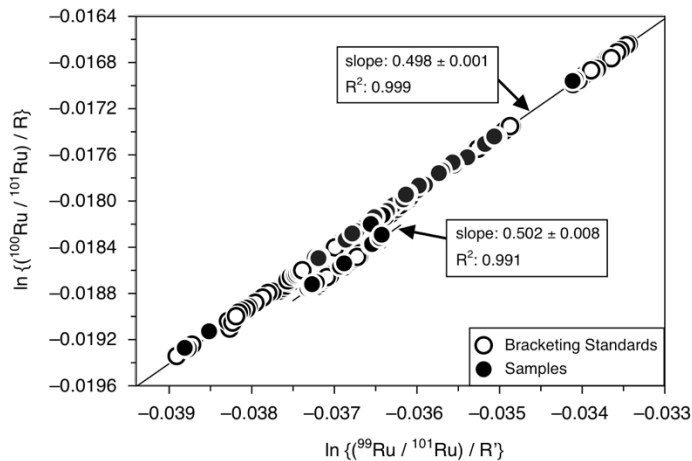
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- 750



752 **Extended data Figure 1 | Ruthenium yields of the total analytical procedure and Ru**
 754 **yields from the distillation plotted against $\epsilon^{100}\text{Ru}$ data for replicate digestions of UG-2**
 756 **and SW Greenland samples.**

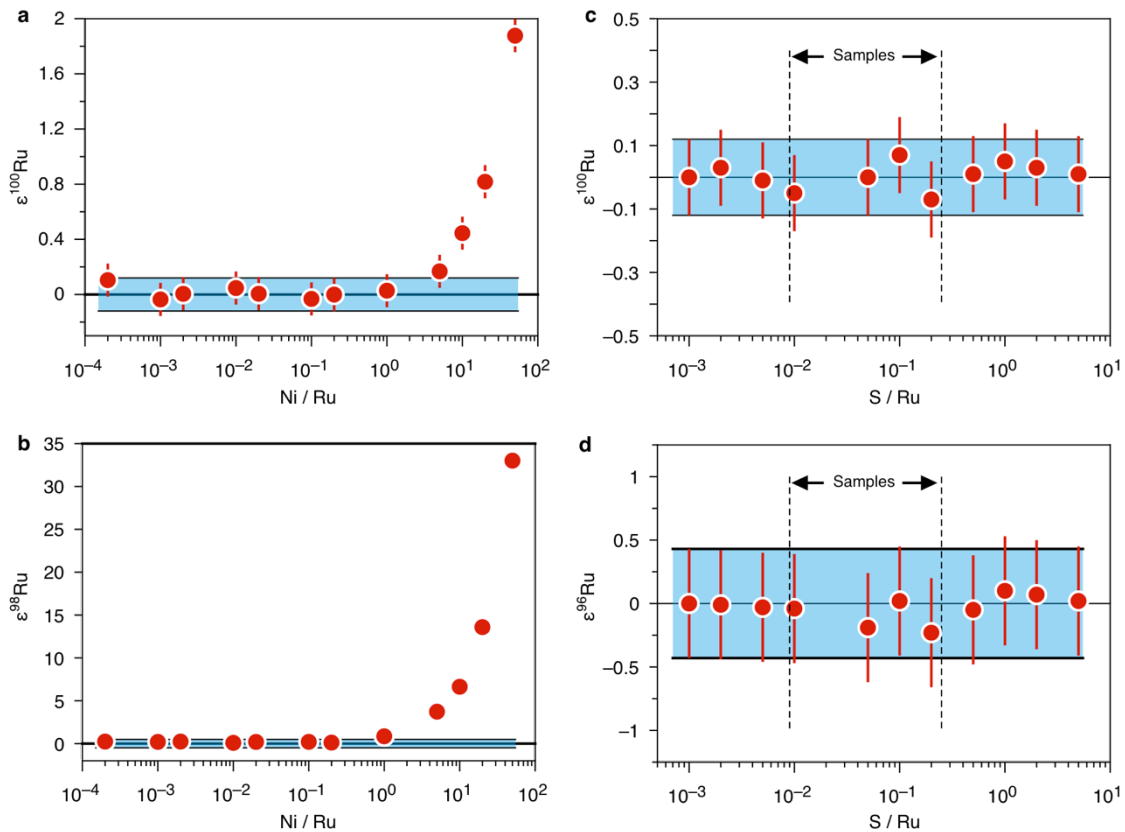
758 The plot shows that the accuracy of the $\epsilon^{100}\text{Ru}$ data is not affected by the Ru yield of the total
 760 analytical procedure (a) or the Ru yield of the distillation (b), respectively. The grey and blue
 762 areas represent the 95% confidence interval uncertainties, light grey and blue areas limited by
 dashed lines indicate the 2 s.d. uncertainty as stated for the calculated mean values of the
 Bushveld igneous complex and the Itsaq gneiss complex (Extended Data Table 1). Note that
 in (b) for the SW Greenland samples it was not possible to determine the Ru distillation yield
 for all replicates of the analyzed samples.



