The origin and degassing history of the Earth’s atmosphere revealed by Archean xenon

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Xenon (Xe) is an exceptional tracer for investigating the origin and fate of volatile elements on Earth. The initial isotopic composition of atmospheric Xe remains unknown, as do the mechanisms involved in its depletion and isotopic fractionation compared with other reservoirs in the solar system. Here we present high precision analyses of noble gases trapped in fluid inclusions of Archean quartz (Barberton, South Africa) that reveal the isotopic composition of the paleo-atmosphere at $\approx 3.3$ Ga. The Archean atmospheric Xe is mass-dependently fractionated by $12.9 \pm 2.4 \text{ u}^{-1}$ (± 2σ, s.d.) relative to the modern atmosphere. The lower than today $^{129}\text{Xe}$ excess requires a degassing rate of radiogenic Xe from the mantle higher than at present. The primordial Xe component delivered to the Earth’s atmosphere is distinct from Solar or Chondritic Xe but similar to a theoretical component called U-Xe. Comets may have brought this component to the Earth’s atmosphere during the last stages of terrestrial accretion.
The building blocks of the Earth accreted in regions where temperatures were too high to permit significant retention of volatile elements (for example, H, C, N, noble gases). The Earth probably acquired its volatile components late from more distant sources such as the Main Belt asteroids and/or comets. Simulations suggest that during the final stages of solar system formation, the orbits of asteroids were disturbed by the migration of the giant planets and, for some of them, their trajectories crossed the Earth’s orbit. Even if the isotopic composition of cometary water argues against comets being the source of terrestrial water, the high Ar/H$_2$O ratio measured in comet 67P/C-G by the Rosetta spacecraft suggests that cometary objects may have contributed noble gases to the terrestrial atmosphere. At least two distinct cosmochemical sources contributed noble gases to the Earth’s mantle: a Solar end-member detected in Ne isotopes and a Chondritic component that is, (astro)parent in the isotopic compositions of Kr (ref. 7) and Xe (ref. 8). The presence of radiogenic and fissiogenic noble gases in the atmosphere ($^{40}$Ar, $^{129}$Xe, $^{131}$–$^{136}$Xe), produced by the radioactive decay of parent nuclides ($^{40}$K, $^{129}$I, $^{244}$Pu, $^{238}$U) in the mantle and crust, attests for exchanges between the surface and the silicate Earth. However, the ultimate origin of the Earth’s atmosphere remains unknown, especially for xenon. The Xe abundance in the Earth’s atmosphere is depleted, the atmospheric Xe/Kr ratio being lower by a factor of ~20 relative to the chondritic composition. Furthermore, atmospheric Xe is enriched in heavy isotopes by 30–40% relative to Chondritic (Q-Xe) or Solar (SW-Xe) (ref. 11). These two features form the so-called xenon paradox. When corrected for mass-dependent isotope fractionation, atmospheric Xe is depleted in its heavy isotopes ($^{131}$–$^{136}$Xe) relative to Solar or Chondritic Xe, and cannot be related to any known cosmochemical component. These observations led to the definition of a theoretical primordial component labelled ‘U-Xe’ (ref. 13), which has solar-like composition for the light isotopes ($^{124}$–$^{130}$Xe), and is depleted in heavy Xe isotopes. However, this composition was derived from statistical correlations and its presence has never been observed in any terrestrial or extraterrestrial material. Recently, Meshik et al. proposed an alternative explanation to U-Xe for the origin of atmospheric Xe. Their model is not based on a different primordial component but involves Chemically Fractionated precursors of Fissiogenic Xe producing the so-called CFF-Xe (see ref. 16 and refs therein). Degassing of this component, enriched in $^{132}$Xe and $^{134}$Xe, accompanied by atmospheric escape seems to match the fission spectrum of atmospheric Xe. However, when SW-Xe is taken as a precursor of atmospheric Xe and is mass-fractionated to reproduce, for example, the $^{128}$Xe/$^{130}$Xe in the modern atmosphere, the result produces anomalous $^{136}$Xe excesses (about 26 ± 6% (1σ) compared with the modern atmosphere) before any fission contribution. Thus, CFF-Xe cannot be the sole explanation for the origin of the isotopic composition of atmospheric Xe since this modified fission component can only increase the $^{136}$Xe budget of the atmosphere.

