nature geoscience

Supplementary information

https://doi.org/10.1038/s41561-025-01811-3

Potassium-40 isotopic evidence for an extant pre-giant-impact component of Earth's mantle

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The comparison between ^{40}K and other isotopic systems

Potassium is the first lithophile element exhibiting mass-independent isotopic variability among terrestrial reservoirs. To our knowledge, for lithophile elements, such as O, Ca, Ti and Cr, no resolvable mass independent isotopic anomalies have been reported in terrestrial samples. Only recently have nucleosynthetic anomalies in Ru been detected in terrestrial rocks. For elements like Ca, Ti, and Cr, limited terrestrial samples were measured to sufficient precision for the identification of nucleosynthetic anomalies. We suggest that concluding no such anomalies exist in these elements is premature.

Assuming that the absence of terrestrial isotopic variability in the above systems (e.g., O, Ca, Ti and Cr) compared to K is not due to limited sampling, a potential explanation for why anomalies persist in K might reflect the mass-balance of a given element in the proto-Earth and the giant impactor. If the proto-Earth was highly depleted in K compared to chondrites[1], addition of K-enriched chondritic material to a K depleted proto-Earth would produce a pronounced change in K isotopic compositions that would require near homogenization of the proto-Earth and the impactor for the isotopic distinction to be erased. In contrast, the abundances of refractory lithophile elements such as Ca, Ti, and Cr are similar in Earth and chondrites, and therefore even limited mixing between impactor and proto-Earth would reduce the isotopic distinction to the point that it may not be resolved with current analytical capability (Supplementary Table S1 & S2).

Here we quantified the isotopic effects of adding chondritic materials to the proto-Earth using the isotopic compositions of O, Ca, Ti, and Cr of different meteorite groups, assuming 10 wt% chondritic material was admixed to the proto-Earth.

The following equations were used for mass balance and isotopic compositions:

$$f_{\mathrm{pE}}[E]_{\mathrm{pE}} + f_{\mathrm{imp}}[E]_{\mathrm{imp}} = [E]_{\mathrm{BSE}},$$

where f denotes mass fraction, $[E]$ denotes the elemental concentration of element E, and pE, imp, and BSE are proto-Earth before the giant impact, the impactor, and the bulk silicate Earth today, respectively. For the giant impact we assume $f_{\mathrm{pE}} = 0.9$ and $f_{\mathrm{imp}} = 0.1$. The elemental concentration in the impactor ($[E]_{\mathrm{imp}}$) is assumed to be chondrite-like compositions and the concentrations of BSE ($[E]_{\mathrm{BSE}}$) are given in Supplementary Table S2. The elemental concentrations of the proto-Earth ($[E]_{\mathrm{pE}}$) are subtracted from the of BSE ($[E]_{\mathrm{BSE}}$) with different assumed types of impactor, and the results are given in Supplementary Table S1.

For isotopic compositions:

$$f_{\mathrm{pE}}[E]_{\mathrm{pE}}\varepsilon_{\mathrm{pE}} + f_{\mathrm{imp}}[E]_{\mathrm{imp}}\varepsilon_{\mathrm{imp}} = (f_{\mathrm{pE}}[E]_{\mathrm{pE}} + f_{\mathrm{imp}}[E]_{\mathrm{imp}})\varepsilon_{\mathrm{BSE}},$$

where ε represents the isotopic composition of element E. The isotopic compositions of the proto-Earth ($\varepsilon_{\mathrm{pE}}$) for O, Ti, Ca, and Cr are calculated with the given impactor types. With the estimates for the isotopic compositions of the proto-Earth, we can then compare the maximum isotopic difference between the proto-Earth and the BSE, in order to evaluate the potential of resolving terrestrial isotopic variation in other lithophile elements, derived from an unmixed, pre-giant-impact, proto-Earth-like domain.

Our results show that the isotopic offsets in O, Ca, Ti, and Cr are much smaller than those in K (Supplementary Table S1). Assuming a NC-like impactor, the isotopic offsets in Ca, Ti, and Cr would be too small to resolve under current analytical precision, making the detection of potential terrestrial isotopic variability in these systems unlikely. In comparison, the offsets in K isotopic compositions remain analytically resolvable regardless of the types of impactor, given the combinations of elemental abundance and ε^{40}K values (i.e., K-depleted groups generally have greater K isotopic anomalies).

