Extinct 244Pu in Ancient Zircons
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9. In the Kondo ground state, the localized spin is screened by the conduction electrons, suppressing magnetic interactions. In the magnetic ground state, spin degeneracy is broken, which suppresses spin fluctuations and Kondo correlations (*26*).
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21. Coulomb blockade conductance peaks are not generally symmetric in V nor do they have similar heights for positive and negative bias, because the capacitances and resistances to the two electrodes are different in general (*27*).
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23. In addition to the Kondo signals, tunneling through the independent electron resonances should be expected to produce peaks in $G(V)$ centered at the Coulomb blockade energy thresholds, with widths on the order of Γ. However, we do not usually resolve these Coulomb blockade peaks in the Kondo samples. Estimates of Γ as large as many tens of milli–electron volts suggest that they would be difficult to observe. Nevertheless, we do expect that electron tunneling through these broad single-electron resonances contributes to the asymmetric conductance background underlying the Kondo signals.
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Extinct ^{244}Pu in Ancient Zircons

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We have found evidence, in the form of fissiogenic xenon isotopes, for in situ decay of ^{244}Pu in individual 4.1- to 4.2-billion-year-old zircons from the Jack Hills region of Western Australia. Because of its short half-life, 82 million years, ^{244}Pu was extinct within 600 million years of Earth's formation. Detrital zircons are the only known relics to have survived from this period, and a study of their Pu geochemistry will allow us to date ancient metamorphic events and determine the terrestrial Pu/U ratio for comparison with the solar ratio.

The isotope ^{244}Pu is one of the longest lived of the so-called extinct isotopes that were present in the early solar system and that recorded nucleosynthetic processes immediately preceding its formation. This nuclide is produced solely in the r process, and its half-life is sufficiently long that it is expected to have been well-mixed locally within the galaxy in the sense that, on an 82-million-year (My) time scale, distances over which ^{244}Pu is dispersed are greater than the mean distance between supernovae in star-forming regions (*1*). On this basis, the equilibrium ratio of ^{244}Pu/^{238}U is expected to be equal to the ratio of the respective half-lives, i.e., 82/4450 = 0.018, multiplied by a number of order unity (related to the production rate of heavy precursors). A well-constrained initial value, combined with other key isotope abundance ratios (^{107}Pd, ^{129}I, ^{182}Hf, ^{235}U, ^{238}U, and ^{232}Th) would provide raw data with which to improve our understanding of the details of the r process and the timing of local nucleosynthetic events before the formation of the solar system (*1*–*5*).

Also, ^{244}Pu has a key role in understanding Earth evolution. Models of volatile transport within and from the mantle and of the origin and evolution of the atmosphere are influenced by inferences made from noble gas studies (*6*–*11*). A key parameter in these models is the Pu/U ratio, which determines the relative ingrowth of ^{136}Xe (from ^{244}Pu and ^{238}U fission) and ^{4}He (from U and Th decay) and hence quantifies the link between the Xe flux from the deep mantle source and that of He. Several attempts have been made to determine the overall ^{244}Pu/^{238}U ratio for the solar system (*12*, *13*) and to use ^{244}Pu as an early solar system chronometer (*14*–*16*); however, the solar value of ^{244}Pu/^{238}U is still uncertain within a factor of two, probably lying between 0.004 and 0.008. The discovery of terrestrial zircons with formation intervals between 4.0×10^9 and 4.4×10^9 years ago (Ga) offers an alternative way to resolve the issue. ^{238}U decay is the dominant source of fissiogenic xenon produced after 3.8 Ga, whereas ^{244}Pu decay dominates before 4.4 Ga. Between 4.0 and 4.4 Ga, contributions from ^{244}Pu and ^{238}U are expected to be comparable, and Pu/U can in principle be obtained directly from xenon analyses on samples with closure ages in this time interval. The ^{131}Xe/^{136}Xe ratio is particularly sensitive, varying between 0.085 for the spontaneous fission of ^{238}U and 0.246 for ^{244}Pu fission. A previous attempt to apply this method to large numbers of coeval zircons from