Recent studies of Archean barite and quartz samples from North Pole, Pilbara (NW Australia) demonstrated that, 3.5 to 3.0 Ga ago, atmospheric Xe had an isotopic composition less isotopically fractionated than the modern atmospheric Xe relative to any of the potential primordial components. These data suggest a progressive long-term evolution of the isotopic composition of atmospheric Xe by mass-dependent isotope fractionation, that may be due to ionization of atmospheric xenon by ancient, ultraviolet-rich, solar radiation and progressive escape of Xe ions to space. However, these studies did not elucidate the original composition of atmospheric xenon, which was then tentatively attributed to Solar/Chondritic. Xenon escape processes could have also led to mass-independent isotope fractionation, in addition to the mass-dependent one, that could account for the unique isotopic composition of modern atmospheric Xe. To investigate the ultimate origin of atmospheric xenon, we selected and analysed with unprecedented high precision Archean quartz samples from the Barberton Greenstone Belt (BGB), South Africa.

Here we demonstrate that fluid inclusions in the Barberton quartz samples record the Xe isotope composition of the Archean atmosphere. This 3.3 Ga-old atmospheric Xe is mass-dependently fractionated by ~13% relative to the modern atmosphere allows us to compute a degassing rate from the Earth’s mantle to the atmosphere over the last 3.3 Ga. Furthermore, Archean Xe originates from a primordial component different from all other known reservoirs of Xe in the solar system and similar to the theoretical U-Xe. Comets may have been the source of this noble gas component, added to the Earth’s atmosphere during late accretionary events.

**Results**

**Samples characteristics.** Samples analysed in this study are from a core (BARB 3) drilled in the BGB, South Africa. The drilling project is part of an ICDP Project (‘Peering into the cradle of life’, PI: N. Arndt). The BARB 3 core was drilled in rocks of the Kromberg formation (3.33–3.47 Ga) and mainly comprises a succession of white and black cherts and ultramafic rocks. All samples of this study consist of macro-crystalline quartz (Supplementary Fig. 1) with different modes of emplacement in rocks from the BGB and probably linked to early hydrothermal activity. Some of the samples are from well-defined cm-sized bedded veins (Supplementary Fig. 1a) with sharp, straight contacts with adjacent white chert; other samples are from meter-sized coarse quartz veins. Analytical techniques used during the $^{40}$Ar/$^{39}$Ar experiments and Xe-Kr analyses are described in Methods.

**$^{40}$Ar/$^{39}$Ar ages.** Results of the $^{40}$Ar/$^{39}$Ar crushing experiments (Methods, Supplementary Table 1) show anomalously high ages, often exceeding the age of the solar system (>4.56 Ga), due to the presence of $^{40}$Ar excess ($^{40}$Ar$_E$) (ref. 26). This excess argon component is correlated with the chlorine (Cl) content (Figs 1 and 2) and probably reflects enrichment of the fluids in crustal-derived radiogenic argon and chlorine during fluid-rock interaction processes before entrapment. Only step-heating steps yielding elevated K/Cl ratios give realistic ages between 3 and 3.5 Ga that are broadly compatible with the age of the formations in which the quartz veins are emplaced (Fig. 2). We correct $^{40}$Ar/$^{39}$Ar data for excess argon using a plane ($R^2 = 0.975$) to the data in three-dimensional (3D) space (Cl–K–$^{40}$Ar) space by applying a Monte Carlo method to propagate errors on measurements (Methods, Fig. 3 and Supplementary Fig. 2). This approach leads to a $^{40}$Ar–$^{39}$Ar age of 3.3 ± 0.1 Ga (± 2σ, s.d.) for Barberton sample BMGA3-9 (Fig. 3). This age is similar within errors to the formation age but may also be consistent with late hydrothermal fluid circulation events linked to the intrusion of adjacent 3.2 Ga-old plutons. The initial $^{40}$Ar/$^{36}$Ar is 458 ± 4 (± 2σ, s.d.) for sample BMGA3-9, which is higher than the modern atmospheric ratio of 298.6 (ref. 28), this may be explained by the presence of some $^{40}$Ar excess uncorrelated with the chlorine content.