764 **Extended data Figure 2 | Ruthenium isotope plot showing the logarithmic (ln) values of**
 766 **the measured raw ratios for $^{99}\text{Ru}/^{101}\text{Ru}$ and $^{100}\text{Ru}/^{101}\text{Ru}$ obtained for 100 ppb sample**
solutions and associated Alfa Aesar Ru bracketing standards.

The measured isotope ratios are shown as raw ratios uncorrected for mass-dependent
 768 fractionation and are normalized to reference ratios R and R'. In the plot two distinct mass
 fractionation lines can be observed. The slopes for both lines are indistinguishable within error
 770 and are in very good agreement with the predicted slope of 0.5, which would be expected if
 the mass-dependent fractionation could accurately be corrected for by the exponential law
 772 (see Methods for details). Most importantly, the samples purified by distillation fall on the same
 respective mass fractionation line as their associated Alfa Aesar bracketing standards. Hence,
 774 this clearly demonstrates that the Ru distillation does not induce any unaccounted mass-
 fractionation effects for the samples in comparison to the bracketing standards. The shift
 776 observed for samples and associated standards plotting on a distinct mass fractionation array
 was caused by a maintenance on the mass spectrometer in May 2019 during which a Faraday
 778 cup was changed. However, this does not affect the accuracy of the isotopic data because the
 analyzed samples and their associated bracketing standards are shifted by the same
 780 magnitude, and the isotopic data are expressed as relative deviations in parts per 10^4 (ϵ
 values) from the bracketing standards.

