LETTER

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Chondritic xenon in the Earth's mantle

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Noble gas isotopes are powerful tracers of the origins of planetary volatiles, and the accretion and evolution of the Earth. The compositions of magmatic gases provide insights into the evolution of the Earth's mantle and atmosphere[1–7]. Despite recent analytical progress in the study of planetary materials[8,9] and mantle-derived gases[2–7], the possible dual origin[1,10] of the planetary gases in the mantle and the atmosphere remains unconstrained. Evidence relating to the relationship between the volatiles within our planet and the potential cosmochemical end-members is scarce[5]. Here we show, using high-precision analysis of magmatic gas from the Eifel volcanic area (in Germany), that the light xenon isotopes identify a chondritic primordial component that differs from the precursor of atmospheric xenon. This is consistent with an asteroidal origin for the volatiles in the Earth's mantle, and indicates that the volatiles in the atmosphere and mantle originated from distinct cosmochemical sources. Furthermore, our data are consistent with the origin of Eifel magmatism being a deep mantle plume. The corresponding mantle source has been isolated from the convective mantle since about 4.45 billion years ago, in agreement with models that predict the early isolation of mantle domains[11]. Xenon isotope systematics support a clear distinction between mid-ocean-ridge and continental or oceanic plume sources[6], with chemical heterogeneities dating back to the Earth's accretion[1,7]. The deep reservoir now sampled by the Eifel gas had a lower volatile/refractory (iodine/plutonium) composition than the shallower mantle sampled by mid-ocean-ridge volcanism, highlighting the increasing contribution of volatile-rich material during the first tens of millions of years of terrestrial accretion.

Owing to their inertness, low abundances and the presence of several different radioactive chronometers in their isotope systematics, the noble gases are excellent geochemical tracers of the formation and subsequent evolution of the Earth[1–7]. However, the origin of terrestrial noble gases is not fully understood. The isotopic composition of atmospheric xenon (Xe) is particularly puzzling because it appears to be strongly isotopically fractionated with respect to solar (derived from the protosolar nebula gas and represented by the solar wind composition) and chondritic (derived from an asteroid-like reservoir) components (see, for example, ref. 12). This feature could be a result of ancient atmospheric escape processes, but even after correction for mass-dependent isotope fractionation the isotope composition of atmospheric Xe cannot easily be related to a chondritic or solar origin[12]. One way to investigate the origin of terrestrial volatiles is to precisely document the compositions of noble gases that have been stored in the terrestrial mantle, presumably since the formation of the Earth.

Mantle-derived CO_2-rich gases are particularly powerful resources for investigating mantle-derived noble gases because the large quantities of sample material available make high-precision measurements possible[2–5,13]. Here we report Xe isotopic measurements in gases from a CO_2-rich well (Victoriaquelle) in the Eifel volcanic region (Germany). Geophysical and geochemical evidence suggests that the Eifel volcanism, which took place from 700 kyr ago to 11 kyr ago, was related to continental rifting and large-scale mantle upwelling[14–17]. The Victoriaquelle well, in the southwest of the Eifel region, emits CO_2-dominated gases (99.7%–99.8% CO_2) with helium isotope ratios of 4.2–4.5 Ra (where Ra is the helium isotope signature of the Earth's atmosphere) and ^{40}Ar/^{36}Ar ratios of up to 2,690 (ref. 18), consistent with low levels of atmospheric contamination and predominantly mantle-derived volatile emissions[18].

Our Xe isotope data (normalized to ^{130}Xe; Fig. 1, Extended Data Table 1) demonstrate that there is a mantle-derived component to this noble gas, marked by a 2.45% excess (relative to air) of ^{129}Xe from the decay of extinct ^{129}I (half-life of 16 Myr). The dataset also highlights an excess of the lightest isotopes ($^{124-128}$Xe) relative to air Xe. Because the light Xe isotopes are not affected by radiogenic or fissiogenic production, this excess $^{124-128}$Xe must represent a primordial Xe component. Excesses of light Xe isotopes have already been recognized in some mantle-derived gases[4,5,13]. Furthermore, given that isotopic fractionation during mantle processing is unlikely, these light Xe spectra must therefore reflect the presence of either solar or chondritic Xe (either average

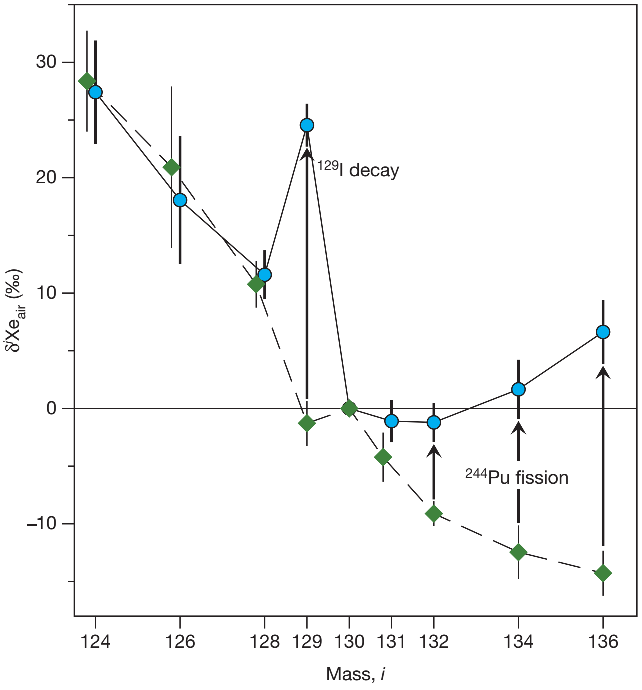

Figure 1 | Xe isotope composition of the Victoriaquelle gas. Data (blue filled circles) are normalized to the isotope composition of atmospheric Xe and to ^{130}Xe. Deviations from the atmospheric composition (Xe_{air}) are expressed in delta notation as parts per mil (‰). For comparison, we show the composition of a mixture composed of 84% atmospheric Xe and 16% chondritic (average carbonaceous chondrite) Xe (green diamonds; see Methods for the derivation of the component fractions). The excesses at masses $i = 129$ and $i = 131–136$ are the products of the extinct radioactivity of ^{129}I (half-life of 16 Myr) and ^{244}Pu (half-life of 82 Myr), respectively. Error bars indicate $\pm 1\sigma$.