A different approach (Methods) was used to constrain the age of sample BMGA3-13, which contains relatively lower excess $^{40}$Ar abundances as indicated by a less-well defined correlation between $^{40}$Ar$_E$ and Cl ($R^2 = 0.95$) and lower $^{40}$Ar/$^{39}$Ar values.
The chlorine content. 40Ar excess prevents the direct determination of an age from any simple 40Ar-K correlation. Samples BMGA3-9 and BMGA3-3 show a similar correlation of 40Ar with chlorine content (solid line). Sample BMGA3-3 contains lower argon excess 40Ar (dashed line). Regression lines represent the evolution of ages with the K/Cl ratio for samples BMGA3-3, BMGA3-9, and BMGA3-13, respectively. Errors bars are at 1σ.

**Figure 2 | Apparent ages versus the K/Cl ratio.** Most ages are anomalously high (> 4.56 Ga) due to the presence of excess argon linked to a hydrothermal component rich in Cl (low K/Cl). For elevated K/Cl ratio (> 3) apparent ages decrease towards more realistic values between 3 and 3.5 Ga (purple range). The solid, dotted and dashed curves schematically represent the evolution of ages with the K/Cl ratio for samples BMGA3-3, BMGA3-9 and BMGA3-13, respectively. Errors bars are at 1σ.

(Contributed by S. D. Brackenridge et al.) This method uses the 40Ar/36Ar derived from crushing data to correct step-heating data for the 40Ar component (Methods). This leads to a similar, but less precise, age of 3.5 ± 1.0 Ga (± 2σ, s.d., mean square weighted deviation (MSWD) = 1.06). The initial atmospheric 40Ar/36Ar ratios of sample BMGA3-13, computed for ages varying between 3.2 and 3.4 Ga (see above) have values ranging from 178 to 202 with a mean of 190 ± 12 (± 2σ, s.d.) (Supplementary Fig. 3). This value is a minimum value for the Archean atmospheric 40Ar/36Ar ratio but is in broad agreement with previous estimates and prediction (143 ± 21, 3.5 Ga ago, (ref. 20)) and models invoking a peak in crustal extraction between 3.8 and 2.5 Ga (refs 20,29).

**Xenon isotopic composition.** The reproducibility of the crushing experiment results (Supplementary Table 2) on different samples and duplicates (Methods and Supplementary Fig. 4) enables a precise determination of the error-weighted average for the isotopic ratios of xenon trapped in Barberton quartz (Fig. 4 and Supplementary Table 2). The isotopic spectrum of xenon in Barberton quartz normalized to 130Xe indicates excesses of the light isotopes (124–129Xe) together with depletions of heavy isotopes (131–136Xe) relative to the modern atmospheric composition (Fig. 4a). The absence of mantle-derived 129Xe excesses from the decay of now extinct 129I (T1/2 = 16 Ma) relative to the atmospheric composition (Fig. 4), together with an isotopic composition of krypton similar to the modern atmosphere (Fig. 5) argues against the presence of a mantle-derived component trapped within the fluid inclusions. Xenon in Barberton quartz thus has an Archean isotopic composition that differs from the modern atmosphere. The isotopic fractionation of xenon in Barberton quartz relative to the isotopic composition of the modern atmosphere was computed using the light stable, non-fissiogenic, non-radiogenic isotopes of Xe (126,128,130Xe) plus 131Xe, for which production by the fission of 238U is small30. Error-weighted correlations were obtained using the Isoplot 4.1 software31, however, note that correlations involving 134Xe were excluded for reasons explained in the Supplementary Discussion (Supplementary Information). The results show that Archean atmospheric xenon was isotopically fractionated by 12.9 ± 2.4 %u–1 (± 2σ s.e.m., MSWD = 1.4) relative to modern atmospheric Xe (Fig. 6).

