LETTER

Potassium isotopic evidence for a high-energy giant impact origin of the Moon

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The Earth-Moon system has unique chemical and isotopic signatures compared with other planetary bodies¹⁻³; any successful model for the origin of this system therefore has to satisfy these chemical and isotopic constraints. The Moon is substantially depleted in volatile elements such as potassium compared with the Earth and the bulk solar composition⁴, and it has long been thought to be the result of a catastrophic Moon-forming giant impact event⁵. Volatile-element-depleted bodies such as the Moon were expected to be enriched in heavy potassium isotopes during the loss of volatiles; however such enrichment was never found⁶. Here we report new high-precision potassium isotope data for the Earth, the Moon and chondritic meteorites. We found that the lunar rocks are significantly $(>2\sigma)$ enriched in the heavy isotopes of potassium compared to the Earth and chondrites (by around 0.4 parts per thousand). The enrichment of the heavy isotope of potassium in lunar rocks compared with those of the Earth and chondrites can be best explained as the result of the incomplete condensation of a bulk silicate Earth vapour at an ambient pressure that is higher than 10 bar. We used these coupled constraints of the chemical loss and isotopic fractionation of K to compare two recent dynamic models that were used to explain the identical non-mass-dependent isotope composition of the Earth and the Moon. Our K isotope result is inconsistent with the low-energy disk equilibration model⁷, but supports the high-energy, high-angular-momentum giant impact model⁸ for the origin of the Moon. High-precision potassium isotope data can also be used as a 'palaeo-barometer' to reveal the physical conditions during the Moon-forming event.

Potassium isotopes have long been recognized as crucial for testing the giant impact theory for the origin of the Moon, and can be used to further refine the physical and chemical parameters of such models⁶. This is because K is a moderately volatile element and the Moon is substantially depleted in K and other volatile elements relative to the Earth and the compositions of carbonaceous chondrite. The K/U ratio is an important indicator of such depletion because U is a refractory element and this ratio is largely preserved during planetary accretion processes. The K/U ratio of the Moon is five times lower than that of the Earth and twenty-five times lower than that of CI chondrites^{4,9–11}. The mechanism that caused the depletion of volatile elements in the Moon is still not entirely understood^{6,12}. More precise measurements of the isotopic fractionation of K associated with such depletion should improve our understanding of the processes involved.

Previous K isotope measurements made with an ion microprobe on lunar samples reported no fractionation of K isotopes at the $\pm 0.5\%$ uncertainty⁶. Recent measurements of the isotopic fractionation of other volatile elements in the Moon, such as Cl and Zn, show that the isotopes of these volatile elements do fractionate^{13,14}, thus we may also expect to find variations in K isotopes. However, both Zn and Cl are considerably more volatile than K. Zinc and Cl in lunar rocks exhibit large isotopic fractionations (up to tens of parts per thousand) and have been linked to multiple late-stage events such as degassing during the differentiation of the lunar magma ocean and volcanic eruptions^{13,15}. Thus while the Zn and Cl isotope variations in lunar rocks may be affected by secondary processes to a large degree, the depletion of the less-volatile element K (and any associated isotopic fractionation) is more likely to be related to the formation of the Moon.

We show that the isotopes of K exhibit very limited fractionation in a suite of terrestrial igneous, metamorphosed rocks and chondrites of various petrologic types and K concentrations (Fig. 1 and Extended Data Tables 1 and 2). The K isotope composition is conventionally expressed as δ^{41} K, where δ^{41} K = [(41 K/ 39 K)_{sample}/(41 K/ 39 K)_{standard} -1] × 1,000. We have previously defined the K isotope composition of the bulk silicate Earth (BSE) by analysing three basalts from different tectonic settings (mid-ocean ridge, ocean island and continental basalts; $\delta^{41}K_{BSE} = 0.000 \pm 0.027\%$; 2 s.d.)¹⁶. In this study, the K isotope compositions of four terrestrial igneous rocks (an andesite, a granite, a granodiorite and a trachyandesite) and a 3.5 billion-year-old Isua metavolcanic rock are found to be indistinguishable from the BSE value. We also found that the K isotope compositions of four chondrites (one CI carbonaceous chondrite and three ordinary chondrites) are identical to those of terrestrial rocks within errors $(-0.075\% \pm 0.056\%)$ versus 0.000‰ \pm 0.027‰). Hence, there is no significant (<2 σ) difference between the K isotope compositions of Earth and chondritic meteorites. Note that there may be a slight enrichment of heavy K isotopes in the Earth relative to chondrites. However, this difference is marginal and cannot be entirely resolved at our precision level. It is subject to further