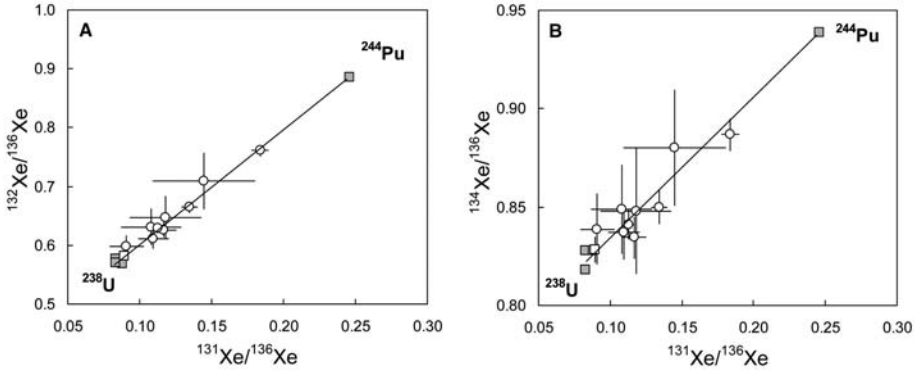

Fig. 1. After corrections for atmospheric Xe (fig. S4), the correlations of (**A**) ^{132}Xe/^{136}Xe with ^{131}Xe/^{136}Xe and of (**B**) ^{134}Xe/^{136}Xe with ^{131}Xe/^{136}Xe indicate that the remaining Xe is a two-component mixture produced by the spontaneous fission of ^{238}U and ^{244}Pu (solid squares). The highest ^{131}Xe/^{136}Xe ratio corresponds to a ^{244}Pu/^{238}U ratio of 0.0066 ± 0.0010 (calculated at 4560 Ma). Open circles are Jack Hills detrital zircons; open square is a 3.6-Gy-old zircon.

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3.8-Gy-old igneous rocks from West Greenland was essentially frustrated by the overwhelming contribution from ^{238}U fission (*17*).

Detrital zircons from Early Archean metasediments in the Jack Hills region of Western Australia have U-Pb ages as old as 4.4 Gy (*18–21*). These minute grains, typically 50 to 200 μm in size and weighing only a few micrograms, are the only known relics of Earth's earliest crust. Because the ancient zircons are detrital and of unknown provenance, it is essential that measurements of xenon isotopes are carried out on individual zircons. The amount of xenon present in a single zircon is very small, around 10^{-15} cm^3 at standard temperature and pressure for a 2-μg zircon initially containing 200 parts per million (ppm) uranium. This is comparable to blank levels and sensitivities of conventional noble gas mass spectrometers. We have developed a sensitive mass spectrometer based on laser resonance ionization (*22*). The instrument, RELAX (refrigerator-enhanced laser analyzer for xenon), can analyze samples of only a few thousand atoms, some two orders of magnitude smaller than conventional noble gas mass spectrometers. We analyzed xenon, released by laser-stepped heating, from eight zircon grains from Jack Hills with ages between 4.12 and 4.22 Gy and one of circa (ca.) 3.6 Gy (*23*). Unambiguous evidence for the presence of fissiogenic xenon was obtained for all extractions (figs. S1 to S4). On the basis of the amount of ^{130}Xe in the spectra, the contribution from atmospheric ^{136}Xe was typically a few hundred atoms and largely or wholly instrumental blank. The contribution of atmospheric ^{136}Xe in those analyses releasing the most gas was less than 1 part in 300 (fig. S4). The actual fission compositions were calculated by subtracting these minor amounts of atmospheric xenon on the basis of the amount of ^{130}Xe.

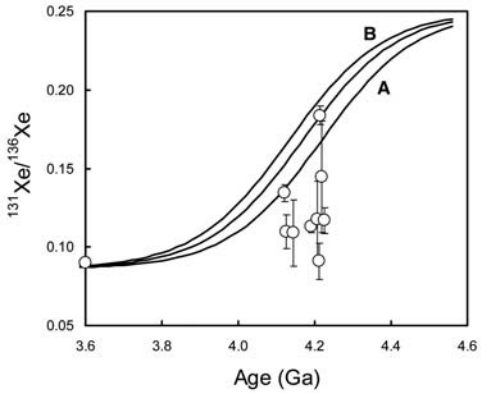

Fig. 2. A comparison of the measured $^{131}Xe/^{136}Xe$ ratios in zircons with the calculated dependence on closure age and Pu/U ratio for xenon produced by the spontaneous fission of ^{244}Pu and ^{238}U. Meteorite analyses suggest that the solar system's initial $^{244}Pu/^{238}U$ ratio at 4560 Ma is in the interval from 0.004 (curve A) to 0.008 (curve B). $^{131}Xe/^{136}Xe$ ratios for two zircons with concordant U-Pb ages lie within the predicted range. Data lying below the theoretical curves are from zircons with discordant U-Pb ages, probably as a result of xenon loss during early metamorphism.