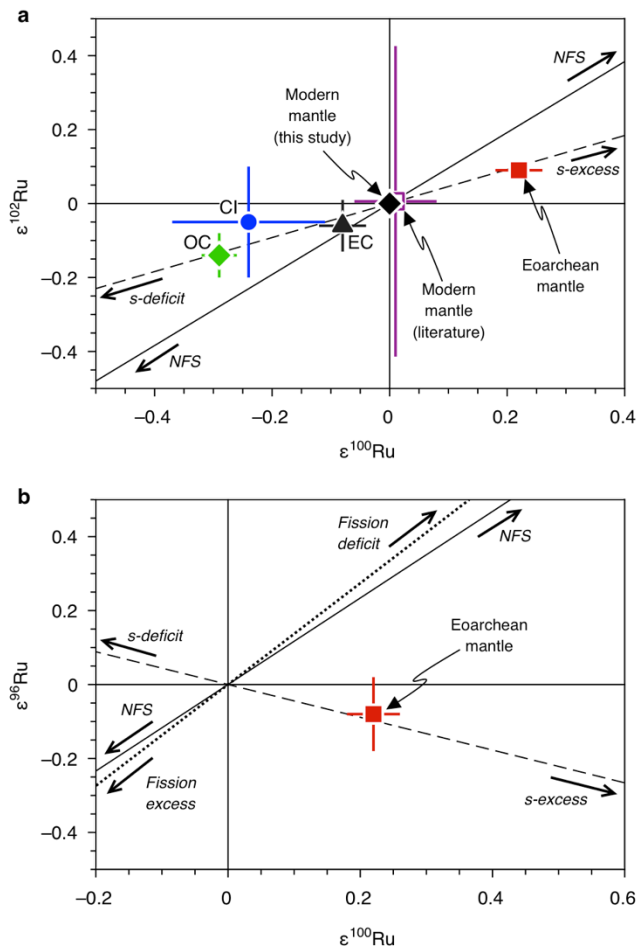
782



784 **Extended data Figure 3 | Ruthenium isotope data obtained for 100 ppb Alfa Aesar Ru**
standard solutions doped with variable amounts of Ni and S.

786 The effect of Ni argide interferences on the measured $\epsilon^{100}\text{Ru}$ (a) and $\epsilon^{98}\text{Ru}$ (b) isotopic
 788 compositions of a 100 ng ml^{-1} Ru standard solution doped with varying amounts of Ni. The
 790 accuracy of the measured isotopic compositions is not affected for samples with $\text{Ni/Ru} < 10^{-2}$.
 Panels (c) and (d) show that even if high amounts of S ($\text{S/Ru} = 5$) are present in the analyzed
 792 sample solutions, this has no effect on the accuracy of the measured $\epsilon^{100}\text{Ru}$ and $\epsilon^{96}\text{Ru}$ data.
 Vertical dashed lines in (c) and (d) indicate the range of S/Ru of the analyzed samples. The
 794 blue areas in (a-d) indicate the external reproducibility of the method as defined by the
 standard deviation (2 s.d.) of replicate digestions and repeated analysis of the UG-2 reference
 sample (see Methods).

796



798 **Extended data Figure 4 | Ruthenium isotope plots illustrating systematic compositional**
 800 **differences between enstatite (EC), ordinary (OC) and CI carbonaceous chondrites (CI),**
 802 **modern mantle and pre-late veneer mantle in comparison to mixing lines calculated**
 804 **between the modern mantle composition and isotopic variations caused by variable**
 806 **contributions of s-process Ru nuclides, a fissiogenic Ru component, and variations of**
 808 **nuclear field-shift induced isotope fractionations.**

804 (a) Ruthenium isotope data for the Eoarchean mantle of SW Greenland, the modern mantle,
 and ordinary, enstatite and CI carbonaceous chondrites in comparison to a mixing line
 806 calculated between the composition of the modern mantle ($\epsilon^{102}\text{Ru} = \epsilon^{100}\text{Ru} = 0$) and an s-
 process component³⁴ (dashed line), and the slope calculated for a nuclear field shift-induced
 808 (NSF) fractionation⁵¹ (black solid line). (b) Ruthenium isotope composition of the Eoarchean
 mantle in comparison to mixing lines calculated between the composition of the modern mantle
 810 ($\epsilon^{96}\text{Ru} = \epsilon^{100}\text{Ru} = 0$) and a fissiogenic Ru component⁵³ (dotted line), an s-process component³⁴
 (dashed line), and the slope calculated for nuclear field shift-induced (NSF) isotope fraction⁵¹
 812 (solid black line).

