

# Meteorite zircon constraints on the bulk Lu–Hf isotope composition and early differentiation of the Earth

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Knowledge of planetary differentiation is crucial for understanding the chemical and thermal evolution of terrestrial planets. The  $^{176}\text{Lu}$ – $^{176}\text{Hf}$  radioactive decay system has been widely used to constrain the timescales and mechanisms of silicate differentiation on Earth, but the data interpretation requires accurate estimation of Hf isotope evolution of the bulk Earth. Because both Lu and Hf are refractory lithophile elements, the isotope evolution can be potentially extrapolated from the present-day  $^{176}\text{Hf}/^{177}\text{Hf}$  and  $^{176}\text{Lu}/^{177}\text{Hf}$  in undifferentiated chondrite meteorites. However, these ratios in chondrites are highly variable due to the metamorphic redistribution of Lu and Hf, making it difficult to ascertain the correct reference values for the bulk Earth. In addition, it has been proposed that chondrites contain excess  $^{176}\text{Hf}$  due to the accelerated decay of  $^{176}\text{Lu}$  resulting from photoexcitation to a short-lived isomer. If so, the paradigm of a chondritic Earth would be invalid for the Lu–Hf system. Herein we report the first, to our knowledge, high-precision Lu–Hf isotope analysis of meteorite crystal-line zircon, a mineral that is resistant to metamorphism and has low Lu/Hf. We use the meteorite zircon data to define the Solar System initial  $^{176}\text{Hf}/^{177}\text{Hf}$  ( $0.279781 \pm 0.000018$ ) and further to identify pristine chondrites that contain no excess  $^{176}\text{Hf}$  and accurately represent the Lu–Hf system of the bulk Earth ( $^{176}\text{Hf}/^{177}\text{Hf} = 0.282793 \pm 0.000011$ ;  $^{176}\text{Lu}/^{177}\text{Hf} = 0.0338 \pm 0.0001$ ). Our results provide firm evidence that the most primitive Hf in terrestrial zircon reflects the development of a chemically enriched silicate reservoir on Earth as far back as 4.5 billion years ago.

hafnium isotopes | chondritic uniform reservoir | bulk silicate Earth | early Earth differentiation | meteorite zircon

The  $^{176}\text{Lu}$ – $^{176}\text{Hf}$  radioactive decay system is a powerful tool to study planetary silicate differentiation and offers a unique means of examining the origin of the Earth's earliest crust (1–12). To allow for the correct interpretation of Lu–Hf data, however, the Hf isotope growth curve of the bulk Earth must be firmly established. On the basis of the refractory lithophile nature of both Lu and Hf, the Lu–Hf isotope composition of chondrites has been proposed as a reference for the composition of the bulk Earth and its silicate portion (13–15). However, the present-day  $^{176}\text{Hf}/^{177}\text{Hf}$  and  $^{176}\text{Lu}/^{177}\text{Hf}$  in chondrites, even in unequilibrated chondrites, are too variable to allow unambiguous definition of the so-called chondritic uniform reservoir (CHUR) (16). Hence, the validity of the Lu–Hf parameters proposed for the CHUR and, by implication, the bulk Earth (13–15) is as yet uncertain.

The initial  $^{176}\text{Hf}$  abundance of the Solar System is the key to understanding Lu–Hf systems of the CHUR and Earth, but this abundance remains poorly constrained. Backward calculations based on the present-day  $^{176}\text{Hf}/^{177}\text{Hf}$  and  $^{176}\text{Lu}/^{177}\text{Hf}$  for the CHUR (13–15), applying the  $^{176}\text{Lu}$  decay constant ( $\lambda^{176}\text{Lu}$ ) of  $1.867 \times 10^{-11} \text{ y}^{-1}$  (17–19), indicate that the  $^{176}\text{Hf}/^{177}\text{Hf}$  value at the formation of the Solar System [ $4,567.30 \pm 0.16$  million years (My) ago (20, 21)] would be between 0.279794 and 0.279820 (Fig. 1). However, the Lu–Hf internal isochron for the angrite SAH99555 (22) and whole-rock isochron for combined eucrites and chondrites (23) yield significantly lower initial  $^{176}\text{Hf}/^{177}\text{Hf}$  values (Fig. 1). Moreover, when the  $\lambda^{176}\text{Lu}$  of refs. 17–19 are used, the Lu–Hf