**Discussion**

Our observations provide strong confirmation, with greater precision, of previous observations on samples from different regions and geological settings (Fig. 6)17–20,32 that the peculiar Xe isotopic composition during the Archean eon was ubiquitous and not due to local fractionation effects. The results provide confirmation for the specific and long-term evolution of the isotopic composition of atmospheric Xe, since the fractionation determined here is significantly different from 21 ± 6 %u–1 (± 2σ, s.d.) Xe in North Pole, Pilbara barite with an age of 3.48 ± 0.18 Ga (± 2σ, s.d.)18 (Fig. 6). A mass-dependent isotope fractionation process acted on atmospheric Xe isotopes from at least 3.3 Ga until the present day. However, neither modern atmospheric Xe, nor Archean atmospheric xenon trapped in Barberton quartz can be derived from Q-Xe (Chondritic) or SW-Xe (Solar) by mass-dependent isotope fractionation, because these primordial components carry 134,136Xe excesses relative to ancient atmospheric Xe (Figs 7 and 8; see also Supplementary Fig. 5). In the following discussion, we show how the Archaen atmospheric composition is consistent with U-Xe being a primordial component present in the atmosphere ≥ 3.3 Ga ago.

We start by making the reasonable assumption that the primordial component had a solar-like 132Xe/130Xe ratio of 6.061 ± 0.029 (± 2σ, s.d.)33 (Fig. 7a, Supplementary Discussion); this is supported by the following: (1) Barberton 126–132Xe/130Xe (and not 134–136Xe/130Xe) ratios can be related to solar Xe by a mass-dependent isotopic fractionation of ≈ 25 %u–1; (2) Solar gas represents the major gas reservoir of the solar system and any higher 132Xe/130Xe ratios as found in Chondritic meteorites are often accompanied by 134Xe and 136Xe excesses34. Note that this starting assumption is valid for 132Xe only and does not imply that the whole isotopic spectrum of primordial Xe component
corresponds to Solar Xe. The heavy isotopes of xenon, for example, $^{134}$Xe and $^{136}$Xe, have been produced over time by spontaneous fission of $^{238}$U ($T_{1/2} = 4.47$ Ga) and $^{244}$Pu ($T_{1/2} = 80$ Ma). $^{244}$Pu was totally extinct $\approx 4.1$ Ga ago, and only the spontaneous fission of $^{238}$U has contributed Xe isotopes to Barberton fluid inclusions from 3.3 Ga ago to the present (Fig. 7b). This contribution could have taken place either in situ in fluid inclusions or in the surrounding crustal rocks leached by the fluids before their entrapment in Barberton quartz samples. Light isotopes excesses in the Barberton Xe isotopic spectrum (Fig. 4) correspond to an isotopic fractionation ($\approx 12.9 \%$ u$^{-1}$) that can be propagated towards heavy isotopes to compute a theoretical primordial isotopic composition for the atmosphere, especially for $^{134}$Xe and $^{136}$Xe (Fig. 7c). The resulting range of possibilities for the initial isotopic composition (range at $\pm 2\sigma$) corresponds to $^{136}$Xe/$^{130}$Xe = 1.685 ± 0.075 ($\pm 2\sigma$, s.d.) (Figs 7d and 8) and $^{134}$Xe/$^{130}$Xe = 2.14 ± 0.07 ($\pm 2\sigma$, s.d.) (Methods, Supplementary Fig. 5). The mass-dependent isotopic fractionation of this composition, combined with the addition of fissionogenic $^{132–136}$Xe isotopes with known yields$^{12}$, accounts for the Xe isotopic composition measured in Barberton quartz (Fig. 8 and Supplementary Fig. 5). Hence, our results demonstrate that an initial isotopic composition different from Q-Xe or SW-Xe, and similar to U-Xe, must have existed in the ancient atmosphere, without making use of the isotopic composition of the modern atmosphere as it was done in previous studies$^{13,14}$. The fidelity of our deconvolution of Archean Xe is revealed by the Xe fission spectra shown in Fig. 9 where $^{131–136}$Xe excesses, following correction for mass-dependent fractionation relative to U-Xe, perfectly match the Xe spectrum for the spontaneous fission of $^{238}$U (ref. 30). Other potential compositions (Solar or Chondritic) lead to fission spectra neither related to the spontaneous fission of $^{238}$U nor to that of $^{244}$Pu. A small contribution of the spontaneous fission of $^{244}$Pu in the total Xe fission component cannot be rejected. However, this contribution must be small (max. 2% based on the $^{134}$Xe/$^{136}$Xe ratio) and the abundances of $^{131–136}$Xe derived from the spontaneous fission of $^{244}$Pu are too low to be estimated accurately due to the overwhelming dominance of fissiogenic Xe isotopes from spontaneous fission of $^{238}$U.