Title: Extended Data Table 1 | Ruthenium isotope data for ultramafic rocks

Sample [†]	Rock [†]	n [‡]	$\epsilon^{96}\text{Ru}^{\S}$	\pm	$\epsilon^{98}\text{Ru}^{\S}$	\pm	$\epsilon^{100}\text{Ru}^{\S}$	\pm	$\epsilon^{102}\text{Ru}^{\S}$	\pm	$\epsilon^{104}\text{Ru}^{\S}$	\pm
Greenland												
Itsaq gneiss complex (IGC)												
<i>Narssaq ultramafic body (NUB), 3.8 Gyr</i>												
10_9	H	1	0.13	0.43	-0.04	0.49	0.19	0.12	0.10	0.16	0.17	0.30
replicate	H	2	0.28	0.43	0.42	0.49	0.30	0.12	0.13	0.16	-0.01	0.30
10_11	D	2	-0.07	0.43	0.29	0.49	0.34	0.12	0.08	0.16	-0.10	0.30
<i>South of the Isua supracrustal belt (SOISB), 3.8 Gyr</i>												
10_27	H	1	(1.19) [¶]	0.43	0.33	0.49	0.23	0.12	0.03	0.16	0.04	0.30
replicate		1	0.03	0.43	0.58	0.49	0.23	0.12	0.18	0.16	0.00	0.30
<i>Ujaragssuit Nunât complex, 3.8 Gyr</i>												
194856	Chr	6	-0.04	0.20	0.18	0.17	0.17	0.09	0.06	0.06	-0.10	0.08
replicate		5	-0.27	0.29	0.04	0.35	0.15	0.11	0.07	0.04	-0.03	0.13
replicate		3	-0.25	0.43	0.40	0.49	0.35	0.12	0.13	0.16	-0.11	0.30
194857	Chr	10	-0.20	0.09	0.06	0.18	0.19	0.03	0.12	0.06	0.00	0.08
replicate		5	-0.17	0.22	0.17	0.31	0.16	0.08	0.06	0.17	-0.08	0.16
replicate		11	-0.09	0.20	0.10	0.18	0.13	0.04	0.05	0.05	-0.11	0.11
194882B	Chr	3	0.03	0.43	0.30	0.49	0.19	0.12	0.07	0.16	0.13	0.30
194884C	Chr	7	-0.17	0.11	0.06	0.14	0.24	0.07	0.09	0.09	-0.08	0.09
<i>Isua supracrustal belt (ISB), 3.7 Gyr</i>												
194907	D	1	-0.23	0.43	0.24	0.49	0.26	0.12	0.10	0.16	-0.20	0.30
Mean IGC (n=14) [¶]			-0.08	0.10	0.22	0.10	0.22	0.04	0.09	0.02	-0.03	0.06
2 s.d. IGC [¶]				0.33		0.35		0.14		0.08		0.20
<i>Seqi ultramafic complex, >3.0 Gyr</i>												
186466	Chr	2	-0.44	0.43	-0.10	0.49	0.20	0.12	0.04	0.16	-0.29	0.30
replicate		2	-0.14	0.43	0.60	0.49	0.13	0.12	0.04	0.16	-0.13	0.30
186479	Chr	3	0.10	0.43	0.30	0.49	0.20	0.12	0.08	0.16	-0.17	0.30
Australia												
Pilbara craton, Warawoona Group, 3.5-3.2 Gyr												
Pil 16-61	Chr	3	-0.03	0.43	-0.11	0.49	0.05	0.12	0.01	0.16	-0.02	0.30
replicate		3	-0.25	0.43	-0.17	0.49	0.05	0.12	-0.06	0.16	-0.05	0.30
Canada												
Abitibi greenstone belt, 2.7 Gyr												
OKUM	Kom	1	0.24	0.43	0.58	0.49	0.07	0.12	-0.03	0.16	0.08	0.30
South Africa												
Bushveld igneous complex, 2.05 Gyr												
UG-2	Chr	20	-0.12	0.08	-0.06	0.10	0.00	0.02	0.03	0.04	0.05	0.07
replicate		29	-0.12	0.08	0.03	0.08	0.01	0.02	-0.01	0.03	-0.06	0.06
replicate		19	-0.11	0.10	0.13	0.11	0.04	0.02	0.04	0.04	0.05	0.07
replicate		11	-0.11	0.15	0.18	0.11	0.02	0.05	0.01	0.04	-0.02	0.10
replicate		5	-0.08	0.47	-0.19	0.44	-0.02	0.12	-0.02	0.11	0.06	0.23
replicate		2	-0.15	0.43	-0.34	0.49	-0.03	0.12	-0.03	0.16	0.08	0.30
replicate		6	-0.31	0.25	0.13	0.31	-0.03	0.05	-0.02	0.07	0.08	0.10
replicate		11	0.02	0.12	-0.01	0.16	0.03	0.03	-0.02	0.05	-0.04	0.09
LG-6	Chr	4	-0.20	0.28	0.05	0.32	0.01	0.09	-0.01	0.09	-0.04	0.18
Mean Bushveld (n=9) [¶]			-0.13	0.07	-0.01	0.13	0.00	0.02	0.00	0.02	0.02	0.04
2 s.d. Bushveld [¶]				0.18		0.33		0.05		0.05		0.12

816

Footnotes:

818 *The term 'replicate' indicates that the Ru isotope data were obtained for a replicate digestion of the same sample powder.