Figure 1 | K isotope compositions of the Earth, the Moon and meteorites. For each sample, the error bars represent 2 standard errors of approximately 10 repeat measurements. The grey shaded area shows the BSE value ($0.000\% \pm 0.027\%$). There is no resolved difference between the K isotope compositions of bulk chondrites and terrestrial igneous rocks; however, the lunar rocks are significantly enriched in heavy isotopes of K compared with the Earth and chondrites.

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investigation and is not the focus of this study due to the small degree of the possible fractionation.

We also report new high-precision K data for seven lunar rocks from the Apollo 11, 12, 14 and 16 missions (Fig. 1 and Extended Data Table 3). Before this study, due to large analytical uncertainties, it was concluded that there was no resolved K isotopic fractionation between the Earth and the Moon, except for the lunar soils⁶. The extreme enrichments of the heavy isotopes of K in lunar soils, caused by impact gardening and the sputtering effects of the solar wind, cosmic rays and micrometeorites, have been recognized since the 1970s^{17–19}. We have also confirmed such extremely large enrichments of heavy isotopes of K in lunar soils (Extended Data Table 3). However, for the first time, this study shows that the K isotope compositions of various lunar rocks from different locations are consistently around 0.4‰ higher than those of the BSE and chondrites. These seven lunar rock samples include two high-K ilmenite basalts (10017 and 10071), two subsamples of a breccia with a granite lithology (12013-170 and 12013-171), one fragmental breccia with regolith component (14301), one crystalline matrix breccia (14305) and one poikilitic impact melt (60315). One breccia with a granite lithology (12013-171) shows a slightly higher value (possibly due to regolith contamination, or more probably due to any secondary fractionation effect during the magmatic differentiation), but all of the other six lunar rocks are indistinguishable from each other. We interpret this δ^{41} K shift of approximately 0.4‰ as a primary feature of the Moon. This is the first time that the K isotopic signatures of different planetary bodies have been truly resolved.

The significant (> 2σ) K isotopic fractionations in the Moon relative to the Earth probably accompany the depletion of volatile elements, and such coupled chemical and isotopic information provides new constraints on the nature of this depletion, which is associated with the formation of the Moon. To decipher this information, we need to understand the mechanisms of K isotope fractionation, which have not been well studied as yet due to the lack of resolvable K isotope fractionation in the past. Recent high-precision K isotope studies show that K isotopes are not fractionated significantly during igneous crystallization processes^{16,20}. This conclusion, based on natural samples, agrees well with the theoretical prediction that K forms ionic bonds and it has only one valence state, both of which prevent a large vibrational isotope effect²¹. The only known high-temperature fractionation mechanism for K isotopes is incomplete evaporation/condensation during Rayleigh distillation^{22,23}. Such fractionations between a vapour and melt can be described with the Rayleigh equation, $\delta^{41}K_{melt} = \delta^{41}K_{vapour} +$ $(1,000 + \delta^{41} K_{vapour}) \times (F^{\alpha-1} - 1)$, where F is the fraction of K in the melt phase and α is the fractionation factor. The value of α during evaporation into a high vacuum can be estimated as the square root of the mass number of the lighter isotope (39 here) over that of the mass number of the heavier isotope (41). Thus, α for K is 0.9753. This high-vacuum fractionation factor was initially expected and would predict an extreme enrichment of heavy K isotopes in lunar samples (of approximately 100‰); however, such high values were never found⁶. Our new result also disproves Rayleigh fractionation in a high vacuum as the mechanism at work (see Fig. 2). By fitting the new data (Fig. 2) through the Rayleigh equation, we obtained effective α values between 0.9997 and 0.9998. This is substantially smaller than the Rayleigh fractionation factor measured in a high vacuum. Both laboratory experiments and theoretical considerations show that higher ambient pressures would suppress the degree of isotopic fractionation of K (refs 22, 24), where α values approach 1. We plotted the experimental pressures versus the effective Rayleigh fractionation factors in Extended Data Fig. 1, based on all of the available data^{22,23}, and there is a good correlation. The size of this suppression effect is difficult to estimate quantitatively because the experiments on K isotopic fractionation during partial evaporation and condensation at a range of high pressures are very limited. Current available evaporation experiments on chondritic analogue materials were only conducted in a high vacuum (approximately 10^{-9} bar) and at a few pressures up to