The modern atmosphere contains $(4.06 \pm 0.05, \pm 1\sigma) \times 10^{12}$ mol of $^{129}$Xe (ref. 12) comprising a radiogenic $^{129}$Xe excess ($^{129}$Xe(I) hereafter) of $6.8 \pm 0.3\%$ (6.8 ± 1\sigma, s.d.) (ref. 35) produced by the radioactive decay of extinct $^{129}$I ($T_{1/2} = 16$ Ma). For the Archean atmosphere, the excess of $^{129}$Xe(I), is calculated to be $6.07 \pm 0.22\%$ ($\pm 1\sigma$, s.d.) after correction for isotopic fractionation (Methods). This value is lower than the modern atmospheric excess (Fig. 4b) and probably results from the overwhelming dominance of fissiogenic Xe isotopes from spontaneous fission of $^{238}$U.
Figure 4 | Isotopic composition of xenon in Barberton quartz samples. (a) Isotope spectrum of xenon in Barberton quartz samples (error-weighted average on 27 measurements) relative to the isotopic composition of the modern atmosphere and expressed using the delta notation \((\delta ^{129}\text{Xe}_{\text{air},\text{corr}} = (\langle {Xe^{129}/Xe^{130}} \rangle_{\text{Barb./}}/\langle Xe^{129}/Xe^{130} \rangle_{\text{air}, -1} - 1) \times 1000\)). The computed isotopic fractionation \((12.9 \pm 2.4 \text{% u}^{-1} (\pm \text{2u}))\) is shown as a red line with its 2σ error envelope in blue. The dashed line corresponds to the isotopic fractionation of SW-Xe relative to the air (38 %u^{-1}, ref. 33). MSWD is mean square weighted deviation. Note the depletion in \(^{129}\text{Xe}\) relative to the Archean atmosphere. Errors at 2σ. (b) Isotope spectrum of \(^{128}\text{Xe}\) and \(^{129}\text{Xe}\) normalized to the isotopic composition of the modern atmosphere (see above) in Barberton quartz samples and corrected for the isotopic fractionation of \(12.9 \pm 2.4 \text{% u}^{-1} (\pm \text{1σ, s.e.m.})\) \((\delta ^{129}\text{Xe}_{\text{air},\text{corr}})\). The \(^{129}\text{Xe}\) depletion \((-6.6 \pm 1.8 \text{% u} (\pm \text{1σ, s.e.m.}))\) corresponds to a degassing rate of \(8 \pm 4 (\pm \text{1σ, s.d.) mol a}^{-1}\) of radiogenic \(^{129}\text{Xe}\) produced by the decay of now extinct \(^{82}\text{Kr}\) \((T_{\text{1/2}} = 16 \text{Ma})\). Errors at 1σ.