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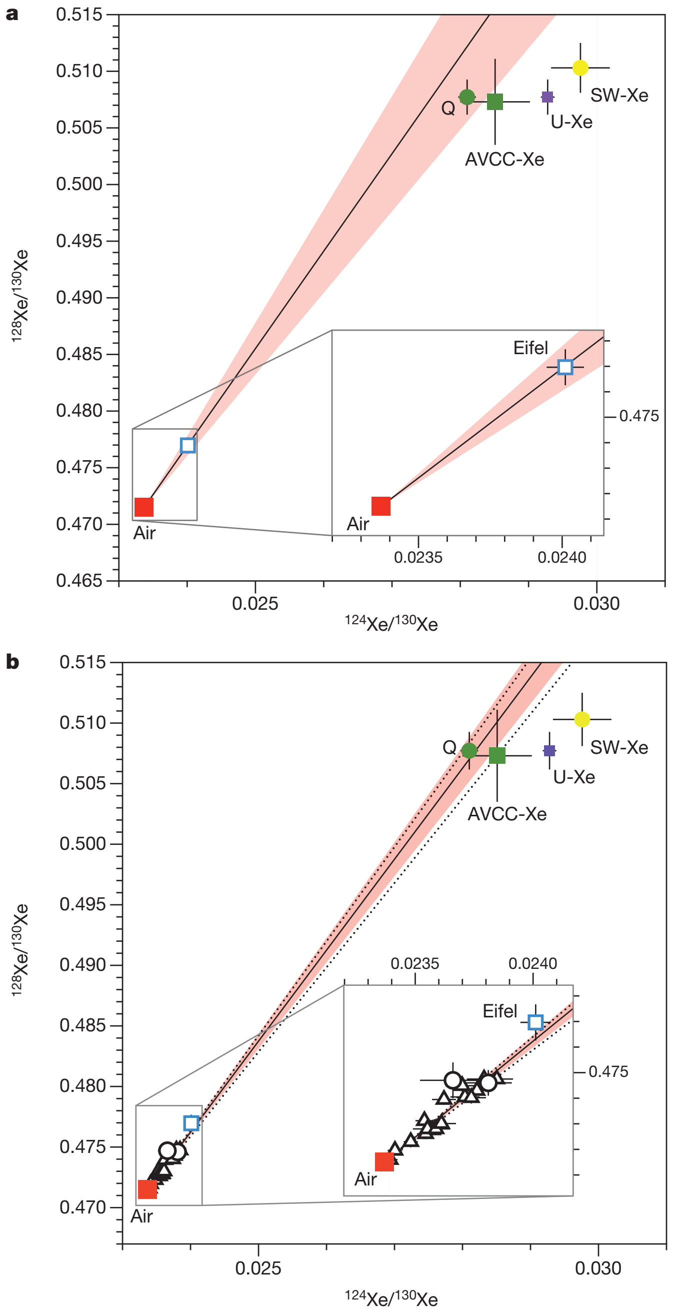

Figure 2 | Light Xe isotope correlations. a, The Eifel composition (open blue square) was derived from the mean of 15 measurements on three different aliquots of the same gas (see Methods). The solid black line is a best-fit line through the air (filled red square) and Eifel compositions; correlation errors were computed using the Isoplot code (courtesy of K. Ludwig, Berkeley Geochronology Center) (the light red envelope represents $\pm 1\sigma$ error). The compositions of phase-Q Xe ('Q', filled green circle; the major carrier of heavy noble gases trapped in primitive meteorites), average-carbonaceous-chondrite Xe ('AVCC-Xe', filled green square; ref. 9 and references therein), solar-wind Xe ('SW-Xe', filled yellow square; ref. 8) and the inferred progenitor of atmospheric Xe ('U-Xe', filled purple square; ref. 9) are also shown for comparison (with $\pm 1\sigma$ error bars). The correlation extrapolates to a chondritic, rather than solar or U-Xe, end-member in the mantle. Because of the overlap in the compositions of the 'Q'-type gases and average carbonaceous chondrites, it is not possible to distinguish the nature of the chondritic Xe carrier phase in the accreting Earth (in our discussion we use 'AVCC' without distinguishing 'Q' from the bulk chondritic composition). **b**, Comparison with other CO_2-rich well gases (Bravo Dome, black triangles; Harding County and Caroline, open circles; refs 5, 13, 19). The Eifel gas is seen either to contain the highest proportion of primordial Xe or to have been less affected by air contamination. The best-fit correlation for the Bravo Dome dataset (black dashed lines represent the upper and lower limit with $\pm 1\sigma$ error range) points to a chondritic composition for Xe in the upper mantle. The best-fit line obtained for the whole dataset (this study and the published well-gas data) also points to a chondritic Xe composition, demonstrating the ubiquitous presence of this component in the mantle.

carbonaceous chondrite or 'phase-Q', a ubiquitous noble gas component found in all classes of primitive meteorites; see, for example, ref. 9) in the Earth's mantle. Because the differences between the isotopic patterns of chondritic and solar-wind Xe are subtle[8,9], it has not previously been possible to differentiate between these two potential primordial sources of Xe. Given the nature of our sample, the high analytical precision of the present study and the recently improved precision on the isotope composition of solar-wind Xe (ref. 8), we are able to assign a chondritic rather than solar origin to the Eifel primordial Xe end-member (Fig. 2a, Methods, Extended Data Fig. 1). According to our calculations for the light isotopes, this chondritic Xe component represents 16% ± 2% of the Eifel gas, the remainder being atmospheric in origin (Methods, Extended Data Fig. 2). This is the highest proportion of primordial Xe identified in mantle-derived volatiles so far (Fig. 2b). Furthermore, the fact that all CO_2 well gases[4,5,13] analysed so far (from Bravo Dome (USA), Harding County (USA) and Caroline (Australia), and which have been ascribed an upper-mantle origin) also point to a chondritic Xe component and lie on a single correlation line with the Eifel gas (shown below to have a mantle plume origin; Fig. 2b), demonstrates the existence of a ubiquitous primordial Xe component in the Earth's mantle. Therefore, chondritic Xe was widely distributed in the proto-mantle during the Earth's accretion. Krypton isotopes also point to a chondritic source for Bravo Dome gases sampling the upper mantle[5], and, together with the present Xe data, support an asteroidal origin for heavy noble gases in the whole mantle.

This study points to several sources of volatile elements on Earth. The ancestor of atmospheric Xe was neither chondritic nor solar in origin because it had to have been relatively depleted in the heavy Xe isotopes (notably ^{134}Xe and ^{136}Xe) compared to documented primordial Xe components[19]. Known nuclear processes cannot resolve this issue because they can only contribute, not deplete, these isotopes. This problem, first recognized four decades ago[20], led to the definition of a primitive Xe component dubbed 'U-Xe' (not to be confused with Xe isotopes produced by ^{238}U fission), which was of solar composition for the light isotopes and depleted in both ^{134}Xe and ^{136}Xe relative to solar and chondritic Xe (ref. 19). Thus, two Xe components appear to co-exist on Earth: chondritic Xe preserved in the mantle and U-Xe found in the atmosphere. Consequently, the non-radiogenic, non-fissiogenic Xe in the atmosphere cannot have been derived from the mantle. To prevent mixing between the two components, the atmospheric Xe must have been added after growth of the Earth had largely been completed.

