Ruthenium isotope vestige of Earth’s pre-late-veene mantle preserved in Archaean rocks

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The accretion of volatile-rich material from the outer Solar System represents a crucial prerequisite for Earth to develop oceans and become a habitable planet1–4. However, the timing of this accretion remains controversial5–8. It has been proposed that volatile elements were added to Earth by the late accretion of a late veneer consisting of carbonaceous-chondrite-like material after core formation had ceased6,9,10. This view could not be reconciled with the ruthenium (Ru) isotope composition of carbonaceous chondrites5,11, which is distinct from that of the modern mantle12, or of any known meteorite group5. As a possible solution, Earth’s pre-late-veene mantle could already have contained a fraction of Ru that was not fully extracted by core formation13. The presence of such pre-late-veene Ru can only be established if its isotope composition is distinct from that of the modern mantle. Here we report the first high-precision, mass-independent Ru isotope compositions for Eoarchaean ultramafic rocks from southwest Greenland, which display a relative 100Ru excess of 22 parts per million compared with the modern mantle value. This 100Ru excess indicates that the source of the Eoarchaean rocks already contained a substantial fraction of Ru before the accretion of the late veneer. By 3.7 billion years ago, the mantle beneath southwest Greenland had not yet fully equilibrated with late accreted material. Otherwise, no Ru isotopic difference relative to the modern mantle would be observed. If constraints from other highly siderophile elements besides Ru are also considered14, the composition of the modern mantle can only be reconciled if the late veneer contained substantial amounts of carbonaceous-chondrite-like materials with their characteristic 100Ru deficits. These data therefore relax previous constraints on the late veneer and are consistent with volatile-rich material from the outer Solar System being delivered to Earth during late accretion.

Ruthenium is a highly siderophile element (HSE) and is therefore expected to be sequestered in 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 with metal–silicate equilibrium conditions15,16. This observation is most commonly explained by HSE replenishment of the mantle through the addition of a late veneer after core formation. Relative abundances of HSEs that are close to chondritic compositions in the mantle suggest that the late veneer must have consisted of primitive meteoritic material17,18, amounting to ~0.5% of Earth’s mass19. 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 volatiles20,21. Previous studies debated whether significant amounts of volatile-rich carbonaceous-chondrite-like material were added by the late veneer during the final stages of Earth’s accretion6,9,10 or had already been incorporated during earlier stages of Earth’s growth5,7,8,11.

Mass-independent ruthenium isotopic variations among meteorites and Earth have provided evidence that the late veneer was derived from reduced and volatile-poor inner Solar System materials most similar to enstatite chondrites22,23,24. This is in contrast to constraints from the relative abundances of volatile elements such as selenium (Se), tellurium (Te) and sulfur (S) and the Se isotope composition in the silicate Earth that were used to argue for a CM or CI carbonaceous-chondrite-like late veneer composition25,26,27. Owing to its distinct Ru
isotope composition, volatile-rich carbonaceous-chondrite-like material from the outer Solar System was excluded as possible late-veneer source material\textsuperscript{11,15} and thus the late veneer seemed unlikely to be the primary source of water and volatiles on Earth\textsuperscript{1,11}. It should be noted, however, that this conclusion depends on the premise that the Ru in Earth’s mantle originates solely from the late accreted materials that were added after cessation of core formation\textsuperscript{11,15,16,18}. If Earth’s pre-late-veneer mantle retained a significant fraction of Ru during metal–silicate differentiation\textsuperscript{12,20}, as recently suggested, this conclusion would be invalid. Investigating Ru isotope signatures in the putative remnants of pre-late-veneer mantle would thus not only provide insights into the timescales and efficiencies of mixing the late veneer into Earth’s mantle, but also introduce constraints on the composition of the material that was added as a late veneer.

To our knowledge, no unambiguous isotopic evidence for the preservation of pre-late-veneer mantle on Earth existed until now. For instance, resolvable excesses in $^{182}$W reported for 3.8 billion-year-old (Gyr-old) Archaean rocks from Isua (Greenland) and Acacsta (Canada) in conjunction with relatively low HSE abundances observed in 3.5–3.2-Gyr-old Archaean 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 Archaean mantle\textsuperscript{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 Archaean peridotites from the Narsaq 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\textsuperscript{46,23}. This suggests that the late veneer was to a large extent mixed into the ambient mantle by 3.8 billion years ago (Ga). 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 proto-Earth’s mantle as a consequence of the Moon-forming giant impact\textsuperscript{20,24}. However, $^{182}$W anomalies could also be generated by early mantle differentiation processes during approximately the first 50 Myr of the Solar System\textsuperscript{25–29} or by core–mantle interactions in the sources of mantle plumes\textsuperscript{30}. In summary, $^{182}$W and HSE concentration data alone fail to provide an unambiguous test of whether pre-late-veneer mantle domains were preserved.

Here we explore the potential use of mass-independent Ru isotope variations in terrestrial rocks as a tool to investigate whether pre-late-veneer isotope signatures can be found in the Archaean mantle. While the Ru isotope composition of the modern mantle is well constrained\textsuperscript{11}, this is not the case for the Archaean mantle. To address this issue, we determined the Ru isotope composition for a set of ultramafic rocks from different Archaean and Palaeoproterozoic terranes (Extended Data Table 1; see Methods for details). We focus on the $^{100}$Ru/$^{101}$Ru and $^{102}$Ru/$^{101}$Ru ratios to constrain the Ru isotope compositions of the mantle sources of these rocks because these isotope ratios are measured at the highest precision and also show the largest variability among meteoritic materials\textsuperscript{59,31}. The results are reported as $\varepsilon$ unit (0.01%) deviations of mass bias-corrected $^{100}$Ru/$^{101}$Ru and $^{102}$Ru/$^{101}$Ru ratios from a terrestrial standard.