Figure 5 | Isotopic ratios of krypton in fluid inclusions of Barberton quartz crystals. Isotopic ratios are expressed with the delta notation relative to \(^{84}\text{Kr}\) and to the isotopic composition of the modern atmosphere. The dashed line represents the isotopic fractionation measured for \(^{130}\text{Xe}\) \((13 \text{% u}^{-1})\) propagated towards \(^{130}\text{Kr}\) following a mass fractionation law proportional to \(m^{1/2}\). Errors at 2σ.

is estimated at \(527 \pm 102 \text{ mol a}^{-1}\) (ref. 36). Estimates for the mantle \(^{138}\text{Xe}^{3}\text{He}\) ratio range from \(0.85 \times 10^{-3}\) to \(3.5 \times 10^{-3}\) (refs 37–39) and values between 1.29 and 1.7 for the \(^{129}\text{Xe}(\text{I})/^{130}\text{Xe}\) (ref. 40), this leads to a modern degassing rate of \(1.37 \pm 0.88 (\pm 1\text{σ, s.d.) mol a}^{-1}\) of \(^{129}\text{Xe}(\text{I})\). By comparison our past degassing rate integrated over the last 3.3 Ga would have been \(8.1 \pm 3.9 (\pm 1\text{σ, s.d.) times higher than the present one. Taking a recent estimate of 450 \pm 50 \text{ mol a}^{-1}\) for the degassing of \(^{3}\text{He}\) (ref. 41) leads to similar results with a past degassing rate \(9.5 \pm 4.5 (\pm 1\text{σ, s.d.) higher than the present one. It is worth noting that the modern degassing rate was computed for the upper-mantle flux only, and whole mantle degassing might have played a major role in the past. A degassing rate up to 14 times the modern one is in agreement with elevated volumetric production rates inherent in convection models proposed for the early Earth (for example, ref. 42) and with degassing rates required to keep a significant portion of primordial \(^{3}\text{He}\) in the Earth’s mantle\(^{3}\). A higher degassing rate during the last 3.3 Ga is also consistent with a more convective mantle\(^{44}\), sustained, for example, by a higher radioactive heat production from parent nuclides (\(^{40}\text{K}, \text{238–235U, 232Th}\) (for example, ref. 45).

Depletions in \(^{134}\text{Xe}\) and \(^{136}\text{Xe}\) for the primordial component similar to U-Xe as recorded by Barberton quartz may reflect either a mass-independent isotope fractionation process, not yet identified, or the presence of a nucleosynthetic anomaly (for example, r-process deficit) in the early atmosphere compared with other major components of the solar system (Chondritic or Solar Xe). This nucleosynthetic anomaly is problematic, as the contribution from meteorites, in particular the carbonaceous chondrites during the final stages of Earth’s accretion is usually advocated to explain the abundances of volatile elements on Earth\(^{10}\). However, neither carbonaceous chondrites nor any other meteorite group contain U-Xe. Comets are primitive volatile-rich objects in the solar system that potentially may carry such an exotic primordial component, possibly inherited from other planetary systems formed in the vicinity of our Sun\(^{46}\). The abundances of the heavy noble gases in comets are not well constrained (only Ar has been measured so far\(^{9}\) and their capacity to transport noble gases will be highly dependent on the physical state of the ice (amorphous ice vs. clathrates). However, a rough estimate of the composition of these objects can be made (Supplementary Tables 4 and 5) based on experimental studies and on the results of the Rosetta space mission\(^{4}\) (see Supplementary Discussion in Supplementary Information).
and Supplementary Fig. 6). If Xe is present as amorphous ices in comets, then a 10% cometary contribution to a mass flux similar in magnitude to the Terrestrial Late Heavy Bombardment (2 \times 10^{24} \text{ g}, see Supplementary Information), added to the Earth following Moon formation, would be sufficient to bring the current budget of atmospheric Xe. For Xe contained in cometary clathrates, a 10% cometary contribution could deliver up to two orders of magnitude higher Xe than the surficial budget of Xe corrected for the loss (Supplementary Fig. 6). Thus, even if the nature of the late accreting events is not well constrained, comets may have contributed significantly to the budget of atmospheric noble gases, and specially Xe, after the Moon formed (Supplementary Fig. 6)!