The heavy Xe isotope composition (^{131,132,134,136}Xe) of the mantle is more complex, being a mixture of four isotopically distinct end-members: (1) atmospheric Xe; (2) primordial Xe; (3) fissiogenic Xe produced from ^{244}Pu (^{Pu}Xe); and (4) fissiogenic Xe derived from ^{238}U (^{U}Xe). ^{244}Pu and ^{238}U each produce fissiogenic Xe isotopes in characteristic proportions, which differ from those of atmospheric or chondritic Xe. Excesses of fissiogenic or radiogenic $^{131-136}$Xe and ^{129}Xe in natural samples can be used to distinguish between magmatic sources and to constrain the timing of mantle differentiation. Both ^{129}Xe and ^{136}Xe were produced in the early Earth by decay of extinct radiochronometers—^{129}I (half-life of 16 Myr) decaying to ^{129}Xe and ^{244}Pu (half-life of 80 Myr) producing $^{131-136}$Xe—while extant ^{238}U also produced $^{131-136}$Xe, but with different ratios to those produced by ^{244}Pu. Thus, the U-Xe system evolved over the entire history of the Earth, whereas the I-Xe and Pu-Xe systems reflect elemental fractionation that occurred during

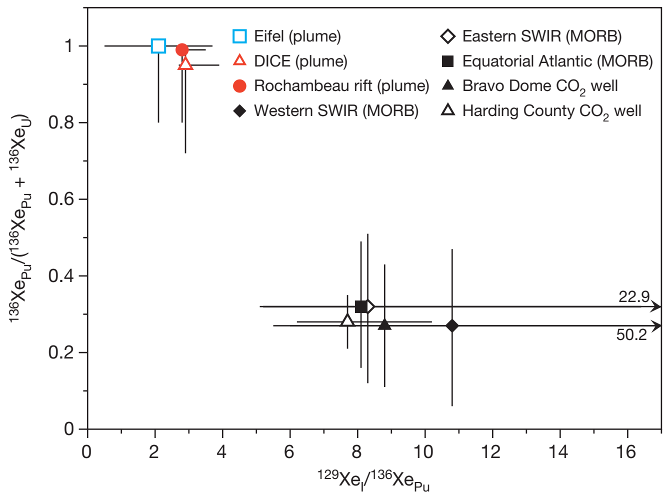

Figure 3 | Differences in the Xe isotopic compositions of the MORB and mantle plume reservoirs. The error-weighted ratios of iodine-derived Xe and plutonium-derived Xe ($^{129}Xe_I/^{136}Xe_{Pu}$) versus the fraction of fissiogenic Xe derived from plutonium ($^{136}Xe_{Pu}/(^{136}Xe_{Pu} + ^{136}Xe_U)$) enable plume-type mantle sources to be resolved from MORB-type mantle sources[6,7] ($\pm 1\sigma$ error bars). The $^{129}Xe_I/^{136}Xe_{Pu}$ and $^{136}Xe_{Pu}/(^{136}Xe_{Pu} + ^{136}Xe_U)$ ratios of worldwide MORB, plume sources and CO_2 well gas (all data except Eifel) are from refs 6 and 7, computed assuming an average-carbonaceous-chondrite primordial component for all data. The data for the convective mantle (equatorial Atlantic MORB, filled black square; western Southwest Indian Ridge (SWIR), filled black diamond; eastern SWIR, open black diamond; Harding County gas, open black triangle; Bravo Dome gas, filled black triangle) and the mantle plume sources (Iceland (DICE), open red triangle; Rochambeau rift, filled red circle; Eifel gas, open blue square) define two distinct fields in this diagram, highlighting the different histories and compositions of their respective reservoirs.

only the first 100 Myr and 500 Myr, respectively. The fissiogenic Xe isotope composition, obtained after correction for the atmospheric Xe contribution and by assuming a chondritic Xe composition for primordial Xe (Methods, Extended Data Figs 3, 4), suggests that excesses of heavy Xe isotopes resulted from ^{244}Pu fission rather than ^{238}U fission (Methods, Extended Data Figs 5, 6). Quantitatively, the fissiogenic Xe contribution to the Eifel gases is 2.26% ± 0.28%, with the remainder being atmospheric or primordial (Methods). Previous estimates of the proportion of ^{238}U- versus ^{244}Pu-derived Xe in the mantle depended on the initial Xe isotope composition of the mantle[8] (chondritic or solar); the fact that we demonstrate that the light Xe isotopes are chondritic in origin (Fig. 2a, Extended Data Fig. 1) allows us to confidently establish a $^{Pu}Xe/(^{Pu}Xe + ^{U}Xe)$ ratio of 0.8–1.0 ($\pm 1\sigma$) for the Eifel mantle source (Fig. 3, Methods).

In comparison, the other CO_2-rich well gases (Bravo Dome and Harding County; refs 4, 5, 13) have significantly lower $^{Pu}Xe/(^{Pu}Xe + ^{U}Xe)$ ratios of 0.06–0.51 ($\pm 1\sigma$) (Fig. 3). Their mantle source has been identified as the convective upper mantle, which also supplies magmas to mid-ocean ridges worldwide. Mid-ocean ridge basalts (MORBs) that have been analysed with sufficient precision also display low $^{Pu}Xe/(^{Pu}Xe + ^{U}Xe)$ ratios, comparable to the CO_2-rich well gases above, and define a well-homogenized convective mantle composition that is depleted in ^{Pu}Xe isotopes relative to ^{U}Xe (ref. 6). In a closed-system mantle with a chondritic Pu/U ratio[21], ^{Pu}Xe should dominate over ^{U}Xe ($^{Pu}Xe/(^{Pu}Xe + ^{U}Xe) = 0.97$). A mantle source degassed over geological timescales would see progressive depletion of ^{Pu}Xe and concurrent enrichment in ^{U}Xe still being produced. Therefore, the Eifel $^{Pu}Xe/(^{Pu}Xe + ^{U}Xe)$ ratio—which is close to 1 and higher than the convective mantle ratio of 0.3 (Fig. 3)—suggests that the Eifel mantle source was much less degassed than the MORB mantle source and, hence, less affected by mantle convection through time. This observation is consistent with the source of the Eifel gas being a deep mantle plume. Two other samples associated with mantle plumes (Iceland plume and the Rochambeau rift in the western Pacific[6]) display comparable $^{Pu}Xe/(^{Pu}Xe + ^{U}Xe)$ ratios (Fig. 3), also pointing to a mantle plume origin for the Eifel volcanism.