internal and whole-rock isochrons give apparent dates significantly older than the age of the Solar System (20, 21), while terrestrial rocks and meteorite phosphates give Lu–Hf internal isochron dates that agree with their U–Pb ages up to 4,557 My (17–19). An explanation proposed for the apparent older dates and lower initial  $^{176}\text{Hf}/^{177}\text{Hf}$  values obtained from the meteorite isochrons is that the  $^{176}\text{Lu}$  decay was accelerated through excitation of the long-lived  $^{176}\text{Lu}$  ground state to its short-lived isomer caused by gamma or cosmic ray irradiation of the surface of planetesimals, which leads to  $^{176}\text{Hf}$  excesses in the meteorites (24, 25). The implication of this proposal is that the assumption of a chondritic Earth cannot be made for the Lu–Hf system, because the planetesimals that accreted to form the Earth are thought to have been composed predominantly of nonirradiated materials (22). This interpretation is, however, inconsistent with the results of Lu isotope studies (26, 27): Although the accelerated  $^{176}\text{Lu}$  decay to account for the apparent older dates would cause a  $\sim 3$  permil decrease in  $^{176}\text{Lu}/^{175}\text{Lu}$  for the irradiated meteorites, all basaltic achondrites analyzed to date, including SAH99555, have identical  $^{176}\text{Lu}/^{175}\text{Lu}$  to those of terrestrial nonirradiated basalts within analytical uncertainties of 0.1–1.0 permil. Alternatively, the excess slopes of the meteorite isochrons, accompanied by a decrease in the initial  $^{176}\text{Hf}/^{177}\text{Hf}$ , may be attributed to secondary Lu–Hf disturbances in some of the meteorites (15, 16). To determine which chondrites are pristine and therefore representative of the CHUR and/or the bulk Earth, the Solar System initial  $^{176}\text{Hf}/^{177}\text{Hf}$  must be defined using a more robust approach.

Here we use meteorite zircon to determine the Solar System initial  $^{176}\text{Hf}/^{177}\text{Hf}$  value and, in turn, to better define the Hf isotope evolution of the CHUR and Earth. Zircon typically

## Significance

The radioactive decay of lutetium-176 to hafnium-176 has been used to study Earth's crust–mantle differentiation that is the primary agent of the chemical and thermal evolution of the silicate Earth. Yet the data interpretation requires a well-defined hafnium isotope growth curve of the bulk Earth, which is notoriously difficult to reconstruct from the variable bulk compositions of undifferentiated chondrite meteorites. Here we use lutetium–hafnium systematics of meteorite zircon crystals to define the initial hafnium isotope composition of the Solar System and further to identify pristine chondrites that are the best representative of the lutetium–hafnium system of the bulk Earth. The established bulk Earth growth curve provides evidence for Earth's crust–mantle differentiation as early as 4.5 billion years ago.

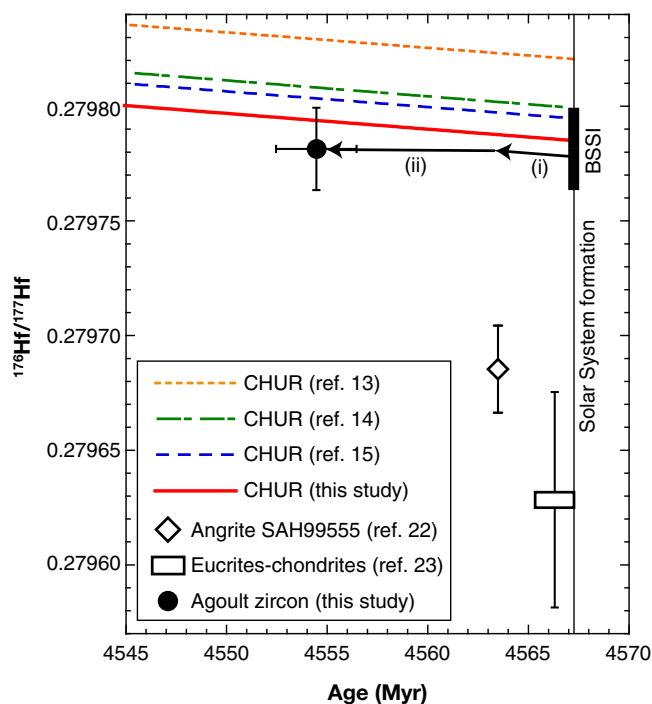
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**Fig. 1.** Initial Hf isotope ratios in meteoritic samples as a function of age. Shown are the initial  $^{176}\text{Hf}/^{177}\text{Hf}$  of Agoult zircon and those obtained from an internal isochron for the angrite SAH99555 (22) and from whole-rock isochron for combined euclrites and chondrites (23). The  $^{207}\text{Pb}/^{206}\text{Pb}$  age was used for the Agoult zircon (28) and SAH99555 [ $4,563.53 \pm 0.26$  My (48)] recalculated using  $^{238}\text{U}/^{235}\text{U}$  of ref. 49]. For the combination of euclrites and chondrites, the range from the Solar System formation age (20, 21) to the Mn–Cr whole-rock isochron age of the combined euclrites and diogenites [ $4,565.4 \pm 0.7$  My (30)] is shown. The proposed Hf isotope growth curves for the CHUR (refs. 13–15 and this study) are also presented. The arrowed lines represent a two-stage Hf isotope evolution model before the zircon crystallization, whereas the thick vertical line shows the BSSI  $^{176}\text{Hf}/^{177}\text{Hf}$  (see *Determining the Initial  $^{176}\text{Hf}$  Abundance of the Solar System*). The starting point of the second stage is taken from the Mn–Cr age of the basaltic eucrite Juvinas [ $4,563.0 \pm 0.9$  My (30)]. All Mn–Cr ages are referenced to the angrite D’Orbigny (50) using the  $^{207}\text{Pb}/^{206}\text{Pb}$  age of ref. 49.