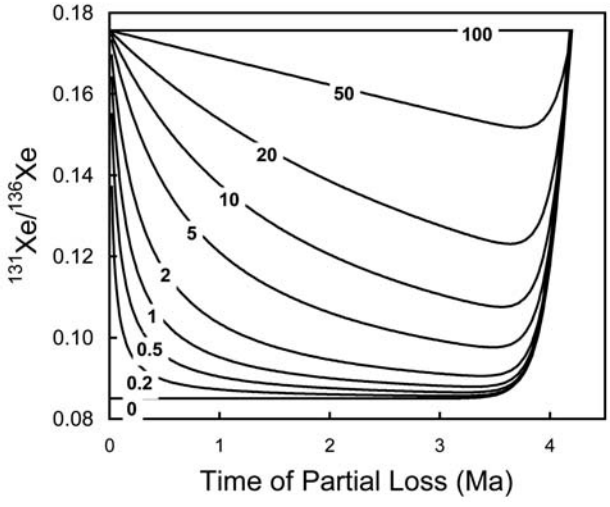

Fig. 3. Theoretical curves for the dependence of $^{131}Xe/^{136}Xe$ on time of partial Xe loss due to a postcrystallization event. The curves assume a crystallization age of 4200 Ma and initial $^{244}Pu/^{238}U$ = 0.006. The numbers on the curves indicate the percentage of xenon retained by the zircon after the loss event. The $^{131}Xe/^{136}Xe$ ratio is most sensitive to loss around 3600 Ma, when ^{244}Pu has fully decayed and maximum time is available for the subsequent buildup of xenon from ^{238}U fission.

The mass spectrum of the ca. 3600-My-old zircon was, as expected, that of ^{238}U fission and, within uncertainty, showed no contribution from fission of ^{244}Pu. The spectra of xenon released from the older zircons demonstrated the presence of varying proportions of ^{244}Pu fission (Fig. 1). The fissiogenic $^{131}Xe/^{136}Xe$, $^{132}Xe/^{136}Xe$, and $^{134}Xe/^{136}Xe$ ratios lie on mixing lines connecting ^{238}U and ^{244}Pu fission xenon. The highest $^{131}Xe/^{136}Xe$ ratio, 0.184 ± 0.006 at 4215 Ma, is obtained for a zircon (sample ANU07 8,2) with concordant $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}Pb$ ages and corresponds to an initial Pu/U ratio of 0.0066 ± 0.0010, intermediate between the extreme meteorite estimates. A second zircon (Cu10 6,1) with U/Pb ages differing by 40 My (i.e., 99% concordant) has an inferred Pu/U ratio of 0.0038 ± 0.006. The remaining zircons have more discordant U/Pb ages (97% to 24%) and $^{131}Xe/^{136}Xe$ ratios below the values anticipated from the meteorite Pu/U estimates (Fig. 2). The inferred Pu/U ratios are 0.002 or less (Table 1). This could be the result of preferential loss of the earlier-formed Pu xenon or the result of chemical fractionation of Pu and U during or before the formation of the zircons.

Correlation between the Pu/U ratios and Pb/U discordance (Table 1) is most readily explained by xenon loss. In recent stepped heating experiments on 3.8-Gy-old zircons from West Greenland, fission Xe was released at temperatures above 1400°C (*17*), probably reflecting the disproportionation of

Table 1. Xenon ratios for major gas releases. Isotope ratios are raw data uncorrected for air contribution. Concordance was defined as 100% minus the percent difference of $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ ages. Cu 10 6,1 and ANU07 8,2 are grains with Pu/U ≥ 0.004. Numbers in parentheses are errors in the most significant figures.

Zircon	Age concordance (Ma)		^{136}Xe (atoms)	$^{130}Xe/^{136}Xe$	$^{131}Xe/^{136}Xe$	$^{132}Xe/^{136}Xe$	$^{134}Xe/^{136}Xe$	Pu/U (range)
Cu10 5,9	3600		298,000	0.001 (1)	0.097 (2)	0.589 (5)	0.829 (6)	
Cu10 9,8	4191 (9)	97%	176,000	0.000 (1)	0.110 (2)	0.626 (6)	0.841 (7)	0.0009 – 0.0012
Cu3 6,8	4125 (9)	95%	62,000	0.000 (2)	0.109 (5)	0.611 (10)	0.837 (12)	0.0008 – 0.0025
Cu10 6,1	4122 (7)	99%	152,000	0.000 (1)	0.137 (3)	0.667 (7)	0.850 (8)	0.0033 – 0.0044
FC30 9.3	4140 (13)	97%	43,600	0.009 (4)	0.153 (9)	0.677 (17)	0.855 (19)	<0.0029
ANU07 8,2	4215 (4)	100%	257,000	0.009 (1)	0.226 (3)	0.804 (7)	0.892 (7)	0.0056 – 0.0077
			55,000	0.077 (5)	0.524 (15)	1.101 (22)	0.930 (18)	0.0007 – 0.0061
FC12 5,6	4218 (8)	24%	191,000	0.003 (1)	0.131 (4)	0.641 (8)	0.837 (9)	0.0007 – 0.0013
ANU09 14,5	4212 (16)	97%	144,000	0.000 (2)	0.091 (6)	0.599 (13)	0.839 (17)	<0.0005
			63,000	0.000 (3)	0.117 (13)	0.646 (24)	0.848 (29)	<0.0023

zircon into baddelyite and silica. Comparison of U-Xe and U-Pb ages (*24*) suggests that Xe is at least as strongly retained as Pb. Nevertheless, Pb loss associated with metamictization is commonly observed in zircons (*25*), and, given the antiquity and complex history of the ancient detrital zircons, it is likely that loss of Xe will also have occurred in a portion of our samples.