We also calculated a $^{129}Xe_I/^{136}Xe_{Pu}$ ratio of 2.1 ± 1.6 ($\pm 1\sigma$) for the Eifel gas (Fig. 3, Methods), a value comparable to the other plume-like signatures (that is, Iceland and the Rochambeau rift[6]) and different from values characteristic of the convective mantle (>5.1; Fig. 3). Assuming a bulk silicate Earth iodine content of between 3 parts per billion (p.p.b.) and 13 p.p.b. (ref. 22 and references therein), we calculated a I-Pu-Xe 'closure age'[12] for the Eifel mantle of 82–139 Myr after the start of Solar System formation, that is, about 4.45 Gyr ago (Methods, Extended Data Fig. 7). Closure ages should be considered as discrete approximations of a continuous process: they assume that the reservoir was open to Xe loss before that time and that it quantitatively retained Xe isotopes produced by extinct radioactivities afterwards. The early closure age calculated here indicates that degassing of the mantle plume source must have been very efficient when the ^{129}I and ^{244}Pu extinct isotopes were still alive, that is, during the first 100 Myr of the history of the Earth. After this time, the Eifel mantle source became efficiently isolated from mantle convection, thus preserving a high $^{Pu}Xe/(^{Pu}Xe + ^{U}Xe)$ ratio comparable within uncertainty to the closed-system value of 0.97. In contrast, the MORB source reservoir continued to lose ^{Pu}Xe while at the same time producing ^{U}Xe from long-lived ^{238}U fission, resulting in a $^{Pu}Xe/(^{Pu}Xe + ^{U}Xe)$ ratio of only 0.3 (Fig. 3). Interestingly, a closure age range of 82–139 Myr is consistent with differentiation times of <150 Myr after the start of Solar System formation recorded by the ^{146}Sm–^{142}Nd (see, for example, ref. 11) and ^{182}Hf–^{182}W (see, for example, ref. 23) extinct radioactivity systems. Therefore, the Eifel closure ages might date the last large-scale melting events of the proto-Earth.

If the I/Pu ratio was homogenous during the Earth's accretion, then the higher $^{129}Xe/^{136}Xe_{Pu}$ ratio of the MORB-type sources (Fig. 3) would imply an earlier closure age for the upper mantle than for the plume-type mantle (Extended Data Fig. 7). However, noble gas isotope systematics indicate that the plume-type source is less degassed than the MORB reservoir. It would be paradoxical to suggest that the more-degassed MORB-type mantle became closed to the loss of volatiles before the less-degassed mantle plume source[7]. Thus, it seems more likely that the I/Pu ratio was heterogeneous[1,7] during accretion, with a higher I/Pu ratio in the MORB reservoir than in the plume source. The initial I/Pu ratio must have been at least 3.5 times higher in the MORB source (Extended Data Fig. 7) for the upper mantle to have a younger closure age than the lower mantle. Because iodine is a volatile element and plutonium is a refractory element, the increase in the I/Pu ratio from the deep mantle reservoir source of the Eifel gas to the shallow convective mantle can be viewed as a progressive contribution of volatile-rich material to an initially dry proto-Earth.

The results of this study, coupled with published data[4–7,13], indicate that Xe isotopes in the Eifel gas have preserved a chemical signature that is characteristic of other mantle plume sources (Fig. 3). This corroborates the presence of a deep mantle plume source for the Eifel volcanism, as has previously been suspected[16,17]. Although the helium isotopic signature of the Eifel gas (<6 Ra; refs 17, 18) lies within the field of 'low $^3He/^4He$' mantle plumes (see, for example, ref. 24), the neon isotopes and neon–argon isotope systematics of the volcanic products point to a deep mantle source below the Eifel region[16,17]. The presence of a mantle plume is also supported by geophysical data[15,16,25,26]. Notably, tomographic images show a low-velocity structure at depths of 660–2,000 km, representing deep mantle upwelling under central Europe, that may feed smaller upper-mantle plumes (such as Eifel, Germany and Massif Central, France)[16].

Our results have implications for both the origin of terrestrial volatiles and the mechanisms and timing of their delivery. Neon, and presumably helium, has a solar-like origin[27], suggesting that these gases were trapped early during terrestrial accretion, before dissipation of the nebular gas. The other mantle noble gases, krypton[5], Xe (this work) and presumably argon, were delivered together with major volatiles such as hydrogen and nitrogen (ref. 28) by asteroidal material before mantle 'closure' (<60 Myr after the start of Solar System formation). Although the non-radiogenic, non-fissiogenic isotope composition of Xe appears to be homogeneous between the deep mantle and the shallower convective mantle, the volatile/refractory (I/Pu) ratio increased during the Earth's accretion, as is independently suggested by palladium–silver isotope data[29]. This is consistent with the existence of a thermal gradient in the forming Solar System, with the innermost zones being too hot to allow condensation of volatile elements during the initial stages of the Earth's accretion. Dissipation of heat over time and/or contributions of volatile-rich bodies from larger heliocentric distances enabled more-efficient trapping of volatile elements in the shallower regions of the growing Earth[30]. The deepest regions of the mantle, now sampled by mantle plumes, have remained efficiently isolated from mantle convection since about 4.45 Gyr ago, thereby preserving a record of the early stages of terrestrial accretion. The origin of the progenitor of atmospheric Xe (U-Xe) remains enigmatic. It is possible that it was added only after the Earth's completion (>82–139 Myr after the start of Solar System formation), thus avoiding any mixing with mantle (chondritic) Xe. This exotic component may have been carried by volatile-rich bodies from the outer Solar System during late veneer episodes or the Late Heavy Bombardment.

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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Author Contributions A.C., P.G.B. and B.M. designed the study. A.C. collected the samples, performed the experiments and analysed the data. G.A. processed the data and wrote the section on the processing procedure in Methods. A.C., P.G.B., G.A. and B.M. wrote the paper. E.F. collected the samples. All authors contributed to the interpretation and discussion of the data and provided comments on and input to the manuscript.

Author Information Data obtained in this study are available at the EarthChem library (http://dx.doi.org/10.1594/IEDA/100582). 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 A.C. (antonio.caracausi@ingv.it).

METHODS

Analytical method. High-precision Xe isotopic ratios were determined in the Noble Gas Laboratory at the Centre de Recherches Pétrographiques et Géochimiques (Nancy, France) using multi-collection mass spectrometry. Xe isotopic compositions were determined in a sample of free gas collected from the Victoriaquelle well in the Eifel volcanic district (Germany). Gas samples were collected in pre-evacuated (10^{-5} Pa) steel bottles equipped with a high-vacuum valve at the end, after thorough flushing of connecting tubes with the well gas. We purified and analysed three aliquots of gas (Extended Data Table 1). Active gases were removed by sequential exposure to hot and cold SAES getters. Xe was condensed on a cold finger at liquid-nitrogen temperature and the abundances of all Xe isotopes were measured on a Thermofisher noble-gas multi-collector mass spectrometer (Helix MC Plus) operating in a combination of multi-collection and peak-jumping modes.

We carried out a total of 15 measurements on the three aliquots of the same gas (Extended Data Table 1; errors are $1\sigma/\sqrt{n}$, where n is the number of duplicate measurements). Procedural blanks were performed before and after each measurement. Xe blanks were typically 0.16% of the ^{130}Xe signal. Therefore, blank corrections were unnecessary and were not applied to the abundances or isotope ratios reported in Extended Data Table 1. Xenon standard runs were analysed before and during the Victoriaquelle analytical session (total of 30 standard runs with 5.37×10^{-15} mol of ^{132}Xe per aliquot).