Oxygen isotopes, however, present a more complex issue. A possible explanation is that the proto-Earth and impactor had too small a difference in O isotopic composition to resolve impactor from proto-Earth in a mixture of the two. The oxygen abundances are also similar across major terrestrial reservoirs, so that mixing processes would not produce relative extreme values toward one end-member, and significant heterogeneity is unexpected.

Modification of ^{40}K due to potassium mobility during alteration and metamorphism

For mantle-derived volcanic rocks (e.g., OIB), hydrothermal alteration and crustal contamination are most likely responsible for the dilution of ^{40}K anomaly, which is shown in Extended Data Figs 2-4. For the La Réunion samples, the only sample (RU0709) without a ^{40}K anomaly has anomalously high K_2O content (Extended Data Fig. 2) and it falls in the crustal contaminated range in Extended Data Fig. 3. Generally, for an oceanic basalt, ~15% crustal contamination would overprint the original ^{40}K isotope signature (Extended Data Fig. 3). For Kama‘ehuakanaloa samples, the major source of contamination is hydrothermal alteration indicated by the seawater-derived ^{234}U isotopic compositions. Extended Data Fig. 4 shows that the only sample (6K491-2) with a ^{40}K anomaly ($\varepsilon^{40}K = -0.6\pm0.3$) has the lowest $^{234}U/^{238}U$ ratio (1.002) among the dataset, while the other two samples that did not have resolvable ^{40}K anomalies (1803-16 and 1804-1) show elevated $^{234}U/^{238}U$ ratios of 1.006-1.008[2].

The ancient felsic igneous rocks in this study are mostly TTGs. The partial melting of their magmatic precursor to form the TTGs likely involved crustal sourced materials, and therefore the mafic samples in the same ancient crustal terranes are more likely to carry the original ^{40}K isotope signature. Additionally, these ancient crustal blocks experienced post-formation (poly-)metamorphism which likely involved open-system behavior. Metamorphic

disturbance might also have diluted/altered the original $\varepsilon^{40}K$ anomaly in the ancient rocks. For example, in our studied mafic rocks, some samples in Isua and Nuvvuagittuq did not show a resolvable ^{40}K anomaly, which can be explained by open-system behavior during post-formation (poly-)metamorphism experienced in these terranes[3]. The K isotope data of all sample measurements are given in the Supplementary Table S3.

The potential ^{100}Ru-^{40}K correlation

For the isotopic systems of Ru, Mo and Zr, Earth appears to be an endmember compared with the primary meteorites (Supplementary Fig. S1). When plotting ^{100}Ru against ^{40}K isotopic compositions, different meteorite groups define a trend (Fig. 2). This correlation likely reflects mixing between the products of different nucleosynthetic paths that contributed material to the molecular cloud from which the solar system formed.

The offset in ^{100}Ru isotopic composition between Earth's ancient and modern mantle is best explained by meteoritic addition by late accretion or a contribution from the core[4,5], given that Ru is highly siderophile and any pre-late-veneer Ru would have been efficiently partitioned into the core during metal-silicate differentiation associated with the last giant impact. Unlike Ru, K is a major, highly lithophile element that is not known to partition into the core, so that the $\varepsilon^{40}K$ offset between the modern upper mantle and the proto-Earth cannot be explained by the addition of late accreted materials or core-mantle exchange. Given the contrasting elemental properties and the currently different views on the sources of the terrestrial ^{100}Ru anomalies, the ^{40}K-^{100}Ru isotopic behavior is underdetermined during the giant impact and subsequent differentiation. Consequently, although ^{100}Ru and ^{40}K are potentially correlated in the solar

reservoir of planetary building blocks, the two systems did not necessarily remain correlated when Earth's core and mantle was differentiated.