contains  $\sim 1$  wt% Hf, and its Lu/Hf is sufficiently low as to make in situ radiogenic growth of  $^{176}\text{Hf}$  insignificant. The crystallization age of zircon can be precisely determined by U–Pb dating. Furthermore, zircon is extremely resistant to secondary Lu–Hf disturbance and, even if such disturbance had taken place, it can be monitored by U–Pb systematics (e.g., refs. 2 and 10). Thus, meteorite zircon would provide the most direct and robust Hf isotope record of the early Solar System (1). Despite this promise, the rarity and typically very small size ( $< 20$   $\mu\text{m}$ ) of meteorite zircon have hampered its use in Lu–Hf studies. Recently, we found exceptionally coarse zircon grains ( $\sim 80$   $\mu\text{m}$ ) in the basaltic eucrite Agoult (28) (Fig. 2). These grains, in concert with high-sensitivity multiple collector inductively coupled plasma mass spectrometry, enabled us to perform, to our knowledge, the first high-precision Lu–Hf isotope analysis of meteorite zircon.

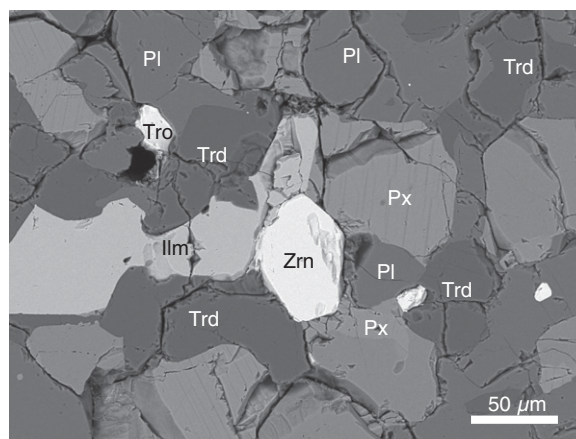
### Determining the Initial $^{176}\text{Hf}$ Abundance of the Solar System

Basaltic euclrites represent crust that crystallized near the surface of a planetesimal and subsequently underwent metamorphic and impact events. Agoult is a highly metamorphosed basaltic eucrite, composed primarily of pyroxene and plagioclase with minor amounts of ilmenite, tridymite, troilite, spinel, Ca-phosphate, zircon, and baddeleyite (28, 29). Zircon ( $\text{ZrSiO}_4$ ) is typically associated with ilmenite and tridymite ( $\text{SiO}_2$ ) (Fig. 2), whereas

ilmenite often contains exsolved needles of baddeleyite ( $\text{ZrO}_2$ ). The application of the Ti-in-zircon thermometer showed that the zircon grains crystallized at subsolidus temperatures of  $\sim 900$   $^\circ\text{C}$  (28). These observations indicate that the Agoult zircon formed by baddeleyite exsolution from ilmenite followed by reaction with the surrounding silica during high-temperature metamorphism. The zircon crystallization age was determined by the U–Pb method to be  $4,554.5 \pm 2.0$  My (28), later by  $\sim 10$  My than the igneous crystallization age of the basaltic euclrites (30).

We analyzed the Lu–Hf isotope compositions of eight Agoult zircon grains having concordant U–Pb systems. All analyses yielded consistent present-day  $^{176}\text{Hf}/^{177}\text{Hf}$  with a mean of  $0.279796 \pm 0.000016$  (2 SD) (Table 1 and Table S1), which is the lowest value among all known Solar System rocks and minerals. The extremely low present-day  $^{176}\text{Hf}/^{177}\text{Hf}$  value of the Agoult zircon is a result of its antiquity and low  $^{176}\text{Lu}/^{177}\text{Hf}$  (0.00015–0.00021), verifying that meteorite zircon is ideal for exploring the primitive Hf isotope composition of the Solar System. Notably, the  $^{176}\text{Lu}/^{177}\text{Hf}$  values are even lower than those for typical terrestrial and lunar igneous zircons ( $> 0.0005$ ) (e.g., refs. 31 and 32). These remarkably low ratios can be interpreted to reflect the metamorphic origin of the zircon through Zr release from ilmenite grains having low Lu/Hf ( $^{176}\text{Lu}/^{177}\text{Hf}$  of  $< 0.003$ ) (28). We also found that the Agoult zircon has  $^{180}\text{Hf}/^{177}\text{Hf}$  and  $^{178}\text{Hf}/^{177}\text{Hf}$  indistinguishable from the terrestrial values (Table S1), providing evidence against secondary neutron capture that could increase the measured  $^{176}\text{Hf}/^{177}\text{Hf}$  (33).