We also purified a different aliquot of gas to measure the Ar isotopic ratio. Ar isotope compositions were measured on a GV-instruments multi-collector mass spectrometer. We determined a ^{40}Ar/^{36}Ar ratio of 1,780 for our Victoriaquelle sample, overlapping values reported in previous investigations[18].

Residuals of the fit on light isotopes. We performed a series of calculations to quantitatively identify the best candidate (Q-Xe, AVCC-Xe or SW-Xe) for the primordial Xe component measured in the Eifel gas. We first calculated the relative percentages of atmosphere and primordial component required to obtain the measured isotopic ratios (^{i}Xe/^{130}Xe, $i = 124$–128) for each potential primordial component. The calculated proportions were typically around 87% air mixed with 13% primordial Xe. By taking the mean percentages for each light isotope, we then determined the corresponding isotopic compositions of different mixtures of atmosphere and each primordial component. Extended Data Figure 1 depicts the residuals of this mixing for each case (Q-Xe, AVCC-Xe or SW-Xe). These residuals correspond to the differences between the isotopic ratios measured in the Eifel gas and the modelled isotopic ratios, divided by the corresponding Eifel isotopic ratios for normalization and representation purposes. SW-Xe is a poor candidate for the primordial component, largely owing to its high residual for ^{124}Xe. Q-Xe or AVCC-Xe are the best candidates.

Deconvolution of the Xe isotope spectrum. We assumed that the isotopic spectrum of Xe (excluding ^{129}Xe) was produced from a mixture of four end-members: (1) modern atmosphere; (2) a primordial component (in the following calculations we used Q-Xe as a proxy for present-day bulk chondrite because present-day bulk chondrite analyses (AVCC) probably contain fissiogenic Xe contributions); (3) fissiogenic Xe derived from ^{244}Pu ($^{\mathrm{Pu}}$Xe); and (4) fissiogenic Xe derived from ^{238}U ($^{\mathrm{U}}$Xe).

To estimate the contribution of each component, we divided the problem into two stages.

First, we used the light isotopes (^{124,126,128}Xe/^{130}Xe) to estimate the contribution of the primordial component relative to the atmosphere $\alpha_{\mathrm{prim/atm}}$

$$\alpha_{\mathrm{prim/atm}} = \frac{(^{i}\mathrm{Xe}/^{130}\mathrm{Xe})_{\mathrm{Eifel}} - (^{i}\mathrm{Xe}/^{130}\mathrm{Xe})_{\mathrm{atm}}}{(^{i}\mathrm{Xe}/^{130}\mathrm{Xe})_{\mathrm{Q}} - (^{i}\mathrm{Xe}/^{130}\mathrm{Xe})_{\mathrm{Eifel}}}$$

where $i = 124$, 126 or 128. We used a Monte Carlo method to propagate uncertainties in the isotopic ratios. As an example, the distribution of $\alpha_{\mathrm{prim/atm}}$ obtained using the isotopic ratio ^{124}Xe/^{130}Xe is shown in Extended Data Fig. 2. The average of all $\alpha_{\mathrm{prim/atm}}$ values obtained for $i = 124$, 126 and 128 is 16% ± 2% ($\pm 1\sigma$). This value was then used to determine the isotopic composition of a mixture of Q-Xe and atmospheric Xe for the heavy isotopes. The uncertainty in this initial composition was calculated using a Monte Carlo propagation on the uncertainty in $\alpha_{\mathrm{prim/atm}}$ (see the normal distribution in Extended Data Fig. 2).

Second, this initial isotopic composition (renormalized to ^{136}Xe) was used to compute the relative contributions of the initial component (atmospheric Xe and Q-Xe), $^{\mathrm{Pu}}$Xe and $^{\mathrm{U}}$Xe required to match the isotopic ratios of the Eifel gases ($^{130-132}$Xe/^{136}Xe). We used ^{131}Xe and ^{132}Xe to constrain the nature of the fissiogenic component because these two isotopes are the most discriminant[31]. The linear system that was solved is

$$\left(\frac{^{i}\mathrm{Xe}}{^{136}\mathrm{Xe}}\right)_{\mathrm{Eifel}} = \beta_{\mathrm{initial}}\left(\frac{^{i}\mathrm{Xe}}{^{136}\mathrm{Xe}}\right)_{\mathrm{initial}} + \beta_{\mathrm{Pu_{Xe}}}\left(\frac{^{i}\mathrm{Xe}}{^{136}\mathrm{Xe}}\right)_{\mathrm{Pu_{Xe}}} + \beta_{\mathrm{U_{Xe}}}\left(\frac{^{i}\mathrm{Xe}}{^{136}\mathrm{Xe}}\right)_{\mathrm{U_{Xe}}}$$

where $i = 130$, 131 or 132 (3 equations), $\left(\frac{^{i}\mathrm{Xe}}{^{136}\mathrm{Xe}}\right)_{\mathrm{initial}}$ is the initial composition built during the first stage, $\left(\frac{^{i}\mathrm{Xe}}{^{136}\mathrm{Xe}}\right)_{\mathrm{Pu_{Xe}}}$ and $\left(\frac{^{i}\mathrm{Xe}}{^{136}\mathrm{Xe}}\right)_{\mathrm{U_{Xe}}}$ are the averages of the fissiogenic spectra from ref. 1, and β_{initial} $\beta_{\mathrm{Pu_{Xe}}}$ and $\beta_{\mathrm{U_{Xe}}}$ are the contributions of each component. We used the same approach as that adopted in ref. 6; that is, we used a MATLAB code with the *lsqlin* function, which minimizes the sum of the squared residuals. Because each component was normalized to the uncertainty in the isotopic composition of the Eifel gas, this sum corresponds to a χ^2 value. We used a Monte Carlo method to propagate the errors in the isotopic composition of the Eifel gas as well as in the initial composition determined during the first stage. A convergence of the results was achieved using 10^5 simulations. The χ^2 values computed for each simulation are shown in Extended Data Fig. 3. 75% of the χ^2 values are less than 3.

The final results are presented in Extended Data Fig. 4 (β_{initial}) and Extended Data Fig. 5 ($\beta_{\mathrm{Pu_{Xe}}}$). The fraction of the initial component (atmospheric Xe and Q-Xe) in the final composition is 97.7% ± 0.26%.

Virtually no simulation leads to a substantial contribution from $^{\mathrm{U}}$Xe; we demonstrate that $\beta_{\mathrm{U_{Xe}}} = {}^{136}\mathrm{Xe_U} = 0$. To fit a normal distribution to $\beta_{\mathrm{Pu_{Xe}}}$, we had to remove some of the very low values (Extended Data Fig. 5), which resulted in a $^{\mathrm{Pu}}$Xe contribution of 2.26% ± 0.28%.