Figure 2 | **K isotope compositions versus the K/U ratio for the Earth and the Moon.** For the terrestrial samples only the average of three basalts is plotted. The K isotope compositions of the Earth and the Moon are from this study. The K/U ratios are from refs 4,11. The Rayleigh fractionation lines are plotted with the Rayleigh equation described in the text using three different fractionation factors (0.9753, 0.9997 and 0.9998). The data points represent the averages of Earth basalts and lunar samples; error bars show 2 s.d.

around 1 bar (refs 22, 23). Direct extrapolation of the experimental data to compare with our result should be viewed with caution because these experimental data are also compositionally dependent. Here we assume that the fractionation factor is due to a pressure effect. We do this to consider different lunar origin models that make different predictions about the pressure of lunar origin. We find that a pressure effect at >10 bar is most consistent with the Rayleigh fractionation factor (α values between 0.9997 and 0.9998) inferred from our data (Extended Data Fig. 1).

The enrichment of the heavy K isotope of around 0.4‰ in the Moon compared with the Earth and chondrites (plus the >10 bar high pressure inferred by this value) provides a new way of testing models for the origin of the Moon. We compare this result with the expectations for the canonical model and two recent models of the post-giant impact that explain the identical non-mass-dependent isotope compositions (for example, Δ^{17} O) of the Earth and the Moon (Fig. 3). Note that K isotope variations here are due to mass-dependent fractionation. So although the two recent models accurately predicted that the Moon and the Earth had the same non-mass-dependent isotope composition (for example, Δ^{17} O), they do not necessarily yield the same δ^{41} K value for the Earth and the Moon.

First, we start with the canonical model. In this model the Moon formed from a lunar disk that resulted from a giant impact (Fig. 3a)⁵, where the disk forms primarily from the impactor (around 80%) and then accreted to form the Moon. This model would yield a Moon that would probably have different non-mass-dependent isotope compositions than the Earth (for example, in Δ^{17} O) because individual Solar System bodies (such as the Earth, Mars, Vesta, chondrite parent bodies) are known to have distinct non-mass-dependent isotope compositions for many elements²⁵. In contrast, we have shown here that chondrites and Earth are similar in δ^{41} K, but that the Moon has a higher δ^{41} K. This is not expected from the canonical lunar disk model (Fig. 3a), which would imply that the Moon would have the same δ^{41} K as the Earth (Fig. 3a) because the Earth and chondrites (the probable building-blocks of terrestrial planets) have so far been found to have the same K isotope composition.

Second, to explain the identical Δ^{17} O values for the Earth and the Moon^{2,26}, a low-energy silicate atmosphere equilibration model was



Figure 3 | Proposed models for the post-giant-impact state to explain the identical non-mass-dependent isotope compositions of the Earth and the Moon. Material that forms beyond the Roche limit can produce the Moon. δ in the figure represents $\delta^{41}K_{BSE}$. **a**, In the canonical lunar disk scenario⁵, the disk forms primarily from the impactor, which is assumed to be isotopically distinct from the Earth for non-mass-dependent isotope compositions. Regarding the loss of volatiles, a new study³⁰ describes a complicated mixture of outer disk material and hot inner disk material that is depleted in K. This model assumes that the outer disk material retains its K (with the same isotopic composition as that of the precursor material) and that there is negligible K from the inner disk. It would predict a depleted K elemental abundance in the Moon (the result of the mixing of the outer and inner disk materials) compared with the Earth. However, it also predicts the same K isotope composition (nearly all of the K from the outer disk and negligible K from the inner disk) as that of the Earth. **b**, To explain the oxygen isotopic homogeneity (Δ^{17} O) of the Earth and the Moon, it was proposed that both bodies reach equilibration through a silicate atmosphere⁷. There are many problems with this model, including that it predicts $\delta^{\,41} \text{K}$ values that are zero or negative for the Moon, rather than the positive value reported here. c, The K isotope composition of the Moon is, however, consistent with the recently proposed high-energy, high-angular-momentum giant impact model⁸. This model is based on a giant impact leaving the Earth in a state that exceeds the hot spin stability limit in which the mantle, atmosphere and disk form a wellmixed continuous extended structure that reaches beyond the Roche limit. See also Extended Data Fig. 2.