We have developed a two-stage model to show how the $^{131}Xe/^{136}Xe$ ratios are affected by Xe loss during diffusion or recrystallization events and provide an illustration for zircons with a crystallization age of 4.2 Gy and initial Pu/U = 0.006 (Fig. 3). Early events cause the loss of predominantly Pu-fission xenon, and the subsequent buildup is dominated by xenon from U. In consequence, the present-day $^{131}Xe/^{136}Xe$ ratio is lowered, reaching a minimum for loss occurring around 3.5 to 3.8 Ga. As the time of Xe loss approaches the present, the short time available for U fission ingrowth relative to the amount of Pu xenon results in measured $^{131}Xe/^{136}Xe$ ratios that approach the value they would have if no loss had occurred. The $^{131}Xe/^{136}Xe$ ratio is thus most sensitive to Xe loss during Archean events. This suggests that the low $^{131}Xe/^{136}Xe$ ratios in the discordant Jack Hills zircons may be the result of events before the formation of the Jack Hills metasediments. To be more definitive requires an additional relationship between the time of Xe loss and the degree of loss. Such a relationship can in principle be provided by the simultaneous determination of U-Xe ages.

We have detected Xe with an isotopic composition characteristic of the spontaneous fission of ^{244}Pu in individual 4.1- to 4.2-Gy-old detrital zircons. The initial Pu/U ratios, at 4.56 Ga, implied by our analyses range from essentially zero to 0.0066 between individual zircons. This is probably the result of Xe loss during subsequent metamorphic processes, e.g., those associated with formation of the host metasediments. Combining the present procedures with U-Xe dating methods has the potential to date these early metamorphic processes. The highest implied Pu/U ratio is within the range of estimates from meteorites, but, in order to quantify a global Pu/U ratio for the early Earth, future work will require an improved understanding of the geochemical behavior of Pu relative to U and the rare earth elements in zircon crystallization.

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Supporting Online Material

www.sciencemag.org/cgi/content/full/306/5693/89/DC1
Materials and Methods
Figs. S1 to S4

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Geochemical Evidence for Excess Iron in the Mantle Beneath Hawaii

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Chemical interaction of Earth's mantle with the liquid outer core should influence the mantle's iron content. Osmium isotope ratios in Hawaiian lavas indicate a mass flux of ≤1% core to the mantle, which is the immediate source of these lavas. We present precise measurements of the Fe/Mn ratio for Hawaiian lavas, revealing an increase of 1 to 2% in the mole fraction of iron in the mantle beneath Hawaii. This corresponds to a density anomaly of about 0.5%, about the same magnitude observed in seismic tomography models of the Pacific superswell region. These data also rule out a role for Mn-rich sediments as the source of the Hawaiian Os isotope signal.

On the basis of geophysical evidence, some mantle plumes are argued to arise from the core-mantle boundary (CMB). Chemical interaction between the core and the mantle at the CMB may involve physical entrainment of differentiated outer core (*1*), disequilibrium chemical reactions (*2*), equilibrium chemical reactions (*3*, *4*), isotopic exchange (*5*), or exsolution of a light element component during inner core growth (*4*, *6*), each of which may impart distinct isotopic and chemical signatures to the adjacent mantle. Assuming that the effects of chemical interaction are localized to mantle adjacent to the CMB, plumes arising from the CMB may entrain mantle that has experienced core-mantle interaction and advect such chemical signatures to the surface where they may be detected in the chemistry of erupted lavas. Osmium isotopic composition of Hawaiian picrites has provided the best indication for the entrainment of differentiated outer core material in the source of the Hawaiian plume, implying a mass flux ≤1% by weight (*1*). The absence of unradiogenic $^{182}W/^{184}W$ in the Hawaiian picrites, however, has been taken as evidence against core-mantle interaction (*7*). It has also been used to support the suggestion that the observed Re-Pt-Os isotope systematics (*1*) can be explained by the recycling of surficial Mn sediments (with high Pt/Os and Pt/Re ratios) into the source of the Hawaiian plume (*7*, *8*). Evidence of Mn enrichment was not found in Gorgona Island komatiites, which exhibited coupled ^{186}Os-^{187}Os isotope variations (*9*).

Iron, the dominant constituent of the core, is probably the most important element with a geochemical cycle that can be affected by exchange across the CMB. The Fe flux is of primary concern in geodynamic models, because it influences the density of the mantle (*10*–*12*). The constant molar 100 Mg/Mg+Fe (Mg#) is 89 ± 2 (1σ) of

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