The emerging picture for the history of Xe on Earth is schematically depicted in Fig. 10. The Earth accreted Chondritic heavy noble gases Xe (ref. 8) and Kr (ref. 7) still present in the modern mantle. Atmospheric Xe is not derived from Solar/Chondritic sources but from U-Xe, an exotic Xe component that may have been contributed by cometary bodies. The dichotomy for Xe between the primitive components stored in the mantle and in the atmosphere may thus be explained by distinct mixing for the two reservoirs: Solar/Chondritic for the Earth’s mantle and Chondritic/Cometary for the atmosphere. The latter was already present 3.3 Ga ago. If this component was contributed by late bombardment events, these events must have preceded the formation of Barberton terranes, and could have occurred during the Late Heavy Bombardment of the Earth around 3.87 Ga ago, or earlier. At 3.3 Ga, atmospheric Xe had not reached its modern fractionated composition and subduction of ancient atmospheric Xe must have been limited to reconcile Xe data on mantle-derived samples (Fig. 10a).

The intense 129Xe(I) degassing rate of 8 ± 4 (± 1σ, s.d.) mol a⁻¹ integrated over 3.3 Ga probably reflects degassing of the whole mantle in the active early Earth. The overall budget and isotopic composition of modern terrestrial xenon (Fig. 10b) have thus probably been shaped by various contributions of cosmochemical sources (Chondritic and possibly Cometary), atmospheric escape processes and complex

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**Figure 7** | Schematic view of the successive steps leading to the determination of the initial 136Xe/130Xe for the ancient atmosphere trapped in Barberton quartz. (a) The starting point uses only one data, the isotopic composition of Xe in Barberton quartz (the isotopic composition of the atmosphere is shown only for comparison) and makes the assumption that the starting 133Xe/130Xe is identical to SW-Xe (dashed line with the green range corresponding to the 2σ error of SW-Xe, ref. 33). (b) The dotted line and the grey range represents the production of 132Xe and 136Xe by the spontaneous fission of 238U. Barberton quartz samples exhibit these excesses and must, therefore, lie on this line. (c) The dotted line and the grey range represents the initial 132Xe/130Xe for Xe in Barberton quartz before addition of fission products. It was obtained by applying the mass fractionation recorded on stable isotopes 129Xe and 128Xe. (d) The intersection of the black line and the green range is used to estimate the primordial 136Xe/130Xe ratio for the Earth’s atmosphere before the progressive mass-dependent isotopic fractionation occurred as recorded in Barberton quartz. The resulting space of possibilities (range at 2σ) appears in pink. The purple square corresponds to the isotopic composition of U-Xe (ref. 13).

**Figure 8** | Three-isotope plot of Xe. This figure demonstrates how the Archean atmospheric xenon trapped in Barberton quartz can only be produced by mass-related isotopic fractionation (black line) of a starting isotopic composition (pink area) similar to U-Xe (purple square) followed by the addition of xenon from the spontaneous fission of 238U (brown line). Mass-dependent isotopic fractionation (dashed and dotted lines) of SW-Xe (Solar Xe, blue square) and of Q-Xe (Chondritic Xe, green square) cannot lead to the isotopic compositions of Barberton or of the modern atmosphere. The grey area represents the range for the non-fissiogenic 132Xe/130Xe ratio of Barberton Xe obtained after propagation of the isotopic fractionation relative to SW-Xe measured on light Xe isotopes. Errors at 2σ.