proposed, see Fig. 3b, in which the disk only achieved temperatures of $T \approx 2,500$ K (ref. 7), and isotopic equilibration of the Earth and the Moon was mediated by a silicate vapour atmosphere. There are several problems with this model, which have been discussed in the literature^{27,28}. Here we only focus on the aspect of this model that relates to its prediction for K isotopes. This model would probably lead to an enrichment of volatile elements in the Moon rather than the observed depletion²⁹. Vapours coming from the much larger Earth would most probably also be depleted in the heavy isotopes of K, potentially resulting in a negative value of δ^{41} K in the Moon rather than the observed positive value given here.

Another recent model⁸ may alleviate these concerns and also be consistent with our δ^{41} K measurements. This model describes a high-energy, high-angular-momentum giant impact that would have left the proto-Earth system spinning so fast that its mantle, atmosphere and disk form a well-mixed continuous structure that extended beyond the Roche limit (Fig. 3c). The growing molten Moon condensed from this vapour of BSE composition at locales beyond the Roche limit at relatively high pressure and temperature, presumably around 20 bar and about 3,700 K. The prediction of the model is consistent with the bulk lunar composition, including the magnitudes of the depletions in moderately volatile elements such as K (ref. 8). The absolute majority of the 'mantle atmosphere' falls back to the Earth, so the Earth has the same K isotopic value as the 'building block' materials. The Moon, which is a tiny fraction of the mantle atmosphere, forms as a condensate. Because the Moon was partially condensed from a vapour phase, according to Rayleigh distillation it is naturally concentrated in the heavy isotope of K, which is consistent with our observation. The degree of K isotopic fractionation (around +0.4‰) is also consistent with a Rayleigh distillation with an effective fractionation factor between 0.9997 and 0.9998 (Fig. 2), which corresponds to a pressure higher than 10 bar (Extended Data Fig. 1). This model generates both the observed bulk lunar chemistry⁸ and the observed K isotope fractionation in this study. Thus, as shown schematically in Fig. 3c, the coupled constraints of the K depletion and ⁴¹K enrichment in the Moon are consistent with a high-energy, high-angular-momentum giant impact forming the Moon⁸.

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

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RESEARCH LETTER

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Author Contributions S.B.J. and K.W. (王昆) designed the study. K.W. performed the analysis. K.W. and S.B.J. wrote the manuscript.

Author Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to K.W. (wangkun@wustl.edu).

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METHODS

We analysed eight terrestrial samples, four chondrites and nine Apollo lunar samples. The data for the terrestrial samples, chondrites and lunar samples are listed in Extended Data Tables 1, 2, and 3, respectively.

The eight terrestrial samples are three basalts, one andesite, one granite, one granodiorite, one trachyandesite and one metavolcanic rock. The three basalts are BCR-2, BHVO-1 and CHEPR; the data for these samples has previously been reported¹⁶ and only the average of the three basalts is listed in Extended Data Table 1. BCR-2 is a Columbia River continental flood basalt and BHVO-1 is a tholeitic basalt from the Kilauea crater of Hawaii. CHEPR is a mid-ocean-ridge basalt from the East Pacific Rise³¹. AGV-1 is an andesite from Guano Valley, Oregon. G-2 is a granite from near Bradford, Rhode Island. GSP-1 is a granodiorite from Silver Plume, Colorado. K1714 is a trachyandesite lava flow of the Permian Oslo Rift, near Oslo, which contains coarse-grained feldspars embedded in a fine-grained matrix. Sm–Nd and Rb–Sr systematics show that it is derived from a mantle source magma³². Isua 3 is a metavolcanic rock from Isua, Greenland, containing 40% quartz, 20% plagioclase, 17% muscovite, 17% biotite, 2% garnet, 1% hornblende, 1% allanite and 1% ilmenite³³. Most of these terrestrial samples are geostandards distributed by the US Geological Survey and have been well studied in the past.