Implications for the high U/Pb of the proto-Earth

Our data indicates that the K/U of the reservoir with anomalous $\varepsilon^{40}K$ is significantly more depleted than the modern BSE, suggesting a volatile depleted component, which supports the high-μ proto-Earth model[1]. The volatile-depleted component would be strongly depleted in Pb with a very high U/Pb ($^{238}U/^{204}Pb$, $\mu \geq 100$)[1]. If Pb and K concentrations were correlated in the volatile-element depleted component, the deep mantle source carrying the negative $\varepsilon^{40}K$ signature would also have highly radiogenic Pb isotopic compositions. We estimated that for such an isolated, mantle domain, the $^{206}Pb/^{204}Pb$ at the present-day could be up to 218 ($^{206}Pb/^{204}Pb_{initial}$=9.307[1], μ = 100). Such highly radiogenic Pb data is not seen in global OIB datasets.

This evident disagreement can be explained by mixing scenarios as the mantle plume rises to the surface. For a μ value up to 100, Pb concentration must be strongly depleted in the isolated mantle domain (i.e., 0.1 ppb Pb in the high-μ proto-Earth model[1]). Although K was also depleted (i.e., 130 ppm), the magnitude of depletion of Pb is much stronger. Compared to the Pb/K ratios of BSE = 6.25×10^{-4} (K = 240 μg/g, Pb = 150 ng/g[6]) and MORB = 3.7×10^{-4} (K = 1520 μg/g, Pb = 570 ng/g[7]), the isolated source would have a significantly lower Pb/K of 7.7×10^{-7} (K=130 μg/g, this study; Pb=0.1 ng/g[1]). Given the extremely low Pb/K ratio of the isolated mantle source, mixing with a small amount of material with "normal" mantle Pb/K ratio would significantly dilute the radiogenic Pb without erasing the ^{40}K anomaly. Here we have quantified three possible mixing scenarios between the volatile-depleted and isolated mantle source and: (1)

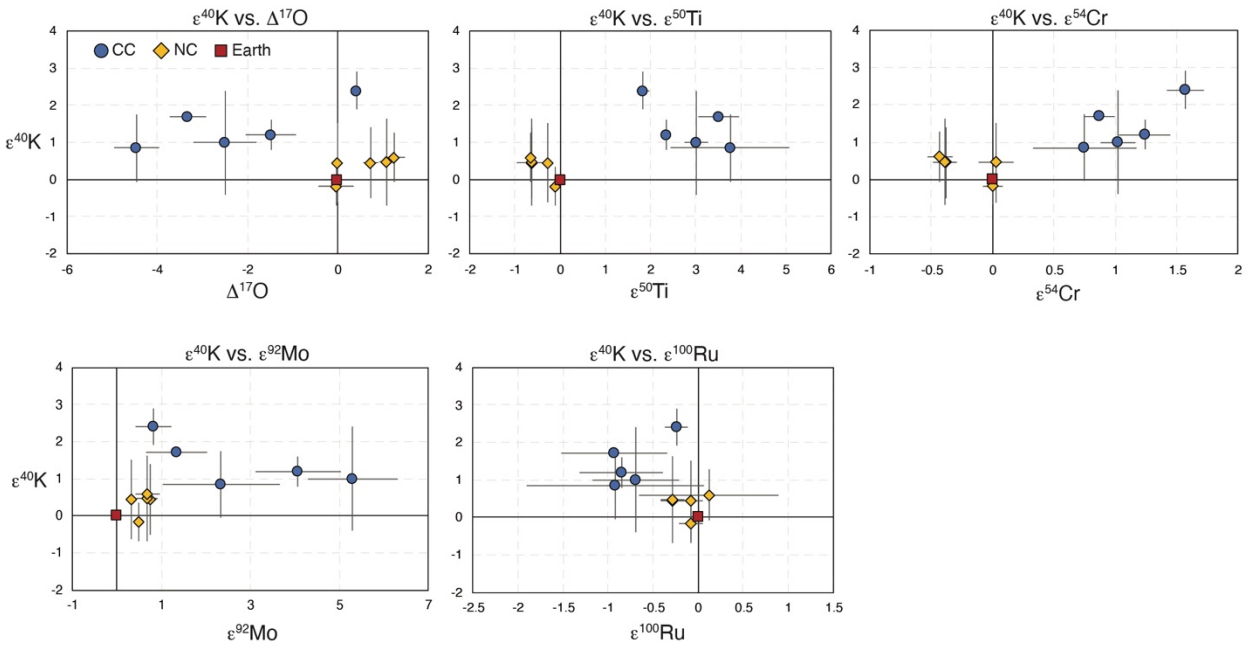
BSE-like mantle; (2) subduction recycled MORB; (3) subduction recycled sediment equal in composition to the average sediment (GLOSS)[8].