On the basis of the present-day  $^{176}\text{Hf}/^{177}\text{Hf}$  and  $^{176}\text{Lu}/^{177}\text{Hf}$ , and using the crystallization age of  $4554.5 \pm 2.0$  My (28) and the  $\lambda^{176}\text{Lu}$  of ref. 18, we derive an initial  $^{176}\text{Hf}/^{177}\text{Hf}$  value of  $0.279781 \pm 0.000018$  (2 SD) for the Agoult zircon (Fig. 1 and Table 1). The value is significantly higher than the initial  $^{176}\text{Hf}/^{177}\text{Hf}$  of  $0.27966 \pm 0.00002$  inferred from the euclrite whole-rock “errorchron” (i.e., the regression line with the scatter of the data more than expected from analytical uncertainties) (34). Note that the zircon initial  $^{176}\text{Hf}/^{177}\text{Hf}$  estimate is insensitive to the choice of a  $\lambda^{176}\text{Lu}$  value due to the low  $^{176}\text{Lu}/^{177}\text{Hf}$ . Thus, the zircon initial  $^{176}\text{Hf}/^{177}\text{Hf}$  value serves as a firm upper limit on the Solar System initial  $^{176}\text{Hf}/^{177}\text{Hf}$ . Moreover, the time interval between the zircon crystallization and the Solar System formation is short ( $\sim 13$  My), so the effect of radiogenic  $^{176}\text{Hf}$  growth over this period would be negligible, unless the  $^{176}\text{Lu}$  decay had been significantly accelerated. Considering that Agoult ilmenite grains serve as the source of Hf and Zr during zircon formation, the Hf isotope evolution before the zircon



**Fig. 2.** Back-scattered electron image showing a zircon grain AG6-Zrn#01 in the eucrite Agoult. Mineral abbreviations are as follows: Ilm, ilmenite; Pl, plagioclase; Px, pyroxene; Trd, tridymite; Tro, troilite; Zrn, zircon. Reprinted from ref. 28, with permission from Elsevier; [www.sciencedirect.com/science/journal/0012821X](http://www.sciencedirect.com/science/journal/0012821X).

**Table 1. Summary of Lu–Hf isotope data for Agoutl zircon**

Grain	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Lu}/^{177}\text{Hf}$ 2 $\sigma$ error	$^{176}\text{Hf}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$ 2 $\sigma$ error	Initial $^{176}\text{Hf}/^{177}\text{Hf}$	Initial $^{176}\text{Hf}/^{177}\text{Hf}$ 2 $\sigma$ error
AG2-Zrn#02	0.000212	0.000058	0.279794	0.000031	0.279775	0.000031
AG2-Zrn#07	0.000153	0.000042	0.279797	0.000013	0.279783	0.000013
AG3-Zrn#07	0.000150	0.000044	0.279812	0.000025	0.279798	0.000025
AG3-Zrn#08	0.000177	0.000048	0.279786	0.000019	0.279770	0.000019
AG3-Zrn#09	0.000177	0.000048	0.279792	0.000015	0.279777	0.000015
AG4-Zrn#10	0.000156	0.000042	0.279792	0.000025	0.279779	0.000025
AG5-Zrn#03	0.000166	0.000046	0.279801	0.000010	0.279786	0.000010
AG6-Zrn#01	0.000167	0.000046	0.279790	0.000009	0.279775	0.000009
Mean (2 SD)	0.000170	0.000040	0.279796	0.000016	0.279781	0.000016

Initial  $^{176}\text{Hf}/^{177}\text{Hf}$  were calculated using the  $\lambda^{176}\text{Lu}$  of ref. 18 and the zircon  $^{207}\text{Pb}/^{206}\text{Pb}$  age of  $4,554.5 \pm 2.0$  My (28). Errors combine the 2 SE internal errors and the 2 SD external reproducibilities of standard analyses.

crystallization can be described by a two-stage model (indicated by the arrowed lines in Fig. 1): (i) Hf initially evolved in the basaltic eucrite precursor, with a chondritic  $^{176}\text{Lu}/^{177}\text{Hf}$  of  $\sim 0.034$  (13–15) between the formations of the Solar System and the basaltic crust, and (ii) subsequently, it developed in Agoutl ilmenite with a  $^{176}\text{Lu}/^{177}\text{Hf}$  of  $\sim 0.003$  (28) until the time of metamorphic zircon crystallization. Assuming a constant decay rate for  $^{176}\text{Lu}$  (18), the net  $^{176}\text{Hf}/^{177}\text{Hf}$  increase would be  $0.000003$ —6 times smaller than the uncertainty associated with the zircon initial value. Even if the zircon precursor had maintained a chondritic  $^{176}\text{Lu}/^{177}\text{Hf}$  over the entire  $\sim 13$ -My period, the radiogenic  $^{176}\text{Hf}/^{177}\text{Hf}$  increase would still equal only one half of the analytical uncertainty. In addition, our whole-rock Lu isotope analyses show that Agoutl and terrestrial (never irradiated) basalts have identical  $^{176}\text{Lu}/^{175}\text{Lu}$  within analytical uncertainties of  $\leq 0.2$  permil (Table 2 and Table S2). As Agoutl should inherit the Lu isotope composition from its precursor, the Lu isotope data indicate that neither Agoutl nor its precursor was exposed to accelerated  $^{176}\text{Lu}$  decay. Overall, we conclude that the zircon initial  $^{176}\text{Hf}/^{177}\text{Hf}$  of  $0.279781 \pm 0.000018$  (2 SD) represents the best Solar System initial (BSSI) value.