**Exotic composition of Archaean mantle**

We report Ru isotope data for samples from four different cratons. The Ru isotope compositions obtained for ultramafic samples from the Pilbara Craton (3.5–3.2 Gyr old), the Superior Province (Abitibi greenstone belt, 2.7 Gyr old) and the Kaapvaal Craton (Bushveld Complex, 2.05 Gyr old) are indistinguishable from the Ru solution standard (Fig. 1), indicating that their Ru isotope compositions reflect that of the modern terrestrial mantle. By contrast, Eoarchaean 3.8–3.7-Gyr-old ultramafic rocks from the North Atlantic Craton, originating from various localities of the Itsaq gneiss complex (IGC) in southwest Greenland (the NUB, SOISB, ISB and the Ujaragssuit Nunât layered intrusion) exhibit a uniform and well-resolved excess in $\varepsilon^{100}$Ru of $+0.22 \pm 0.04$ (95% confidence interval, Fig. 1) combined with a smaller excess in $\varepsilon^{102}$Ru of $+0.09 \pm 0.02$ (95% confidence interval, Fig. 2a). Chromitites from the younger 3.0-Gyr-old Sequi ultramafic complex in southwest Greenland show the same excesses in $\varepsilon^{100}$Ru and $\varepsilon^{102}$Ru. The combined $\varepsilon^{100}$Ru and $\varepsilon^{102}$Ru excesses in these rocks represent mass-independent isotope anomalies of nucleosynthetic origin and indicate that the Ru in the southwest Greenland mantle source is enriched in nuclides produced by the slow neutron capture process (s-process) of nucleosynthesis compared with the modern mantle (Fig. 2a). The isotope excesses cannot be explained by mass-independent fractionation effects or by inherited fissiogenic Ru nuclides (see Methods and Extended Data for details about the accuracy of the Ru isotope data).

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**Fig. 1 | $\varepsilon^{100}$Ru data for Archaean and Palaeoproterozoic rocks, the modern mantle and chondrites.** The individual results for all analysed samples (Extended Data Table 1) are shown with the composition of the modern mantle\textsuperscript{12}. The uncertainties for individual data points reflect the external uncertainty of the method (2 s.d. for samples measured $n \leq 4$ times) or 95% confidence intervals of replicate analyses of a given sample ($4 < n \leq 8$). The mean values for 3.8–3.7-Gyr-old Archaean samples from the IGC in southwest Greenland and chromitite samples from the Bushveld complex are shown as solid vertical black lines. The darker grey and blue areas represent the respective 95% confidence intervals; the light grey and blue areas limited by dashed lines indicate the 2 s.d. uncertainty of the mean values. The uncertainty for the modern mantle composition is 2 s.d. (ref. 11). Numbers on the right of the data points refer to the sample identifiers given in Extended Data Table 1.
The $^{100}\text{Ru}$ excess provides unequivocal evidence that the mantle source of the Greenland rocks did not receive the full complement of late veneer material\(^{21}\). Furthermore, it also requires that Ru (and possibly other HSEs) was not completely stripped from the mantle during the latest stages of core formation\(^ {22,32}\). Otherwise, no Ru isotope anomaly would be observed. The uniform and ubiquitous presence of the $e^{100}\text{Ru}$ anomaly in various 3.8–3.7-Gyr-old ultramafic rock types from different Eoarchaean terranes in Greenland (Isuakasia, Færingehaven) suggests that a larger mantle domain is lacking a full late veneer component\(^ {20,21}\). The presence of the $e^{100}\text{Ru}$ anomaly in the younger Mesoarchaean chondrites from Seqii (minimum age of 3.0 Gyr, Akia terrane) also indicates that even 700 Myr later, the southwest Greenland mantle 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 Archaean mafic rocks from the Pilbara and Kaapvaal cratons\(^ {17}\), which previously had been explained by sluggish inmixing of late veneer material.

As outlined above, the $e^{100}\text{Ru}$ excess identified in Eoarchaean ultramafic rocks from southwest Greenland indicates that Ru was not completely sequestered in the core, most probably because some late accretionary component had been delivered during the waning stages of core formation\(^ {14,23,32}\). Depending on the composition of this early veneer material, the $e^{100}\text{Ru}$ excess measured in the Greenland rocks would then represent a minimum estimate for the $e^{100}\text{Ru}$ excess of the pure pre-late-veneer mantle. The nature of the early component that supplied the $e^{100}\text{Ru}$ excess and was already mixed into the Greenland mantle before 3.8 Gt, probably inner Solar System material (Fig. 2b), can be further constrained by osmium isotope systematics. This is because the initial osmium isotopic compositions of chromitite and peridotite samples from the IGC overlap the $^{187}\text{Os}/^{188}\text{Os}$ composition of chondrites at 3.8 Ga (refs. 14, 23, 32) (Extended Data Table 2). Assuming that the positive $e^{100}\text{Ru}$ anomaly and the chondritic Os signature were both imparted by this component, it is unlikely that it is represented by any known chondritic meteorites because these all exhibit negative $e^{100}\text{Ru}$ values and chondritic Os isotope compositions. Importantly, owing to its positive $e^{100}\text{Ru}$ value, this material cannot derive from a carbonaceous-chondrite-like Moon-forming impactor\(^ {20}\) because carbonaceous chondrites also exhibit the most negative $e^{100}\text{Ru}$ values among all known chondrite groups\(^ {5}\) (Fig. 2).