The compositions of the mixing components are given below.

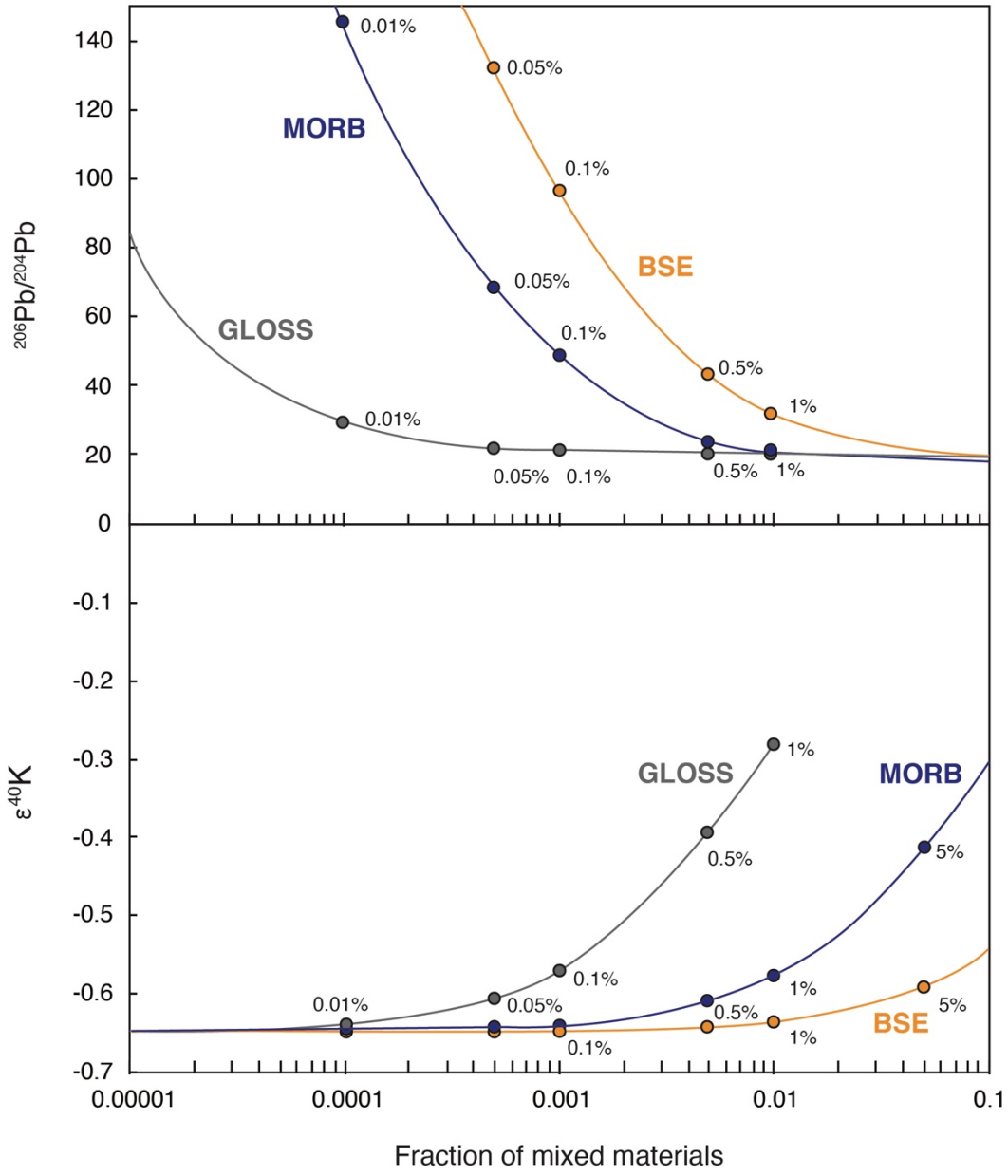
	K μg/g	Pb μg/g	Pb/K (10^{-6})	$\varepsilon^{40}K$	$^{206}Pb/^{204}Pb$ (present-day)*
Isolated mantle source	130 this study	0.0001[1]	0.77	0.65	218.6
MORB	1520[7]	0.570[9]	375	0	17
BSE	240[6]	0.15[6]	625	0	18
GLOSS	16900[8]	19.9[8]	1177	0	18.9

* the present-day value was calculated using initial $^{238}U/^{204}Pb = 100$ and initial $^{206}Pb/^{204}Pb = 9.307$[1] at 4.567 Ga.