### Lu–Hf Isotope Evolution of Chondrites

The BSSI is distinctly higher than the initial  $^{176}\text{Hf}/^{177}\text{Hf}$  defined by the meteorite internal and whole-rock isochrons, which yield apparent old dates (22, 23) (Fig. 1). At the same time, the BSSI overlaps, within the uncertainty, with the initial value calculated from the most precise Lu–Hf CHUR parameters, which are based on analyses of unequilibrated chondrites (ref. 15:  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282785 \pm 0.000011$ ;  $^{176}\text{Lu}/^{177}\text{Hf} = 0.0336 \pm 0.0001$ ). This general agreement eliminates accelerated  $^{176}\text{Lu}$  decay as a primary cause of the apparent older whole-rock isochron date of combined eucrites and chondrites. When examining the data in detail, however, it is evident that some of the unequilibrated chondrites, in particular ordinary chondrites, exhibit initial  $^{176}\text{Hf}/^{177}\text{Hf}$  higher than the BSSI (Fig. 3 and Table S3). There are three possible explanations for the higher chondrite initial  $^{176}\text{Hf}/^{177}\text{Hf}$  values. First, the higher values may reflect nucleosynthetic Hf isotope heterogeneity in the solar nebula when the chondrites formed. Second,

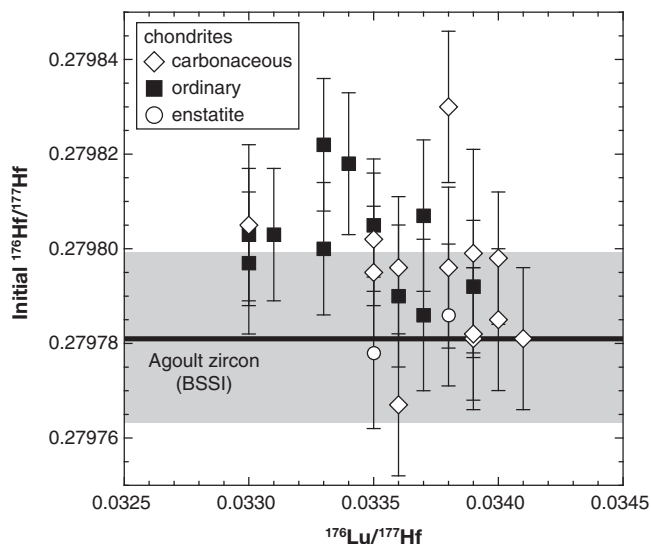
**Table 2. Summary of Lu isotope data for Agoutl and terrestrial basalts**

Sample	N*	$\delta^{176}\text{Lu}$	2 SD
Agoutl	5	0.19	0.20
JB-1b	3	0.22	0.09
JB-2	3	0.14	0.16
NIST 3130a	10	0.19	0.11

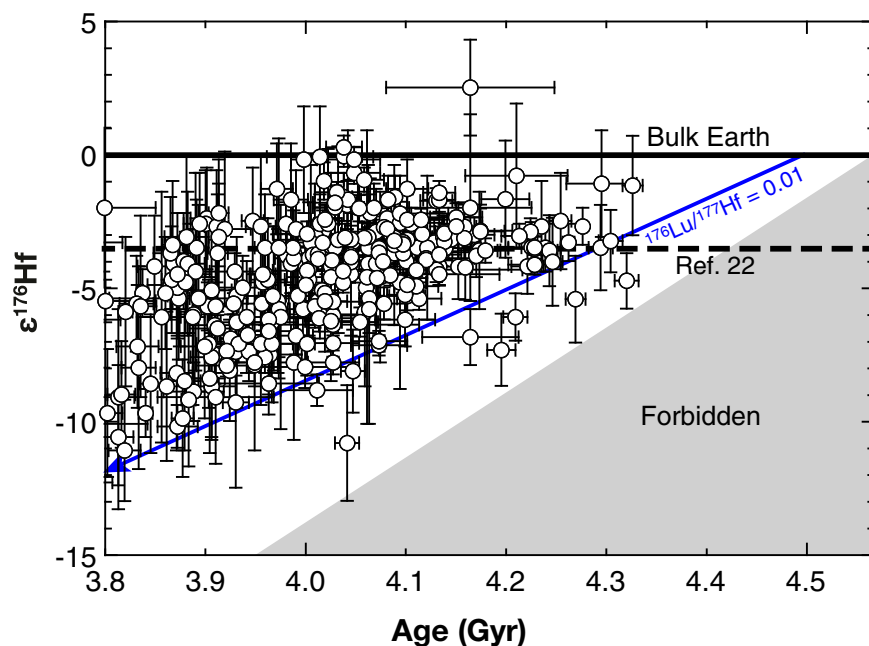
The  $^{176}\text{Lu}/^{175}\text{Lu}$  are expressed in parts per thousand deviations from the SPEX Lu standard solution.