**Carbonaceous-chondrite-like late veneer**

Regardless of the precise nature and origin of the early accreted component, the $e^{100}\text{Ru}$ excess inferred for the Eoarchaean southwest Greenland mantle source could only be balanced by the addition of chondritic materials with negative $e^{100}\text{Ru}$ to yield the composition of the modern mantle ($e^{100}\text{Ru} = 0$). This mixing relationship is further illustrated in Fig. 3, where possible $e^{100}\text{Ru}$ compositions for the pre-late-veneer mantle are calculated by subtracting enstatite, ordinary 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 about 20% of the Ru (~1.4 ng g$^{-1}$) in the modern mantle derives from the pre-late-veneer stage\(^ {17}\). Assuming a minimum late accretionary contribution of 60% for the 3.8-Gyr-old Itsaq mantle source\(^ {17}\), only the addition of a late veneer consisting of carbonaceous chondrites could account for $e^{100}\text{Ru} = 0$, as observed for the modern mantle\(^ {42}\) (Fig. 3). The required proportion of late accreted material would amount to a maximum estimate of 0.3% of Earth’s mass of average carbonaceous chondrite or CM carbonaceous chondrite material, consistent with a recent estimate based on Se isotopes\(^ {10}\).

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**Fig. 2|** Ru isotope plot illustrating compositional differences between enstatite, ordinary, average carbonaceous, CI and CM carbonaceous chondrites, the modern mantle and the Eoarchaean mantle. **a.** The dashed line represents a mixing line between the modern mantle composition ($e^{100}\text{Ru} = 0$) and an s-process component defined by Ru isotope data for pre-solar silicon carbide grains\(^ {34}\). The compositions of enstatite chondrites (EC, $e^{100}\text{Ru} = -0.29 \pm 0.03$, 95% confidence interval); ordinary chondrites (OC, $e^{100}\text{Ru} = -0.24 \pm 0.13$, 95% confidence interval); CI chondrites (CI, $e^{100}\text{Ru} = -0.49 \pm 0.38$, 95% confidence interval); and average carbonaceous chondrites (average CC, $e^{100}\text{Ru} = -0.90 \pm 0.12$, 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 in ref. \(^ {5}\)). Uncertainties for the modern and the Eoarchaean mantle composition are the same as stated in Fig. 1. Note that the uncertainty for the modern oceanic mantle composition from the literature is shown as 2 s.d. (ref. \(^ {9}\)). **b.** Heliocentric zoning of $e^{100}\text{Ru}$ anomalies\(^ {34}\). The presence of an s-process-enriched reservoir that contributed to Earth’s growth is inferred from the Ru isotopic composition obtained for the Eoarchaean mantle of southwest Greenland (Fig. 1). Chondrite groups formed at increasing heliocentric distances exhibit more negative $e^{100}\text{Ru}$ because they are more depleted in s-process Ru relative to Earth’s modern mantle\(^ {5}\). The $e^{100}\text{Ru}$ uncertainty for carbonaceous chondrites is shown as 2 s.d. to account for the significant within-group variation of their $e^{100}\text{Ru}$ values (image adapted from ref. \(^ {5}\), Springer Nature).
A late veneer consisting of CM-like material is also supported by the abundances of volatile elements in the silicate Earth\(^2,9,10\). This conclusion remains robust, even if a larger fraction of Ru was present in the pre-late-veneer mantle or the late accretion component in the mantle by 3.8 Ga (>60%), but 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 contained a significantly lower late veneer contribution by 3.8 Ga (<50%). A late veneer consisting of carbonaceous chondrites is consistent with the relative abundances of S–Se–Te and the Se isotopic composition of the modern mantle\(^2,9,10\), but the addition of a late veneer composed of ordinary chondrites cannot be reconciled with these constraints, because the relative abundances of S–Se–Te and the Se isotopic composition of ordinary chondrites are distinct from those of Earth’s mantle\(^2,9,10\). If a major part of the late veneer consisted of core fragments from differentiated impactors\(^2,9,10\), one potential caveat would be that this material cannot readily account for chondritic S–Se–Te and broadly chondritic HSE relative abundances in Earth’s mantle\(^2,9,10\).

Collectively, our data imply that the distinct \(^{100}\text{Ru}\) isotope excess in the Eoarchaean southwest Greenland mantle source is best explained by late mixing of a carbonaceous-chondrite-like late veneer fraction into Earth’s mantle. Thus, contrary to previous Ru isotope constraints on the late veneer\(^1,10\), these data imply that significant amounts of volatile-rich outer Solar System materials including water and volatiles were added with the late veneer. This revised view also agrees with other constraints, such as those independently obtained from the 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 chondrite source\(^1,4\). Finally, our data demonstrate that investigating the Ru isotope composition of terrestrial rocks represents a powerful analytical tool for identifying primordial mantle heterogeneities arising from incomplete equilibration of the ambient mantle with Earth’s late-stage building blocks.

### Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41586-020-2069-3.

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Methods

Samples

The samples analysed in this study comprise ultramafic rocks from four different cratons. The North Atlantic Craton is represented by peridotite and chromitite samples from various localities of the Eocarchean IGC and the Mesoarchean Seqi ultramafic complex in southwest Greenland. The sample set is complemented by chromitites from the Kaapvaal Craton (Bushveld Complex, South Africa) and the Pilbara Craton (Australia) and a komatite reference sample from the Superior Province (Abitibi greenstone belt, Canada). Where available, the Ru concentration and osmium isotope data for the samples analysed in this study are given in Extended Data Table 2. There were no data available for some samples, so Ru and Os data obtained for similar samples from the same location are listed.