Four chondritic meteorites were analysed. One CI1 carbonaceous chondrite, Orgueil, is an 1864 fall in France. The three ordinary chondrites include one equilibrated H6 (Guareña, an 1892 fall in Spain) and two equilibrated L6 (Bruderheim, a 1960 fall and Peace River, a 1963 fall, both in Canada). All but Guareña are bulk samples. Guareña is from the silicate separate after removing metals from the bulk for a previous study.

Nine Apollo lunar samples were allocated by NASA's Johnson Space Center. They include seven rock samples and two soil samples. The seven rock samples comprise two high-K ilmenite basalts (10017 and 10071), two breccias with some granite lithology (12013-170 and 12013-171), one fragmental breccia with a regolith component (14301), one crystalline matrix breccia (14305) and one poikilitic impact melt (60315). The two soil samples are a trench soil (12033) collected 15 cm below the surface and a bulk soil sample (14163).

All of the samples (approximately 100 mg each) were digested through a CEM MARS 6 microwave system in two steps: digestion first in a concentrated HF/HNO₃/HCl mixture and then in diluted aqua regia. The sample of Orgueil (CI1 chondrite) was dry-ashed first in a Thermolyne muffle furnace (800 °C; 3 h) to remove its abundant of organic material. The other chondrites were also treated

with extra steps in order to fully dissolve the organic portion (see Extended Data Table 2 for digestion notes).

Fully digested samples were loaded on to chromatography columns (ID = 1 cm; filled with 13 ml of Bio-Rad AG50W-X8 100–200 mesh cation exchange resin). Potassium was eluted with 0.5 M HNO₃ and collected in the 180–340 ml cut. This purification procedure was repeated in a smaller column (ID = 0.4 cm; filled with 1.6 ml of Bio-Rad AG50W-X8 100-200 mesh cation exchange resin) once to further purify the K. This column chemistry used here was first established in the literature^{34,35} and was recently adopted by our group¹⁶. Matrix effects are closely monitored.

Samples were analysed with a GV Instruments IsoProbe P (HCP01) multiplecollector inductively coupled plasma mass spectrometer (MC-ICP-MS) at Harvard University. The IsoProbe is equipped with a hexapole collision cell to remove interference from Ar⁺ and ArH⁺. Sample solutions were introduced into the plasma source via an APEX-IR spray chamber and ACM desolvator system. A 100 µl min⁻¹ PFA MicroFlow nebulizer was used. The method used here has been described and evaluated in detail in a recent work¹⁶, and makes it possible to precisely measure K isotopes at the level of 0.05‰. The isotopic ratios of ⁴¹K/³⁹K are measured with the standard sample bracketing technique. The laboratory standard is Merck KGaA Suprapur 99.995% purity potassium nitrate. The final data (δ^{41} K_{BSE}) are normalized relative to the BSE value (δ^{41} K_{BSE}=1.000479 × δ^{41} K_{Suprapur} + 0.479230), which is defined by the average of the terrestrial basalts¹⁶. Uncertainties are reported as two standard errors of repeated measurements unless otherwise noted.

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Pressure (bar)

Extended Data Figure 1 | The estimation of the pressure effect on α . The experiments on K isotope fractionation during evaporation and condensation are very limited. One study²² conducted evaporation experiments on chondritic analogue materials in a high vacuum (around 10^{-9} atm) and at various higher pressures (1×10^{-5} , 9×10^{-5} , 7.2×10^{-5} , 1.8×10^{-5} , 1.8×10^{-4} , 1.4×10^{-3} , 1.3×10^{-2} and 1 atm). One of their major observations is that the degree of K isotope fractionation during evaporation decreases with higher pressures. Another study²³ indicates that not only the pressure but also the composition (that is, H₂, He, CO₂) of the surrounding gas would affect the degree of K isotope fractionation. Here the red dots show the calculated effective Rayleigh fractionation factors based on the experimental data^{22,23} versus pressures. The effective Rayleigh fractionation factor is correlated with pressures and the observed value from this study suggests a >10 bar pressure during the loss of K from the Moon. Note that because not all the experiments are conducted at the same surrounding gas environment and the composition of the surrounding gas would also affect the effective fractionation factor (downward arrows in the figure), the correlation between the effective fractionation factor and pressure is not perfect. This >10 bar pressure from this study is at best a first-order estimation.