Because $^{136}\mathrm{Xe_U} = 0$, the range for the $^{136}\mathrm{Xe_{Pu}}/(^{136}\mathrm{Xe_{Pu}} + {}^{136}\mathrm{Xe_U})$ ratio is 0.8–1.0 ($\pm 1\sigma$). The $^{129}\mathrm{Xe_I}/^{136}\mathrm{Xe_{Pu}}$ ratio was computed using

$$\frac{^{129}\mathrm{Xe_I}}{^{136}\mathrm{Xe_{Pu}}} = \frac{(^{129}\mathrm{Xe}/^{132}\mathrm{Xe})_{\mathrm{Eifel}} - \beta_{\mathrm{initial}}(^{129}\mathrm{Xe}/^{132}\mathrm{Xe})_{\mathrm{initial}}}{\beta_{\mathrm{Pu_{Xe}}}(^{136}\mathrm{Xe}/^{132}\mathrm{Xe})_{\mathrm{Pu_{Xe}}}}$$

and the errors in $(^{129}\mathrm{Xe}/^{132}\mathrm{Xe})_{\mathrm{Eifel}}$, β_{initial} and $\beta_{\mathrm{Pu_{Xe}}}$ were propagated using the Monte Carlo method. The value obtained for $^{129}\mathrm{Xe_I}/^{136}\mathrm{Xe_{Pu}}$ is 2.1 ± 1.6 ($\pm 1\sigma$), which was then used to compute the closure ages of the Eifel gas mantle source regions.

Code availability. The code for this Letter is available by contacting G.A. (gavice@crpg.cnrs-nancy.fr).

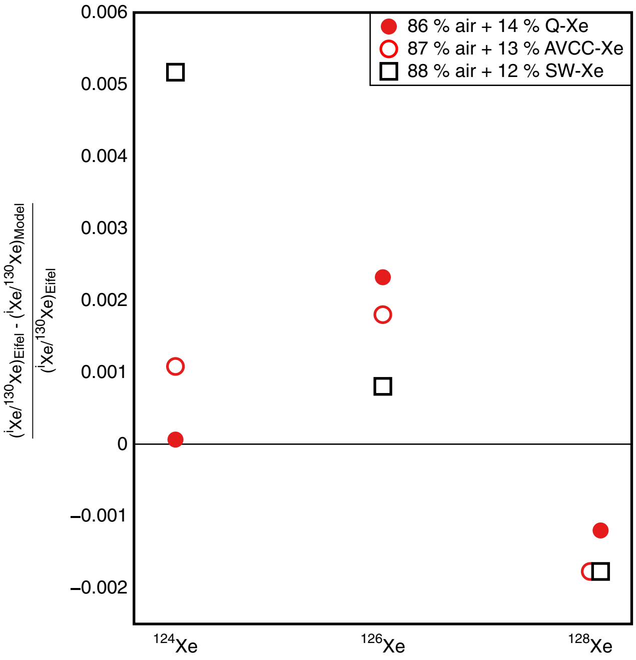
Sample size. No statistical methods were used to predetermine sample size.

Closure ages and I/Pu heterogeneity. The closure ages (in millions of years) of the Eifel gas mantle source regions were calculated using (see, for example, ref. 12)

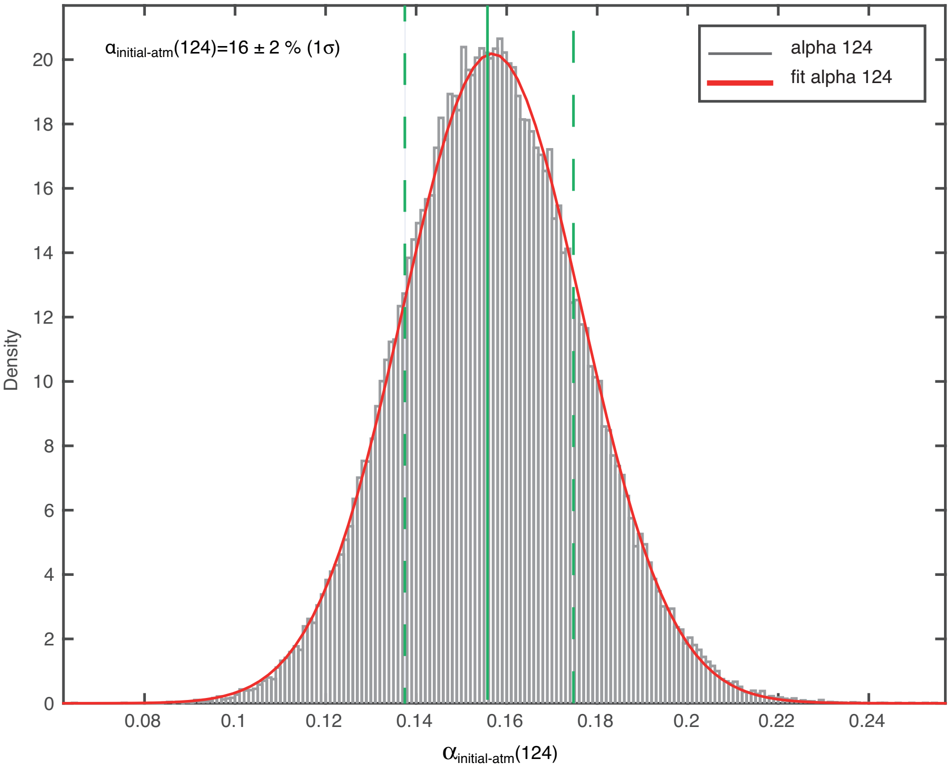
$$t = \frac{1}{\lambda_{244} - \lambda_{129}} \ln\left[\left(\frac{^{129}\mathrm{Xe_I}}{^{136}\mathrm{Xe_{Pu}}}\right)\left(\frac{^{238}\mathrm{U}}{^{127}\mathrm{I}}\right)_0\left(\frac{^{244}\mathrm{Pu}}{^{238}\mathrm{U}}\right)_0\left(\frac{^{127}\mathrm{I}}{^{129}\mathrm{I}}\right)_0 {}^{136}\mathrm{Y}_{244}\right]$$

where $\lambda_{244} = 8.45 \times 10^{-3}\,\mathrm{Myr}^{-1}$ and $\lambda_{129} = 4.41 \times 10^{-2}\,\mathrm{Myr}^{-1}$ are the decay constants of ^{244}Pu and ^{129}I, respectively, $^{136}\mathrm{Y}_{244}$ is the yield of fission of ^{244}Pu for production of ^{136}Xe (ref. 1), and $^{238}\mathrm{U}_0$, $^{244}\mathrm{Pu}_0$, $^{129}\mathrm{I}_0$ and $^{127}\mathrm{I}_0$ are the initial abundances (in mol) of parent and stable nuclides. Using $\mathrm{U}_0 = 40$ p.p.b. and $\mathrm{I}_0 = 6.4$ p.p.b. (ref. 22), we obtained a closure age of 98^{+41}_{-16} Myr. This age is relatively insensitive to the initial uranium content (U_0) of the bulk-silicate Earth, whereas the initial iodine content (I_0) is important (see Extended Data Fig. 7 for the sensitivity of the closure age to variable initial I/Pu ratios).