The IGC in southwest Greenland represents one of the few localities where remnants of Eocarchean mantle are preserved. The IGC comprises two Eocarchean crustal terranes (Isuakasia and Færingehavn), where possible mantle rocks are exposed as ultramafic lenses in the 3.8–3.7-Gyr-old Isua supracrustal belt and ultramafic bodies in the 3.8-Gyr-old SOISB, both located in the Isuakasia terrane. In the Færingehavn terrane, such rocks are exposed in the 3.8-Gyr-old NUB. The peridotite and chromitite samples investigated in this study were selected to cover all of these different localities.

Samples 10-9 and 10-11 from the NUB are massive, coarse-grained peridotites. Olivine is the dominant phase in these rocks. They also contain orthopyroxene, amphibole, spinel and magnetite. The chemical compositions of these samples, including concentration data for highly siderophile elements and Os isotopes, were reported in a previous study. Sample 10-27 is a harzburgite from the SOISB. The mineral assemblage of this rock is comparable to other harzburgites collected from the same locality. These rocks are typically spinel-peridotites with harzburgitic mineral assemblages composed mainly of olivine and variable amounts of orthopyroxene, amphibole and opaques. A minimum age of 3.8 Gyr was estimated for the studied SOISB and NUB peridotites on the basis of field relationships with surrounding 3.8-Gyr-old tonalitic gneisses and crosscutting dykes.

Two of the investigated chromitites (194856, 194857) were collected from the Ujarrasuit Nunat layered intrusion. For chromitites from this locality, Pt–Os model ages as old as 4.36 Gyr were reported. Samples 194882B and 19488C are chromitites from a locality close to the inland ice that most probably belongs to the same sequence as the chromitites from the Ujarrasuit Nunat layered intrusion.

The dunite sample 194907 was collected from an antigorite lens located within the northeastern part of the 3.7-Gyr-old Isua supracrustal belt, which has previously been referred to as Dunitite Lens B. The ISB dunites also contain orthopyroxene and spinel, and very minor amounts of clinopyroxene that has mostly been altered. Two of the analysed chromitites (186466, 186479) derive from the Seqi ultramafic complex. The major and trace element compositions, including concentration data for platinum group elements of these samples, were reported in a previous study. The Seqi ultramafic complex 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 granitoid sheets, 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 are interpreted as representing the remnant of a fragmented layered complex or a magma conduit.

The ultramafic rocks formed from a magnesian-rich, near-anhydrous magma as olivine dominated cumulates with high modal contents of chromite. Their parental magma was generated by high degrees of partial melting of a mantle source that probably represents the precursor of the regional sub-continental lithospheric mantle.

Ruthenium separation and purification

The required amount of sample material to yield sufficient Ru for a high-precision measurement was estimated on the basis of previously reported Ru concentrations (10–9, 10–11, UG-2, LG-6, OKUM, 186466, 186479) or Ru concentrations reported for similar compositions from the same locality (10–7, 194907). When information was not available (for example, for samples 194856, 194857 and Pil16-61), the Ru concentrations were determined from a 1 g powder test portion digested in a high-pressure ash in reverse aqua regia (5 ml concentrated HNO3 and 2.5 ml concentrated HCl). Before quantification of Ru for these samples, the digestion solution was dried down, converted twice with 5 ml of 6 M 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 fractions by external calibration using a quadrupole inductively coupled plasma mass spectrometer (ThermoScientific iCap). We note that the concentrations determined by this 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. These concentrations are therefore considered to be only approximate values. In a similar manner, the Ru contents of two chromitites (194882B, 194884C) were estimated from a sample aliquot taken after NIS digestion and cation column chemistry as described below. However, we note that these estimates represent only approximate values too because the Ru yield of the NIS procedure is around 100%.

For the NIS procedure, powder aliquots of 5–10 g were digested using a NIS fire assay technique. For chromatite 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 amounts of Ru. Multiple NIS digestions with 10 g of sample powder had to be prepared for ultramafic samples with lower Ru concentrations (harzburgites, dunites, komatitites and some chromitites). 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. Appropriate amounts of Ni, S, borax and Na2CO3 were added to each 5–10 g sample portion and thoroughly mixed. The mixture was fluxed in a muffle furnace for 75 min at 1,000 °C. After cooling, the NiS beads were physically removed from the quenched silicate melt.

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

Ruthenium was separated from the dissolved NiS beads using cation exchange chromatography. Each dissolved NiS bead from a single fire assay digestion was split over three cation columns filled with 10 ml AG50 X8 resin, respectively. The resin was equilibrated with 20 ml of 0.2 M HCl. Ruthenium and other platinum group elements were loaded and eluted in 14 ml of 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 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 column. The Ru yields from the cation column were usually >95%. The eluted sample solutions were dried down on a hotplate, recombined and Ru was further purified using a macrodistillation unit as described elsewhere. After the distillation, the purified Ru fractions were dried down on a hotplate and dissolved in 0.5 ml of 0.28 M HNO₃, from which a small aliquot was prepared as a sample for the analytical procedure. The purified Ru fractions were dried down on a hotplate and dissolved in 0.5 ml of 0.28 M HNO₃, from which a small aliquot was prepared as a sample for the analytical procedure. The yield of the analytical procedure, including NiS digestion, column chemistry and distillation, is typically 30–70%, estimated from samples with known Ru concentrations (UG-2, OKUM, 10-9, 10-11, 186466, 186479). The total yield of the three UG-2 digestions was only 6–21%. The yields of the distillation for these samples were 50–80%, so the low total Ru yields are caused 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 distillation have any effect on the accuracy of the Ru isotope data (Extended Data Fig. 1).

The procedural blank for a single NiS digestion, including column chemistry and distillation, 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 ≥30 ng of Ru were processed for each respective NiS digestion.