\*Number of analyses.

the  $^{176}\text{Hf}$  excesses may be attributed to irradiation processes that lead to either moderate acceleration of  $^{176}\text{Lu}$  decay (24, 25) or secondary neutron capture (33). However, all chondrites analyzed for nonradiogenic stable Hf isotopes show no evidence for nucleosynthetic heterogeneity or secondary neutron capture (33). Moreover, the chondrites having higher initial  $^{176}\text{Hf}/^{177}\text{Hf}$  tend to have substantially lower  $^{176}\text{Lu}/^{177}\text{Hf}$  (Fig. 3), even though the accelerated  $^{176}\text{Lu}$  decay and secondary neutron capture to account for the  $^{176}\text{Hf}$  excesses would cause little change in the  $^{176}\text{Lu}/^{177}\text{Hf}$  (33). The observed trend is instead well explained by secondary Lu/Hf fractionation in these chondrites, which resulted in decreases in the  $^{176}\text{Lu}/^{177}\text{Hf}$  and apparent increases in the initial  $^{176}\text{Hf}/^{177}\text{Hf}$  (Fig. S1). This third scenario is further supported by the fact that the unequilibrated ordinary chondrites Sharps and Mezö-Madaras yield not only higher initial  $^{176}\text{Hf}/^{177}\text{Hf}$  values but also substantially younger Pb–Pb ages (35). The unequilibrated chondrites yielding initial values equal to the BSSI exhibit a narrow range of present-day  $^{176}\text{Hf}/^{177}\text{Hf}$  and  $^{176}\text{Lu}/^{177}\text{Hf}$ , that is,  $0.282793 \pm 0.000011$  and  $0.0338 \pm 0.0001$  (2 SE,  $n = 14$  after rejection of one outlier). We consider that these values represent the chondrites with the most well-preserved Lu–Hf systems and, therefore, are best suited to serve as CHUR references (Fig. 1).



**Fig. 3.** Comparison of the initial Hf isotope composition of Agoutl zircon with those of unequilibrated chondrites. The solid line and gray shaded area show the mean and 2 SD of the zircon initial  $^{176}\text{Hf}/^{177}\text{Hf}$ , which are interpreted as representing the BSSI. The chondrite data are plotted against the  $^{176}\text{Lu}/^{177}\text{Hf}$ , which were determined by isotope dilution (14, 15) (Table S3).



**Fig. 4.** Hf isotope evolution diagrams for terrestrial zircons from the Jack Hills, Western Australia. Data taken from refs. 6–8, in which the Hf and Pb isotope ratios were measured concurrently. The  $^{176}\text{Hf}/^{177}\text{Hf}$  are expressed in parts per 10,000 deviations from the Hf isotope growth curve of the bulk Earth based on our newly established CHUR parameters. For comparison, the bulk Earth growth curve proposed by ref. 22 is also shown. The blue arrowed line represents the Hf isotope evolution of a 4.5-Gy-old enriched reservoir with  $^{176}\text{Lu}/^{177}\text{Hf} = 0.01$  equivalent to typical granites (51). The gray shaded area indicates  $^{176}\text{Hf}/^{177}\text{Hf}$  lower than the Solar System initial value.

### Lu–Hf Isotope Evolution and Early Differentiation of Earth

The Earth's most primitive Hf isotope compositions are recorded in detrital zircons with  $^{207}\text{Pb}/^{206}\text{Pb}$  ages as old as 4.3 Gy from the Jack Hills in Western Australia (3–8) (Fig. 4). The terrestrial zircon record has been interpreted to reflect that the protoliths to magmas from which the most ancient zircons crystallized were chemically enriched and were extracted from the undifferentiated primitive mantle more than 4.5 Gy ago. However, this interpretation strongly depends on the bulk Earth composition. For instance, if the Earth has a chondritic Lu/Hf but its  $^{176}\text{Hf}/^{177}\text{Hf}$  is 3.5  $\epsilon$  units (parts per 10,000) lower than the CHUR as proposed by ref. 22 on the basis of the possible accelerated  $^{176}\text{Lu}$  decay, the terrestrial zircon record instead requires that the magmatic protoliths have a history of both enrichment and depletion dating as far back as 4.3 Gy ago. In the present study, we have directly determined the initial  $^{176}\text{Hf}/^{177}\text{Hf}$  value of the Solar System using meteorite zircon, which in turn shows that the Lu–Hf systematics of chondrites are consistent with a constant  $^{176}\text{Lu}$  decay rate at  $1.867 \times 10^{-11} \text{ y}^{-1}$  (17–19) since the formation of the Solar System. This finding removes the requirement for a nonchondritic bulk Lu–Hf isotope composition of Earth as a result of accelerated  $^{176}\text{Lu}$  decay. Furthermore, our directly defined initial  $^{176}\text{Hf}/^{177}\text{Hf}$  of the Solar System and Earth provides strong evidence that the terrestrial zircon record reflects the development of an enriched silicate reservoir as early as 4.5 Gy ago (Fig. 4). This conclusion holds even if the Earth has a superchondritic Lu/Hf as well as Sm/Nd due to the preferential loss of more incompatible elements during Earth accretion (36–38).