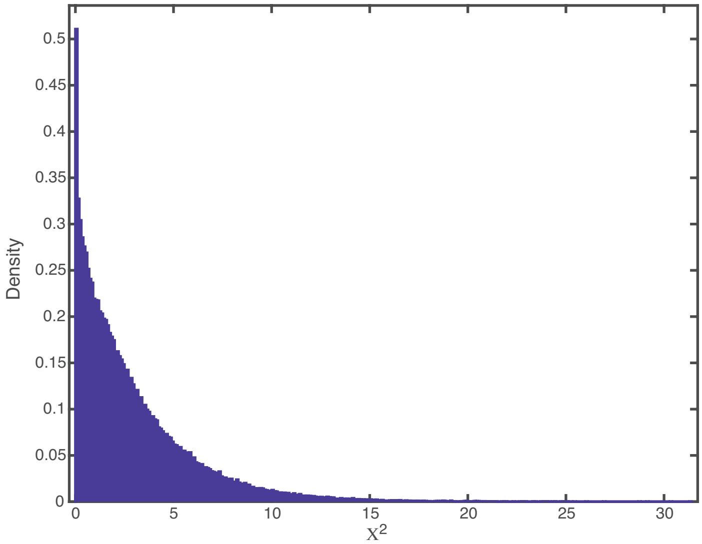
31. Ozima, M. & Podosek, F. A. *Noble Gas Geochemistry* 2nd edn, 22 (Cambridge Univ. Press, 2002).



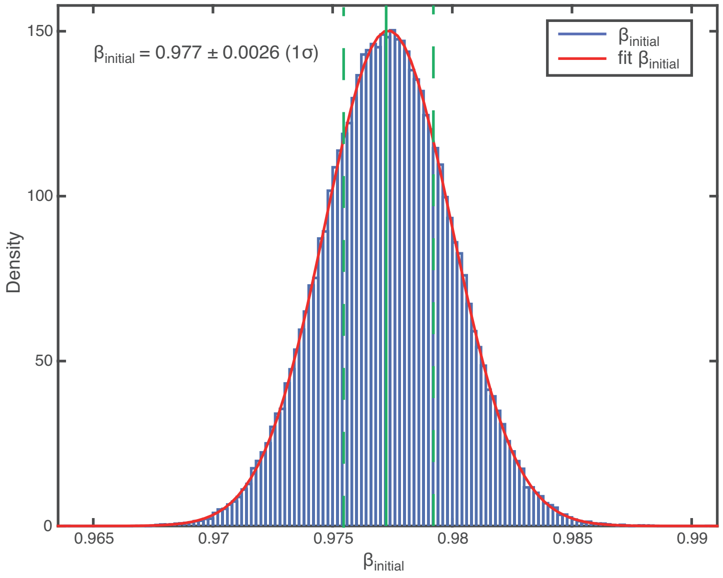
Extended Data Figure 1 | Residuals of the different mixing possibilities. Calculations were performed for the light isotopes ($^{124-128}$Xe) using the isotopic compositions of air (typically about 87%) and Q-Xe, AVCC-Xe or SW-Xe (typically about 13%). The best fit is achieved by taking either AVCC-Xe or Q-Xe as the primordial component. SW-Xe does not produce an adequate fit and therefore is not a suitable candidate for this component (as also shown in Fig. 1).



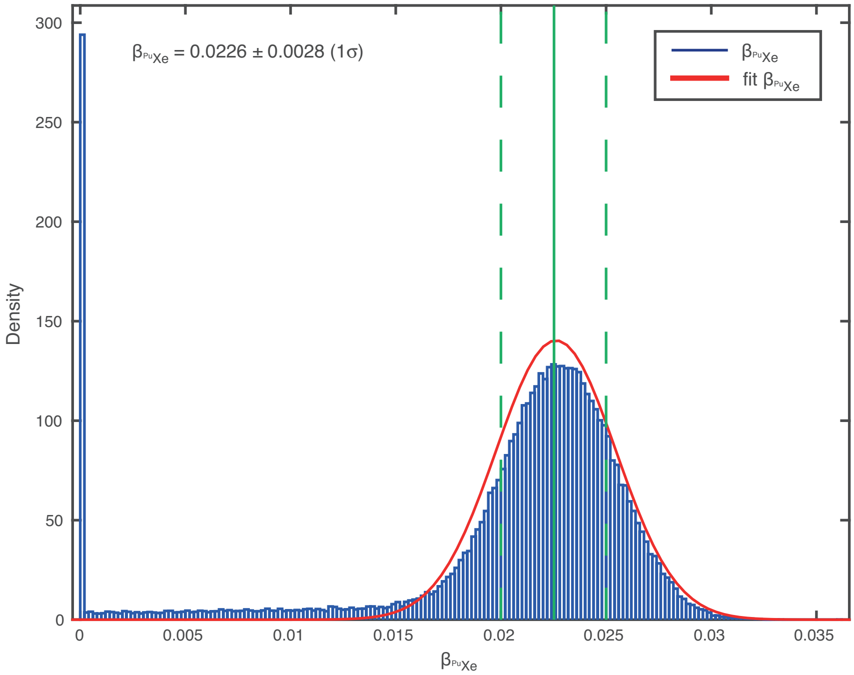
Extended Data Figure 2 | Deconvolution of the proportion of the primordial component (Q-Xe) relative to the atmosphere for ^{124}Xe/^{130}Xe. The red line represents the result of the normal fit. The solid green line depicts the mean value and the dashed green lines depict the error range of $\pm 1\sigma$.



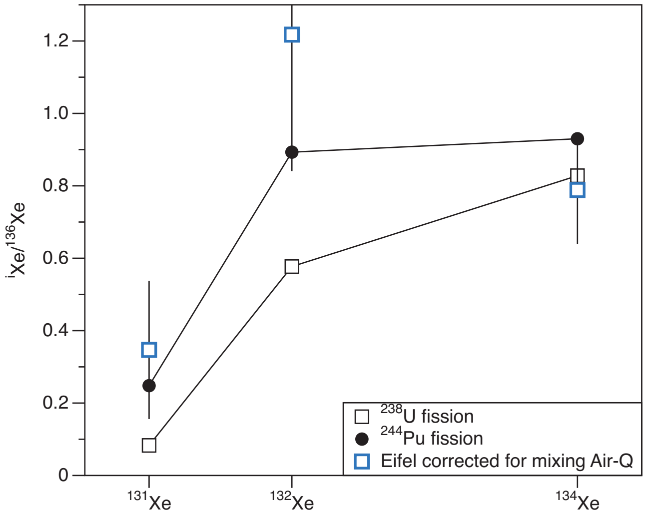
Extended Data Figure 3 | Range of χ^2 values obtained from the simulations. Approximately 75% of the values are less than 3.