Mass spectrometry

The Ru isotope measurements were performed using a ThermoScientific Neptune Plus multicollector inductively coupled plasma mass spectrometer in 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 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. The solution samples were introduced into the mass spectrometer at an uptake rate of 50 μl min⁻¹ using an ESI microflow PFA nebulizer attached to a Cetac Aridus II desolvator. The isotope measurements were conducted with total ion beam intensities between 8 × 10⁻¹⁰ and 2 × 10⁻⁰, obtained for 100 ng ml⁻¹ Ru sample and standard solutions using conventional NiH-cones. The set-up was optimized to yield oxide production rates <1% (CeO/Ce). The measurements were conducted in static mode and the seven stable Ru isotopes (⁹⁵Ru, ⁹⁶Ru, ⁹⁷Ru, ⁹⁸Ru, ¹⁰⁰Ru, ¹⁰¹Ru, ¹⁰²Ru and ¹⁰⁴Ru) as well as ⁴⁰Mo and ¹⁰⁰Pd were monitored simultaneously. Each Ru isotope analysis consisted of an on-peak baseline on a solution blank (40 integrations 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-house Ru standard solution (Alfa Aesar Ru). The data were internally normalized to ¹⁰⁰Ru/¹⁰⁴Ru = 0.7450754 (ref. 3) using the exponential law to correct for mass-dependent isotope fractionation. The isotope data are reported as ε = ([RuSample/RuStandard] - 1) × 10⁴, calculated relative to the bracketing standard of each analytical session. The accuracy and precision of the Ru isotopic measurements were evaluated by replicate digestions and multiple analyses of the UG-2 chromitite (Bushveld), which was used as a reference sample. The Ru isotope data obtained for UG-2 in this study agree well with previously reported data, where a different digestion method (alkali fusion) was used for sample decomposition. This demonstrates that the isotope data obtained by the NiS method yield accurate results. The external reproducibilities (2 s.d.) obtained for a total number of 103 individual measurements from 8 replicate UG-2 digests are ±0.43 ε¹⁰⁴Ru, ±0.49 ε¹⁰⁰Ru, ±0.12 ε¹⁰¹Ru, ±0.16 ε¹⁰²Ru and ±0.30 ε¹⁰⁴Ru.

Correction for mass-dependent isotope fractionation

The exponential law is one of the most commonly used methods to correct for natural and instrumental mass-dependent isotope fractionation. One potential caveat in using this correction for Ru isotope measurements could be that the distillation technique used to purify the Ru could induce an isotope fraction that would not follow the exponential law. This could cause apparent isotope anomalies for a given sample as a consequence of inaccurate mass fractionation correction. The exponential law assumes that the logarithmic fractionation δ = ln(r/R) of a given isotopic ratio is expressed as a function of the mass log difference Δ(lnM) = ln(M₂/M₁) = ln(r'/r). Considering two isotopic ratios (r₁ = Ru/¹⁰⁴Ru and r₂ = Ru/¹⁰⁴Ru) the exponential law predicts that mass fractionation produces a linear array in a ln(r'/r) plot. This is illustrated in Extended Data Fig. 2 for the measured raw ratios of ¹⁰⁶Ru/¹⁰⁴Ru and ¹⁰⁸Ru/¹⁰⁴Ru. The ratios in this figure are not corrected for mass fractionation and are normalized to a reference ratio (R and R', respectively). If the mass fractionation experienced by the samples is accurately described by the exponential law, the ratios should fall on a linear array with a slope of -0.5. Two distinct mass fractionation lines can be observed in the plot for different sessions. The slopes for both groups of sessions 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 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-fractionation effects for the samples in comparison with the bracketing standard. This observation is also independent from the Ru yield of the samples and does not change if other Ru isotope ratios are considered. Thus, the Ru isotope anomalies obtained for the southwest Greenland samples cannot reflect inaccurate mass fractionation correction. The shift observed for samples and associated standards plotting on a distinct mass fractionation array in Extended Data Figure 2 was caused by maintenance in May 2019 during which a Faraday cup was replaced. However, because the data are reported as relative deviations in parts per 10⁴ from the Alfa Aesar bracketing standard, and because samples and bracketing standards are shifted by the same magnitude, this does not affect the accuracy of the data. This is also confirmed by replicate digestions of sample 10-9 that were analysed in both groups of sessions. The ε¹⁰⁴Ru values for this sample are indistinguishable within analytical uncertainty.

Another argument against non-exponential mass-fractionation effects is that nucleosynthetic Ru isotopic anomalies caused by variable contributions of s-process Ru nuclides would not lead to any ε¹⁰⁴Ru anomalies in the ¹⁰⁴Ru/¹⁰⁴Ru normalization scheme. As the ε¹⁰⁴Ru values for all analysed samples fall within the external reproducibility of the method (±0.30 for ε¹⁰⁴Ru), this demonstrates that sample distillation does not cause non-exponential mass fractionation effects.

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 effects relating to remaining S in the analysed sample...
solutions. While interferences from Mo and Pd are simultaneously monitored and corrected for during the measurements, isobars from Zr and Ni argides are not. Owing to the design of the collector block and limited availability of collectors, Zr and Ni could not be simultaneously monitored during the measurements. However, Zr is very effectively separated from Ru by cation exchange chemistry. Hence, all analysed sample solutions (except for one digestion of sample 10-27) had Zr intensities indistinguishable from the background of the 0.28 M HNO₃ and the Ru standard solution. Only one analysed sample (10-27) had a slightly elevated Zr/Ru ratio of 0.0008 and, hence, its ε⁹⁶Ru value is slightly elevated due to an isobaric interference from ⁹⁰Zr that could not be corrected. The Zr contained in the one analysed sample solution most probably reflects a random contamination from the laboratory equipment used during sample preparation that was not observed for other samples.