820 [†]H: harzburgite, D: dunite, Chr: chromitite, Kom: komatiite.

[‡]Number of analysis of the same sample solution.

822 [§]Ruthenium isotope data are internally normalized to ⁹⁹Ru/¹⁰¹Ru using the exponential law and are reported as ϵ -unit (0.01%) deviations from the terrestrial bracketing standard: $\epsilon^i\text{Ru} = ({}^i\text{Ru}/{}^{101}\text{Ru}_{\text{Sample}} / {}^i\text{Ru}/{}^{101}\text{Ru}_{\text{Standard}} - 1) \times 10^4$, where $i = 96, 98, 100, 102$ or 104 . For samples measured $n < 4$ times

824 quoted errors reflect the external uncertainty as defined by the standard deviation (2 s.d.) of replicate digestions and repeated analysis of a reference sample (see Methods). Uncertainties for

826 samples measured $n \geq 4$ times are given as 95% confidence intervals of the mean calculated as:

828 $(\text{s.d.} \times t_{0.95, n-1}) / \sqrt{n}$.

830 ^{||}Calculated averages for samples from Itsaq and Bushveld with 95% confidence interval
uncertainties calculated as: $(s.d. \times t_{0.95, n-1})/\sqrt{n}$ and 2 s.d. uncertainties.

832 [†]Elevated $\epsilon^{96}\text{Ru}$ value due to an isobaric Zr interference that could not be corrected during the
isotopic measurement (see Methods). Consequently, this value was not included for the calculation
of the IGC mean value.

834

836 Extended Data Table 2

Title: Extended data Table 2 | Ruthenium concentration data, details about the NiS procedure and
838 Re-Os isotope data for ultramafic rocks

Sample	Rock*	Ru (ng g ⁻¹) [†]	NiS n x (g) [‡]	¹⁸⁷ Os/ ¹⁸⁸ Os [§]	¹⁸⁷ Re/ ¹⁸⁸ Os [§]	Age (Gyr)	¹⁸⁷ Os/ ¹⁸⁸ Os _{ini.} [¶]	yOs [#]	Ref.**
Greenland									
Itsaq gneiss complex (IGC)									
<i>Narssaq ultramafic body (NUB), 3.8 Gyr</i>									
10_9	H	7.76	5 (8) x10g	0.1013	0.044	3.80	0.09845	-2.3	14
10_11	D	8.27	8 x10g	0.1013	0.042	3.80	0.09857	-2.2	14
<i>South of the Isua supracrustal belt (SOISB), 3.8 Gyr</i>									
10_27	H	3.13 - 6.80	5 (6) x10g	0.1010 - 0.1153	0.023 - 0.233	3.81	0.09942 - 0.10002	-5.3 to +5.8	14
<i>Ujaragssuit Nunât complex, 3.8 Gyr</i>									
194856	Chr	<i>215</i>	1 x5g	0.10471 - 0.10493	0.0008 - 0.0013	3.81	0.1046 - 0.1047	+3.9 to +4.0	33
194857	Chr	<i>189</i>	1 x5g	0.10490 - 0.10809	0.01424 - 0.02906	3.90	0.10395 - 0.10614	+3.9 to +6.1	38
194882B	Chr	<i>12</i>	6 x10g	0.104842 - 0.105590					39
194884C	Chr	<i>23</i>	4 x10g						
<i>Isua supracrustal belt (ISB), 3.7 Gyr</i>									
194907	D	2.43 - 7.06	7 x10g	0.10899 - 0.37064	0.049 - 2.96	3.80	0.1045 - 0.1772	+3.8 to +76.2	23
		2.9 - 5.3		0.10245 - 0.13411	0.042 - 0.707	3.70	0.089 - 0.101	-12.8 to +0.2	46
Seqi ultramafic complex, >3.0 Gyr									
186466	Chr	53.83	2 x5g						42
186479	Chr	53.54	2 x5g						42
Australia									
Pilbara craton, Warawoona Group, 3.5-3.2 Gyr									
Pil 16-61	Chr	<i>115</i>	1 x5g	0.10517 - 0.11926	0.0281 - 0.1688	3.46	0.0979 - 0.1130	-5.2 to +9.6	33
Canada									
Abitibi greenstone belt, 2.7 Gyr									
OKUM	Kom	4.25	4 x10g	0.269					44, 54
South Africa									
Bushveld igneous complex, 2.05 Gyr									
UG-2	Chr	760	1 x5g	0.1483 - 0.1489	0.0916				45, 55
LG-6	Chr	270 - 430	1 x5g	0.1254 - 0.1265	0.101 - 0.117				45, 55