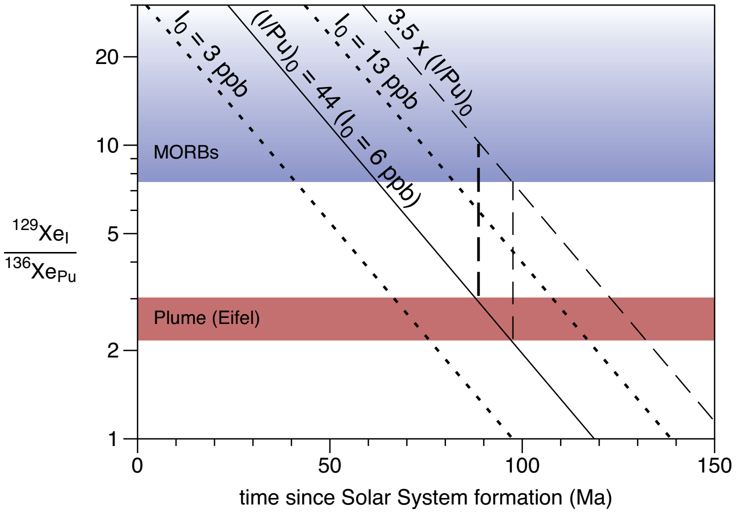
Extended Data Figure 4 | Fraction of initial component required to fit the isotopic composition of the Eifel gas. The solid green line depicts the mean value and the dashed green lines depict the error range of $\pm 1\sigma$.



Extended Data Figure 5 | Fraction of Pu-Xe required to fit the isotopic composition of the Eifel gas. Some very low values (those less than 10^{-5}) were excluded from the calculations, resulting in a mean of 2.26% (green line) and a standard deviation of 0.28% (1σ).



Extended Data Figure 6 | Isotopic composition of heavy isotopes ($^{131-134}$Xe). The data are normalized to ^{136}Xe of the Eifel gas after correction for atmospheric and primitive chondritic contributions, and compared to the fission spectrum of $^{131-136}$Xe produced by spontaneous fission of ^{238}U and ^{244}Pu. Excesses in heavy isotopes are compatible with spontaneous fission of ^{244}Pu.



Extended Data Figure 7 | Closure ages calculated from the $^{129}Xe_I/^{136}Xe_{Pu}$ ratios. See Methods for details of the computation method. A younger closure age for the upper mantle is achieved only if the I/Pu ratio is at least 3.5 times higher than the lower-mantle source.

Extended Data Table 1 | Xenon isotopic ratios measured in aliquots of the Eifel gas

	^{130}Xe	^{124}Xe/^{130}Xe	^{126}Xe/^{130}Xe	^{128}Xe/^{130}Xe	^{129}Xe/^{130}Xe	^{131}Xe/^{130}Xe	^{132}Xe/^{130}Xe	^{134}Xe/^{130}Xe	^{136}Xe/^{130}Xe
Eif_1	7.9E-14	0.024225	0.022345	0.474745	6.654409	5.215284	6.618798	2.560233	2.187465
		0.000109	0.000078	0.000949	0.007304	0.005177	0.007846	0.002519	0.002158
Eif_2		0.023910	0.021997	0.474385	6.590819	5.159161	6.548295	2.532569	2.168481
		0.000130	0.000091	0.000948	0.009207	0.006145	0.008410	0.003489	0.002567
Eif_3		0.024502	0.022549	0.478018	6.681859	5.221782	6.655400	2.558332	2.245266
		0,000100	0.000156	0.001194	0.012001	0.008812	0.010520	0.005035	0.004652
Eif_4		0.024168	0.022220	0.474905	6.657195	5.198561	6.611074	2.553088	2.168967
		0.000291	0.000243	0.002040	0.014614	0.011353	0.013715	0.005527	0.006634
Eif_5		0.024139	0.022287	0.483613	6.646030	5.204344	6.622836	2.590335	2.191245
		0,000073	0.000071	0.000580	0.004642	0.004649	0.005234	0.002039	0.001730
Eif_6	4.8E-14	0.023824	0.021997	0.473584	6.643284	5.210670	6.574350	2.604929	2.205901
		0.000147	0.000093	0.000994	0.007954	0.005690	0.008443	0.003588	0.002612
Eif_7		0.024149	0.022200	0.478799	6.713198	5.209149	6.602612	2.552671	2.171623
		0.000172	0.000126	0.001052	0.013397	0.009307	0.013689	0.004772	0.004285
Eif_8		0.024435	0.022229	0.477518	6.664280	5.223837	6.607845	2.567031	2.193414
		0.000120	0.000129	0.000954	0.008644	0.006741	0.007181	0.003031	0.003246
Eif_9		0.023748	0.022094	0.476777	6.672970	5.199317	6.610295	2.587957	2.206022
		0.000309	0.000283	0.002715	0.021306	0.014451	0.019591	0.007130	0.007618
Eif_10		0.023691	0.022016	0.474975	6.597032	5.166969	6.544023	2.538413	2.165106
		0.000134	0.000089	0.001092	0.009874	0.008206	0.011637	0.003996	0.002991
Eif_11	3.2E-14	0.024006	0.022239	0.481571	6.667457	5.230183	6.637291	2.566452	2.178160
		0.000254	0.000232	0.001588	0.011310	0.008307	0.010491	0.005051	0.004298
Eif_12		0.023815	0.022016	0.475436	6.657245	5.221550	6.583217	2.569755	2.197417
		0.000130	0.000170	0.001235	0.009964	0.008811	0.010406	0.004551	0.003469
Eif_13		0.023881	0.022278	0.477177	6.673390	5.224593	6.648375	2.570202	2.197580
		0.000123	0.000127	0.000715	0.009322	0.006742	0.006568	0.004046	0.003036
Eif_14		0.023729	0.021977	0.477007	6.665152	5.215294	6.600769	2.594237	2.190850
		0.000152	0.000141	0.001239	0.009311	0.007765	0.007173	0.004340	0.003242
Eif_15		0.023939	0.022462	0.475946	6.648185	5.208323	6.582498	2.562519	2.188883
		0.000133	0.000158	0.000761	0.008624	0.006204	0.008454	0.003026	0.003239
Eifel		0.024011	0.022194	0.476964	6.655500	5.207268	6.603179	2.567248	2.190425
		0.000065	0.000046	0.000707	0.007827	0.005231	0.008213	0.005221	0.005209

Individual Xe isotopic ratio measurements (‘Eif_*n*’) for three different aliquots of the same gas. Errors (1σ) are reported in the cell below each ratio. The ‘Eifel’ ratios represent the average of 15 measurements (‘Eif_1’ to ‘Eif_15’) of three aliquots of the same gas. The amounts of ^{130}Xe are in mol and errors are 5%.