In the case of Ni we noticed during the initial stage of the project that a few processed reference samples still contained considerable amounts of Ni after the cation chemistry. For these 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 analysed. During the isotopic measurements Ni readily forms argide species in the plasma that interfere with Ru isobars. To assess potential effects from Ni argide species on the measured Ru isotope data, 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 measured Ru isotope compositions for 100 ng ml⁻¹ Ru solutions are not affected for samples with Ni/Ru ratios <0.01 (Extended Data Fig. 3a, b). For sample solutions with higher amounts of Ni, positive anomalies are observed, which are most pronounced for Ru and to a lesser extent for ¹⁰⁰Ru. Other Ru isotope masses (¹⁰⁰Ru and ¹⁰⁸Ru), owing to the lower abundance of the higher mass Ni isotopes, are not significantly affected by Ni argide species. To avoid any interferences from Ni argides during the isotopic measurements, the final dilutions of all samples analysed in this study were carefully checked for their Ni contents before the analysis. The intensity of Ni, monitored by scanning the mass of ⁶⁰Ni, in the finally diluted sample solutions was indistinguishable from the background intensity observed for the Ru solution standard and for 0.28 M HNO₃ (10–30 mV on ⁶⁰Ni). These negligible amounts of Ni are insignificant and have no effect on the measured data. The minimal Ni background originates from the Ni cones of the experimental set-up.

To eliminate any potential effects of S in the analysed solutions on the isotopic measurements, the S from the crushed NiS beads was almost completely removed by evaporation as H₂S 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 sample solutions were <25 ng ml⁻¹ for all analysed samples. Tests with S-doped Alfa Aesar Ru standard solutions showed that even a 100 ng ml⁻¹ Ru standard solution contains large excesses of S (S/Ru = 5), the accuracy of the Ru isotope measurements is not compromised (Extended Data Fig. 3c, d).

**Nuclear field shift**

Previous studies have shown that mass-independent Ru isotope anomalies could be caused by nuclear field shift-induced fractionation effects. In meteorites and their components, such effects could be a primary feature resulting from evaporation/condensation processes. However, experimental studies have shown that mass-independent effects could also be generated in the laboratory during sample preparation. In this section, we explore the potential effects of nuclear field shift-induced fractionation of Ru isotopes. These fractionations can be predicted on the basis of differences in the 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 equation:

\[
\varepsilon_m = \left( \frac{\delta m^2}{m_{Ru,m}} \right) \frac{m_R(m_m - m_R)}{m_R(m_m - m_R)} \left( \frac{\delta m^2}{m_{Ru,m'}} \right) \alpha
\]

where \(m_R\) and \(m_m\) are the atomic masses of the two isotopes of an element chosen for internal normalization, \(m_{Ru,m}\) refers to the atomic mass of another isotope indexed with variable \(i\), \(\delta m^2\) denotes the difference in the mean-squared nuclear charge radii of the respective isotope pair and \(\alpha\) 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 \(\varepsilon_{99Ru}\) and \(\varepsilon_{98Ru}\) versus \(\delta_{99Ru}\) (Extended Data Fig. 4), the slopes calculated for the nuclear field shift fractionation are clearly distinct from the slope predicted by a variation in s-process Ru isotopes. The Ru isotopic composition obtained for Eoarchaean southwest 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 anomalies identified in the southwest Greenland rocks cannot be explained by nuclear field shift-induced fractionation and therefore reflect isotope anomalies of nucleosynthetic origin.

**Fissiogenic Ru**

The spontaneous fission of uranium has been shown to produce Ru nuclides with relative abundances that are distinct from naturally occurring Ru (ref. 52). Fissiogenic Ru primarily consists of ¹⁰⁰Ru (33.4%), ¹⁰¹Ru (28.9%), ¹⁰²Ru (24.7%) and ¹⁰⁴Ru (12.4%). The presence 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 field shift origin. Because ¹⁰⁰Ru and ¹⁰⁴Ru are not a significant fission product, the presence of an inherited fraction of fissogenic Ru in a rock sample would cause negative \(\varepsilon_{99Ru}\) and \(\varepsilon_{98Ru}\) anomalies. These are not observed in any of the analysed samples. On the other hand, a deficit of such an inherited fissogenic Ru component would yield positive \(\varepsilon_{99Ru}\) and \(\varepsilon_{98Ru}\) anomalies, which are also not observed. This is shown in Extended Data Fig. 4b, where samples with an excess or a deficit of such a fissogenic Ru component would fall on a mixing line with a distinct slope. Hence, the isotopic composition of the samples with a positive \(\varepsilon_{99Ru}\) anomaly cannot be explained by either an excess or a deficit of fissogenic Ru nuclides.

**Data availability**

The data that support the findings of this study are available from the EarthChem library (https://doi.org/10.1594/IEDA/111462). Source data for Figs. 1–3 and Extended Data Fig. 1–4 are provided with the paper.

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Author contributions 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. All authors contributed to the discussion of the results and editing of the manuscript.