### Materials and Methods

**Zircon Lu–Hf Isotopes.** Eight zircon grains were extracted from five thin sections of the eucrite Agoutt. All eight zircon grains displayed no zoning structure with back-scattered electron and cathodoluminescence imaging (28). The grains were cleaned with 2 N  $\text{HNO}_3$  and decomposed by concentrated HF +  $\text{HNO}_3$  at 220 °C. Subsequently, the decomposed samples were evaporated and dissolved in 6 N HCl at 180 °C, followed by further evaporation and redissolution in 2.5 N HCl. Then, each dissolved grain was divided into two aliquots for determinations of Hf isotope ratios (ca. 90%) and  $^{176}\text{Lu}/^{177}\text{Hf}$  (ca. 10%), respectively. The sample aliquots for Hf isotope ratio measurements were processed for chemical separation with a two-step ion exchange procedure (Table S4). The first separation step, designed for U–Pb dating, used 0.05 mL of Eichrom anion exchange resin AG1-X8 with 200–400 mesh, in which matrix elements including Hf were eluted in 2.5 N HCl followed by elution of Pb and U in 0.5 N  $\text{HNO}_3$ . Hafnium and Zr were

purified in the second step using 0.1 mL of Eichrom Ln-spec resin (100–150  $\mu\text{m}$ ), where Zr was eluted with 6 N HCl + 0.06 N HF followed by Hf elution in 2 N HF (39). The purified Hf fractions were evaporated and redissolved in 0.3–0.5 mL of 0.5 N  $\text{HNO}_3$  containing a trace amount of HF for isotope analysis. The sample aliquots for  $^{176}\text{Lu}/^{177}\text{Hf}$  determination were not processed for chemical separation to avoid any artificial Lu/Hf fractionation.

The Hf isotope analyses were performed on a Neptune Plus multicollector inductively coupled plasma mass spectrometer (Thermo Fisher Scientific) attached to an Aridus II desolvating nebulizer (Cetac Technologies) at The University of Tokyo. The instrumental sensitivity was enhanced by installing a high-efficiency vacuum interface rotary pump (TRIVAC D 65B, Oerlikon Leybold Vacuum) and by using high-transmission Jet sample and X-skimmer cones. The achieved sensitivity was 3,500–4,000 V/ppm for Hf at a sample uptake rate of  $\sim 150 \mu\text{L}/\text{min}$ . For isotope ratio measurements of purified Hf fractions, isotopes of  $^{174}\text{Hf}$ ,  $^{176}\text{Hf}$ ,  $^{177}\text{Hf}$ ,  $^{178}\text{Hf}$ ,  $^{179}\text{Hf}$ , and  $^{180}\text{Hf}$  as well as  $^{172}\text{Yb}$ ,  $^{175}\text{Lu}$ , and  $^{182}\text{W}$  were monitored with static mode on nine Faraday cups. We found that the interferences of Yb, Lu, and W on Hf isotopes are negligible due to efficient separation of Hf in the ion exchange chemistry. Data were acquired using an integration time of 1.0 s for periods of 75–150 s. The total Hf signal intensities obtained during the sample analyses range from 4 V to 21 V. The ion beams of five procedural blanks were measured using the same procedure as the samples, and the Hf signal intensities of 3–7 mV with an average of 4 mV were obtained, indicating that the procedural Hf blanks were less than 1 pg. The blank contribution was corrected by subtracting the average signal intensity of the five blank measurements, even though this blank correction would cause only a  $\sim 10$  ppm change in the resulting mean  $^{176}\text{Hf}/^{177}\text{Hf}$  value. The mass bias factor was calculated by normalizing the measured  $^{179}\text{Hf}/^{177}\text{Hf}$  to 0.7325 (1) with an exponential law. Hafnium isotope ratios corrected for mass bias were further normalized to reference values of  $^{180}\text{Hf}/^{177}\text{Hf} = 1.886666$ ,  $^{178}\text{Hf}/^{177}\text{Hf} = 1.467168$ , and  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282160$  for Johnson Matthey Company (JMC)-Hf 475 (40) to allow accurate comparison with literature values. Analytical uncertainties on sample Hf isotope ratios (Table S1) combined the internal precisions (2 SE) and the reproducibility of the JMC-Hf 475 standard analyses (2 SD), added in quadrature. The internal precisions are variable, depending on the Hf amounts available for analyses.

The  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios in the sample aliquots without chemical separation were calculated from measured  $^{175}\text{Lu}/^{177}\text{Hf}$  ratios and the  $^{176}\text{Lu}/^{175}\text{Lu}$  value of 0.026549 (41). The  $^{175}\text{Lu}/^{177}\text{Hf}$  measurements were carried out on the Neptune Plus under wet plasma conditions using a Scott-type spray chamber. Data were acquired with dynamic mode on the secondary electron multiplier over 10 cycles using the integration time of 8.4 s for  $^{175}\text{Lu}$  and 4.2 s for  $^{177}\text{Hf}$ . The instrumental  $^{175}\text{Lu}/^{177}\text{Hf}$  fractionation was corrected by reference to multiple measurements of Lu–Hf solution (0.5 N  $\text{HNO}_3$  with a trace amount of HF) prepared by mixing ultrapure Hf and Lu from 1,000-ppm standard solutions from SPEX. Analytical uncertainties on  $^{175}\text{Lu}/^{177}\text{Hf}$

combine the internal precisions of the sample analyses (2 SE) and the reproducibility of the Lu–Hf solution (2 SD).