The mixing results (Supplementary Fig. S2) show that the addition of small amounts of recycled MORB (>1%) or GLOSS (>0.09%) will drive the $^{206}Pb/^{204}Pb$ of the mixture below 20. A larger mixing fraction (>6%) of BSE mantle is required for the same effect. In all three cases, the $\varepsilon^{40}K$ of the mixture is increased by only 0.07 (GLOSS and BSE) to 0.1 (MORB) ε units. Therefore, highly radiogenic Pb isotopic compositions are unlikely to be preserved in deep mantle, plume-derived volcanic rocks.



Supplementary Fig S1. The ^{40}K anomalies versus isotopic anomalies of other systems. Two types of isotopic anomalies are distinguished: (1) For ^{17}O, ^{50}Ti and ^{54}Cr, the Earth is 0, between the CCs and NCs; (2) For ^{92}Mo, ^{100}Ru and ^{40}K, the Earth has more extreme values than CCs and NCs, suggesting an additional isotopic end-member. The data points represent mean values ± 2SE. The isotopic data of the meteorite groups and the sources of data are given in Supplementary Table S1.



Supplementary Fig S2. The amount of materials mixed in the isolated, volatile depleted, mantle source to erase highly radiogenic Pb and anomalous $\varepsilon^{40}K$ isotope signatures. Three different mixing scenarios are considered: (1) mixing with BSE-like mantle; (2) subduction recycled MORB; and (3) subduction recycled GLOSS. The mixing results show that the addition of small amounts of recycled MORB (>1%) or GLOSS (>0.09%) will drive the present-day $^{206}Pb/^{204}Pb$ of the mixture below 20. A larger mixing fraction (>6%) of BSE mantle is required for the same effect. In all three cases, the $\varepsilon^{40}K$ of the mixture is not significantly affected, with increases of only ~0.07 (GLOSS and BSE) to 0.1 (MORB) ε units.

Supplementary Table S1. Calculated elemental concentrations of proto-Earth and isotopic offsets between the BSE and the proto-Earth, assuming 10% mass contribution from an impactor with isotopic compositions of different meteorite groups.

Impactor type	$[K]_{pE}$ (μg/g)	$\varepsilon^{40}K_{pE-BSE}$	$[O]_{pE}$ (mg/g)	$\Delta^{17}O_{pE-BSE}$	$[Ca]_{pE}$ (mg/g)	$\varepsilon^{48}Ca_{pE-BSE}$	$[Ti]_{pE}$ (μg/g)	$\varepsilon^{50}Ti_{pE-BSE}$	$[Cr]_{pE}$ (mg/g)	$\varepsilon^{54}Cr_{pE-BSE}$
CI	158	-0.92	442	-0.05	28.0	-0.07	1357	-0.07	2.51	-0.18
CM	174	-0.26	448	0.25	27.6	-0.16	1337	-0.15	2.46	-0.14
CO	181	-0.18	454	0.38	27.3	-0.25	1321	-0.24	2.41	-0.12
CV	184	-0.31	452	0.30	26.9	-0.30	1306	-0.27	2.40	-0.15
CR	185	-0.22	452	0.13	27.5	-0.12	1333	-0.13	2.38	-0.22
H	132	-0.29	456	-0.06	27.6	0.01	1339	0.03	2.39	0.06
L	127	-0.34	452	-0.10	27.5	0.02	1336	0.03	2.37	0.07
LL	131	-0.40	451	-0.12	27.6	0.01	1337	0.03	2.38	0.07
EH	130	0.11	461	0.00	28.1	0.01	1356	0.00	2.45	0.00
EL	137	-0.27	456	0.00	27.8	0.02	1344	0.01	2.45	0.00

pE: proto-Earth.

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