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Extended Data Fig. 1 | Ruthenium yields of the total analytical procedure and Ru yields from the distillation plotted against \( \varepsilon^{100}\text{Ru} \) data for replicate digestions of UG-2 and southwest Greenland samples. a, b. The accuracy of the \( \varepsilon^{100}\text{Ru} \) data are not affected by the Ru yield of the total analytical procedure (a) or the Ru yield of the distillation (b). The grey and blue areas represent the 95% confidence intervals, and the light grey and light 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 IGC (Extended Data Table 1). Note that it was not possible to determine the Ru distillation yield for all replicates of the analysed samples in b for the southwest Greenland samples.
Extended Data Fig. 2 | Ruthenium isotope plot showing the ln values of the measured raw ratios for $^{99}$Ru/$^{101}$Ru and $^{100}$Ru/$^{101}$Ru obtained for 100 ng ml$^{-1}$ Ru sample solutions and associated Alfa Aesar Ru bracketing standards. The measured isotope ratios are shown as raw ratios uncorrected for mass-dependent fractionation and are normalized to reference ratios $R$ and $R'$. Two distinct mass fractionation lines can be observed. The slopes for both lines are indistinguishable within error and are in very good agreement with the predicted slope of 0.5, which would be expected if the exponential law could accurately correct the mass-dependent fractionation (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. This clearly demonstrates that the Ru distillation does not induce any unaccounted mass-fractionation effects for the samples in comparison with the bracketing standards. The shift 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 cup was changed. However, this does not affect the accuracy of the isotopic data because the analysed samples and their associated bracketing standards are shifted by the same magnitude, and the isotopic data are expressed as $\varepsilon$ values from the bracketing standards.
Extended Data Fig. 3 | Ruthenium isotope data obtained for 100 ng ml⁻¹ Alfa Aesar Ru standard solutions doped with variable amounts of Ni and S. 

a, b. The effect of Ni argide interferences on the measured ε¹⁰⁰Ru (a) and ε⁹⁸Ru (b) isotopic compositions of a 100 ng ml⁻¹ Ru standard solution doped with varying amounts of Ni. The accuracy of the measured isotopic compositions is not affected for samples with Ni/Ru < 10⁻². c, d. High amounts of S (S/Ru = 5) in the analysed sample solutions have no effect on the accuracy of the measured ε¹⁰⁰Ru (c) and ε⁹⁸Ru (d) data. Vertical dashed lines in c and d indicate the range of S/Ru ratios in the analysed samples. The blue areas indicate the external reproducibility of the method as defined by 2 s.d. of the replicate digestions and repeated analysis of the UG-2 reference sample (see Methods).
Extended Data Fig. 4 | Ruthenium isotope plots illustrating systematic compositional differences between EC, OC and CI, modern mantle and the pre-late-veneer mantle in comparison with mixing lines calculated between the modern mantle composition and isotopic variations caused by variable contributions of s-process Ru nuclides, a fissionogenic Ru component and variations of nuclear field-shift induced isotope fractionations.

a, Ruthenium isotope data for the Eoarchaean mantle of southwest Greenland, the modern mantle and the three types of carbonaceous chondrite in comparison with a mixing line calculated between the composition of the modern mantle (ε$^{100}$Ru = ε$^{102}$Ru = 0) and an s-process component$^{34}$ (dashed line) and the slope calculated for a nuclear field shift-induced (NSF) fractionation$^{51}$ (solid black line).

b, Ruthenium isotope composition of the Eoarchaean mantle in comparison with mixing lines calculated between the composition of the modern mantle (ε$^{96}$Ru = ε$^{100}$Ru = 0) and a fissionogenic Ru component$^{53}$ (dotted line), an s-process component$^{34}$ (dashed line) and the slope calculated for an NSF isotope fraction$^{51}$ (solid black line).
Extended Data Table 1 | Ruthenium isotope data for ultramafic rocks

| Sample* | Rock† | n‡ | $\varepsilon^{96}$Ru | $\varepsilon^{98}$Ru | $\varepsilon^{98}$Ru | $\varepsilon^{100}$Ru | $\varepsilon^{102}$Ru | $\varepsilon^{104}$Ru |
|---------|-------|----|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Greenland | | | | | | | | | |
| Itsaq gneiss complex (IGC) | | | | | | | | | |
| Narissaq ultramafic body (NUB), 3.8 Gyr | | | | | | | | | |
| 10_9 | H | 1 | 0.13 | -0.04 | 0.49 | 0.19 | 0.12 | 0.10 | 0.16 | 0.17 | 0.30 |
| replicate | | | | | | | | | | |
| 10_11 | D | 2 | -0.07 | 0.43 | 0.29 | 0.49 | 0.34 | 0.12 | 0.08 | 0.16 | 0.03 |
| South of the Isua supracrustal belt (SOISB), 3.8 Gyr | | | | | | | | | | |
| 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 | | | | | | | | | | | |
| Ujarassuit Nuntal complex, 3.8 Gyr | | | | | | | | | | |
| 194856 Chr | 10 | -0.20 | 0.09 | 0.18 | 0.19 | 0.03 | 0.12 | 0.06 | 0.03 | 0.08 |
| replicate | | | | | | | | | | | |
| 19488B Chr | 5 | -0.17 | 0.22 | 0.17 | 0.31 | 0.16 | 0.08 | 0.06 | 0.17 | 0.08 | 0.16 |
| Isua supracrustal belt (ISB), 3.7 Gyr | | | | | | | | | | |
| 194907 D | 1 | 0.23 | 0.43 | 0.24 | 0.49 | 0.26 | 0.12 | 0.16 | 0.10 | 0.20 | 0.30 |
| Mean IGC (n=14)i | | | | | | | | | | | |
| 2 s.d. IGCi | 0.33 | 0.35 | 0.14 | 0.02 | 0.03 | 0.06 |
| Seqi ultramafic complex, >3.0 Gyr | | | | | | | | | | |
| 186466 Chr | 2 | 0.44 | 0.43 | 0.10 | 0.49 | 0.20 | 0.12 | 0.04 | 0.16 | 0.29 | 0.30 |
| replicate | | | | | | | | | | | |
| 186479 Chr | 3 | 0.25 | 0.43 | -0.17 | 0.49 | 0.05 | 0.12 | -0.06 | 0.16 | 0.05 | 0.30 |
| Australia | | | | | | | | | | | |
| Pilbara craton, Warawoo 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 | | | | | | | | | | | |
| 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 | | | | | | | | | | | |
| Mean Bushveld (n=9)i | | | | | | | | | | | |
| 2 s.d. Bushveldi | 0.18 | 0.33 | 0.05 | 0.05 | 0.12 |

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

†H, harzburgite; D, dunite; Chr, chromitite; Kom, komatite.