840 Footnotes:

*H: harzburgite, D: dunite, Chr: chromitite, Kom: komatiite.

842 [†]Ruthenium concentrations reported for the same samples or samples from the same locality.
Italicized values indicate Ru concentrations determined in this study as described in methods
844 section.

[‡]Number of individual NiS digestions (n) and amount of sample material (in g) taken for each single
846 NiS digestion processed for each sample and replicate sample analysis. In cases where different
numbers of NiS digestions were processed for a replicate sample analysis this is indicated by the

848 number in parenthesis. If not stated otherwise the same number of NiS digestions was used for all
849 replicates.

850 §Re-Os isotope data reported for the same samples or for samples of similar composition from
851 the same locality. Note that the different ranges reported for chromitite samples from the
852 Ujaragssuit Nunât complex were not obtained for the same samples and represent data reported
853 by different previous studies for chromitites from the same locality or sampling area.

854 ||Age used for calculation of the initial $^{187}\text{Os}/^{188}\text{Os}$ isotope composition as quoted in literature.

¶Initial $^{187}\text{Os}/^{188}\text{Os}$ isotope composition calculated at the time of emplacement of the samples.

856 #yOs values refer to the relative deviation in % of the calculated initial $^{187}\text{Os}/^{188}\text{Os}$ isotope
857 compositions of samples relative to the chondritic Os isotope composition at the time of
858 emplacement of the samples.

**References for Ru concentration and Os isotope data.

860

862 **Extended Data Table 3**

863 **Title:** Extended Data Table 3 | Parameter for mixing model shown in Figure 3 and resulting $\epsilon^{100}\text{Ru}$
864 values for pre-late veneer mantle endmember composition

	$\epsilon^{100}\text{Ru}$	\pm	Ru (ng/g)	$\epsilon^{100}\text{Ru}$ in pre-LV mantle	$\epsilon^{100}\text{Ru}$ in pre-LV mantle min	$\epsilon^{100}\text{Ru}$ in pre-LV mantle max
Chondrite groups						
Enstatite	-0.08	0.04	818 ⁵⁶	0.31	0.16	0.47
Ordinary	-0.29	0.03	882 ⁵⁶	1.14	1.02	1.26
Carbonaceous average	-0.90	0.61	838 ⁵⁶	3.56	1.19	4.74
Carbonaceous average	-0.90	0.12	838 ⁵⁶	3.56	3.08	4.03
CI	-0.24	0.13	637.4 ⁵⁶	1.00	0.46	1.55
CM	-0.69	0.38	817 ⁵⁶	2.90	1.30	4.49
Terrestrial mantle						
Modern mantle*	0.00	0.02	7.0 ¹⁶			
Eoarchean SW Greenland mantle [†]	0.22	0.04				
Pre-late veneer mantle			1.4			

866 **Footnotes:**

867 *The composition of the modern mantle corresponds to the mean value calculated for samples
868 from the Bushveld complex (Extended Data Table 1).

869 †The Eoarchean SW Greenland mantle composition represents the mean value calculated for
870 samples from the Itsaq gneiss complex (Extended Data Table 1).