The precision and accuracy of our Lu–Hf isotope analyses were evaluated by analyzing the TEMORA standard zircon as an unknown sample during the course of this study. We obtained mean  $^{176}\text{Lu}/^{177}\text{Hf}$  and initial  $^{176}\text{Hf}/^{177}\text{Hf}$  values of  $0.0011 \pm 0.0004$  and  $0.282668 \pm 0.000016$  (2 SD,  $n = 6$ ) (Table S1), in agreement with the previously reported values (42, 43).

**Whole-Rock Lu Isotopes.** Five whole-rock fractions of the eucrite Agoult and three fractions of two individual terrestrial basalts (JB-1b and JB-2) were analyzed for  $^{176}\text{Lu}/^{175}\text{Lu}$ . The fractions were digested in a mixture of concentrated HF + HNO<sub>3</sub> on a hot plate at 130 °C and converted to a soluble form by repeated evaporation with concentrated HNO<sub>3</sub>, followed by dissolution in 6 N HCl. For accurate and precise Lu isotope ratio measurements, efficient separation of Lu from Yb and Hf is required. The separation of Lu was performed using three types of resins following the procedures of ref. 44 (Table S5): (i) removal of Fe and U from bulk sample using Bio-Rad AG1-X8 with 200–400 mesh; (ii) separation of heavy rare earth elements (REE) from most other elements including Hf using Eichrom Ln-spec resin with particle sizes of 100–150 μm; and (iii) separation of Lu from Yb as well as Hf using Eichrom Ln-spec resin with particle sizes of 20–50 μm in 120-mm-long column. The last step was repeated for further purification of Lu from Yb. These separation protocols reduce the Yb/Lu ratio by  $\sim 10^5$  for basaltic samples, with total Lu yields higher than 90%.

The Lu isotope ratio measurements were made on the Neptune Plus multicollector inductively coupled plasma mass spectrometer attached to the Aridus II desolvating nebulizer at The University of Tokyo. We used a standard “H” sample cone instead of the high-transmission Jet sample cone for Lu isotope analyses, because use of the Jet sample cone could cause mass discrimination that significantly diverges from the exponential law for heavy

REE (45). Data were acquired using an integration time of 8.4 s over 60 cycles. Nine Faraday cups were used to simultaneously monitor  $^{172}\text{Yb}$ ,  $^{173}\text{Yb}$ ,  $^{175}\text{Lu}$ ,  $^{176}(\text{Lu} + \text{Yb} + \text{Hf})$ ,  $^{177}\text{Hf}$ ,  $^{179}\text{Hf}$ ,  $^{182}\text{W}$ ,  $^{184}\text{W}$ , and  $^{186}\text{W}$ . Following ref. 44, all Lu standards and samples were doped with National Institute of Standards and Technology (NIST) SRM 3163 W standard to correct for mass bias. The mass bias factor was calculated in each analysis by normalizing  $^{186}\text{W}/^{184}\text{W}$  to 0.92767 (46) with an exponential law. To account for the difference in mass bias factors for Lu and W,  $^{176}\text{Lu}/^{175}\text{Lu}$  ratios corrected for mass bias were further normalized to the  $^{176}\text{Lu}/^{175}\text{Lu}$  value of 0.026549 (41) for the SPEX Lu standard solution using the mean value obtained for this standard on any given analytical session. The contribution of isobaric interferences by  $^{176}\text{Yb}$  and  $^{176}\text{Hf}$  on  $^{176}\text{Lu}$  was evaluated by monitoring  $^{173}\text{Yb}$  and  $^{177}\text{Hf}$ , respectively. While the contribution of  $^{176}\text{Hf}$  was negligible,  $^{176}\text{Yb}$  interference correction was necessary for all samples. For the correction, the mass bias factor for Yb was assumed to be identical to that for W, and the literature  $^{176}\text{Yb}/^{173}\text{Yb}$  value of 0.79640 (47) was used. The interference correction produces accurate results for Yb-doped Lu standard solutions with  $^{173}\text{Yb}/^{175}\text{Lu}$  up to  $1.5 \times 10^{-4}$ , indicating that the correction method is robust for the sample analyses which yielded  $^{173}\text{Yb}/^{175}\text{Lu}$  of  $\leq 3.4 \times 10^{-5}$  (Fig. S2). Analytical uncertainties of each  $^{176}\text{Lu}/^{175}\text{Lu}$  analysis (Table S2) combine the internal precisions (2 SE) and the reproducibility of the SPEX Lu standard solution analyses (2 SD), added in quadrature. To allow accurate comparison with literature values (44), we also reported the  $^{176}\text{Lu}/^{175}\text{Lu}$  obtained for a NIST SRM 3130a Lu standard solution during the course of this study (Table 2 and Table S2).

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