‡Number of analyses of the same sample solution.

§Ruthenium isotope data are internally normalized to $^{99}$Ru/$^{101}$Ru using the exponential law and are reported as $\varepsilon$ unit (0.01%) deviations from the terrestrial bracketing standard:

$$\varepsilon_i^\text{Ru} = \left( \frac{i^{96}_{\text{Ru}}/101_{\text{Ru}} \text{Sample}}{i^{99}_{\text{Ru}}/101_{\text{Ru}} \text{Standard}} - 1 \right) \times 10^4,$$

where $i = 96, 98, 100, 102$ or $104$. For samples measured $n < 4$ times, the 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 samples measured $n \geq 4$ times are given as 95% confidence intervals of the mean calculated as $\text{s.d.} \times t_{0.95,n-1}/\sqrt{n}$.

¶Elevated $\varepsilon^{96}$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.
### Extended Data Table 2 | Ruthenium concentration data, details about the NiS procedure and Re–Os isotope data for ultramafic rocks

| Sample | Rock* | Ru (ng g⁻¹)† | NiS n x (g)² | ¹⁸⁷⁰Os/¹⁸⁸⁰Os§ | ¹⁸⁷⁰Re/¹⁸⁸⁰Os§ | Age (Gyr)¹ | ¹⁸⁷⁰Os/¹⁸⁸⁰OsRe † | γ⁰⁷⁰Os² | Ref. ** |
|--------|-------|-------------|-------------|----------------|----------------|-------------|----------------|----------|--------|
| **Greenland** | | | | | | | | | | |
| Itsaq gneiss complex (IGC) | | | | | | | | | |
| Narssaaq ultramafic body (NUB), 3.8 Gyr | | | | | | | | | |
| 10.9 H | 7.76 | 5 (6) 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 |
| **South of the Isua supracrustal belt (SOIB), 3.8 Gyr** | | | | | | | | | |
| 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 |
| **Ujaragssuit Nunaí complex, 3.8 Gyr** | | | | | | | | | |
| 194856 Chr | 215 | 1 x5g | 0.10471 - 0.10493 | 0.0008 - 0.0013 | 3.81 | 0.1046 - 0.1047 | +3.9 to +4.0 | 33 |
| 194857 Chr | 189 | 1 x5g | 0.10490 - 0.10809 | 0.01424 - 0.02906 | 3.90 | 0.10395 - 0.10614 | +3.9 to +6.1 | 38 |
| 194882B Chr | 12 | 6 x10g | 0.104842 - 0.105590 | | | | | 39 |
| 194884C Chr | 23 | 4 x10g | | | | | | | |
| **Isua supracrustal belt (ISB), 3.7 Gyr** | | | | | | | | | |
| 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 | | | | | | | |
| **Sequim ultramafic complex, >3.0 Gyr** | | | | | | | | | |
| 186466 Chr | 53.83 | 2 x5g | | | | | | | 42 |
| 186479 Chr | 53.54 | 2 x5g | | | | | | | 42 |
| **Australia** | | | | | | | | | |
| Pilbara craton, Warrawoona Group, 3.5-3.2 Gyr | | | | | | | | | |
| Pil 16-61 Chr | 115 | 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 |

*H, harzburgite; D, dunite; Chr, chromitite; Kom, komatite.

1Ruthenium concentrations reported for the same samples or samples from the same locality. Italicized values indicate Ru concentrations determined in this study as described in the Methods.

2Number of individual NiS digestions (n) and amount of sample material (in g) taken for each single 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 number in parentheses. If not stated otherwise, the same number of NiS digestions was used for all replicates.

3Re–Os isotope data reported for the same samples or for samples of similar composition from the same locality. Note that the different ranges reported for chromitite samples from the Ujaragssuit Nunaí complex were not obtained for the same samples and represent data reported by different previous studies for chromitites from the same locality or sampling area.

4Age used for calculation of the initial ¹⁸⁷⁰Os/¹⁸⁸⁰Os isotope composition as quoted in literature.

5Initial ¹⁸⁷⁰Os/¹⁸⁸⁰Os isotope composition calculated at the time of emplacement of the samples.

6γ⁰⁷⁰Os values refer to the relative deviation (in %) of the calculated initial ¹⁸⁷⁰Os/¹⁸⁸⁰Os isotope compositions of samples relative to the chondritic Os isotope composition at the time of emplacement of the samples.

7Data from refs. 14, 23, 30, 36, 42, 44-46, 53, as indicated.
Extended Data Table 3 | Parameters for mixing model shown in Fig. 3 and resulting $\varepsilon^{106}$Ru values for pre-late-veenear mantle endmember composition

|                          | $\varepsilon^{106}$Ru | $\pm$ Ru (ng g$^{-1}$) | $\varepsilon^{106}$Ru in pre-LV mantle | $\varepsilon^{106}$Ru in pre-LV mantle min | $\varepsilon^{106}$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$^{58}$                           | 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                                        |

*The composition of the modern mantle corresponds to the mean value calculated for samples from the Bushveld complex (Extended Data Table 1).
†The Eoarchean southwest Greenland mantle composition represents the mean value calculated for samples from the IGC (Extended Data Table 1). Data from refs. $^{16,56}$. 