Extended Data Figure 2 | An artist's rendering of the two recent models of the origin of the Moon and their implications for K isotopes. Scenario 1 is from ref. 7; scenario 2 is from ref. 8.

Extended Data Table 1 | K isotope compositions of terrestrial igneous rocks

Sample	Description Location		Weight (mg) [K] (ppm)		$\delta^{41} K_{BSE}$	$\delta^{41} K_{BSE}$		n ^b
Average Basalts ^c	Basalt				0.000	±	0.027	115
AGV-1	Andesite	Guano Valley, Oregon	19.9	21501.9	0.017	±	0.111	11
G-2	Granite	Near Bradford, Rhode Island	20.3	32624.7	0.056	±	0.091	12
GSP-1	Granodiorite	Silver Plume, Colorado	14.6	36823.0	0.069	±	0.067	13
K1714	Trachyandesite	Oslo Rift, Norway	24.1	38600.0	0.041	±	0.054	10
Isua 3	Meta volcanic rock	Isua, Greenland	15.7	19639.7	-0.003	±	0.057	10

^aSE, standard errors (standard deviation divided by the square root of the total number of measurements *n*).

⁵C, standard of measurements. ^cThe $\delta^{41}K_{BSE}$ of the average of three basalts (BCR-2, BHVO-2 and CHEPR) is zero by definition¹⁶.

LETTER RESEARCH

Extended Data Table 2 | K isotope compositions of carbonaceous chondrites

Sample	Description	Weight (mg)	[K] (ppm)	$\delta^{41}K_{BSE}$ (%)		2SE ^a	n ^b	Digestion Note
Orgueil	CI1	49.4	919.2	-0.055	±	0.097	11	Ashing in Ni foil, 800 °C, 3 hour
Guareña #1	H6	102.2	909.5	-0.205	±	0.081	9	No ashing, added H ₂ O ₂
Guareña #2	H6	99.3	1292.4	-0.188	±	0.063	8	No ashing, two extra conc. HNO ₃ steps
Bruderheim #1	L6	105.4	730.7	-0.092	±	0.092	8	No ashing, added H ₂ O ₂
Bruderheim #2	L6	105.0	938.6	-0.121	±	0.084	8	No ashing, two extra conc. HNO ₃ steps
Peace River	L6	82.2	754.9	-0.062	±	0.096	14	No ashing, added H ₂ O ₂

^aSE, standard errors (standard deviation divided by the square root of the total number of measurements).

^bNumber of measurements.

Sample	Description	Weight (mg) [K] (ppm)		$\delta^{41}K_{BSE}$ (%)	2SE ^a	n ^b
Rock						
10017-282	Ilmenite Basalt (high K)	21.66	2311.9	0.372 ±	0.061	15
10071-126	Ilmenite Basalt (high K)	86.49	2617.5	0.460 ±	0.037	12
12013-170	Breccia with Granite	74.29	10725.4	0.468 ±	0.032	12
12013-171	Breccia with Granite	80.02	8771.8	0.595 ±	0.051	12
14301-290	Regolith Breccia	90.00	6785.1	0.350 ±	0.035	12
14305-330	Crystalline Matrix Breccia	75.73	5806.7	0.422 ±	0.044	12
60315-191	Poikilitic Impact Melt	78.91	3421.6	0.420 ±	0.049	12
Soil						
12033-686	Trench Soil	83.31	3131.5	1.480 ±	0.037	12
14163-947 ^c	Soil	91.89	3619.2	8.147 ±	0.038	12

Extended Data Table 3 | K isotope compositions of Apollo lunar samples

^aSE, standard errors (standard deviation divided by the square root of the total number of measurements). ^bNumber of measurements.

"The same lunar soil sample was also analysed in ref. 35. The reported value is 8.3‰±0.8‰ (relative to BSE), which is identical to the new value here.