**Figure 9** | Fission spectrum of Barberton Xe corrected for mass-fractionation relative to a starting isotopic composition similar to U-Xe. It corresponds to spontaneous fission of 238U. The fission spectra for fission of 238U and 244Pu are from a compilation in ref. 56. Errors at 2σ.
The abundances of Ca and Cl in samples can also be determined from Hb3gr using additional irradiation parameters, \( x \) (ref. 51) and \( \beta \) (ref. 52) (equations 2 and 3):

\[
\frac{K}{Ca} = x \frac{\text{Ar}_{\text{K}}}{\text{Ar}_{\text{Ca}}}
\]  

(2)

\[
\frac{K}{Cl} = \beta \frac{\text{Ar}_{\text{K}}}{\text{Ar}_{\text{Cl}}}
\]  

(3)

The abundances (in wt.%) of K, Ca and Cl in Hb3gr are, respectively, 1.247 ± 0.008, 7.45 ± 0.09 and 0.2379 ± 0.0032 (ref. 53). Analyses of Hb3gr yielded \( x \) values of 0.473 ± 0.002 (top) and 0.497 ± 0.002 (bottom). \( \beta \) values are 1.271 ± 0.018 (top) and 1.263 ± 0.019 (bottom).

Thus in units of moles cm\(^{-3}\) STP:

\[
K = (3.66 ± 0.03) \times \frac{[^{36}\text{Ar}]}{J}
\]  

(4)

\[
Ca = (3.57 ± 0.03) \times \frac{[^{37}\text{Ar}]}{J x}
\]  

(5)

\[
Cl = (4.04 ± 0.04) \times \frac{[^{38}\text{Ar}]}{J \beta x}
\]  

(6)

Following irradiation, samples were analysed in two successive steps: (1) step-crushing to release fluids trapped in fluid inclusions; (2) step-heating up to 1,700 °C to release K, Cl and Ar trapped in small inclusions, and present in the quartz lattice. Extraction, purification, measurement and correction techniques are already described elsewhere.

Results obtained for samples BMGA3-9, BMGA3-13 and BMGA3-3 are listed in Supplementary Table 1. The \( ^{40}\text{Ar}^{36}\text{Ar} \) ratios measured during the crushing and step-heating experiments are high (up to about 8,500) and cannot be solely explained by \( \text{in situ} \) decay of \(^{40}\text{Ar} \) even during 4.5 Ga. This \(^{40}\text{Ar} \) excess, referred to as \( ^{40}\text{Ar}_{\text{excess}} \), hereafter, is correlated to the chlorine content (Figs 1 and 2) and probably linked to a hydrothermal fluid circulation through the samples. One of the methods to correct the data for this \( ^{40}\text{Ar}_{\text{excess}} \) contribution is to use the K-Cl-\( ^{40}\text{Ar} \) (x-y-z) space where crushing and step-heating data would lie on a plane with the following equation (equation 7):

\[
\frac{^{40}\text{Ar}}{^{36}\text{Ar}} = \frac{^{36}\text{Ar}_{\text{in situ}}}{^{36}\text{Ar}} + A \times \frac{\text{Cl}_{\text{in situ}}}{^{36}\text{Ar}_{\text{in situ}}} + B \times \frac{\text{K}_{\text{in situ}}}{^{36}\text{Ar}_{\text{in situ}}}
\]  

(7)

where \( \frac{^{36}\text{Ar}_{\text{in situ}}}{^{36}\text{Ar}} \) and \( \frac{\text{Cl}_{\text{in situ}}}{^{36}\text{Ar}_{\text{in situ}}} \) are obtained during measurements (Supplementary Table 1). \( ^{36}\text{Ar}_{\text{in situ}} \) is the initial ratio trapped in the sample, \( A \) represents the correlation between \( ^{40}\text{Ar}_{\text{excess}} \) and the chlorine content, and \( B (= ^{40}\text{Ar}_{\text{excess}}/\text{K}) \) reflects the relationship between \( \text{in situ} \) produced \( ^{40}\text{Ar} \) (\( ^{40}\text{Ar}_{\text{excess}} \)) and the potassium content computed from the abundance of \(^{36}\text{Ar} \) produced by neutron irradiation. The errors on the parameters of the plane defined by the data points were determined by a Monte Carlo propagation method using a Matlab code. First, for each point, coordinates on the \( x, y \) and \( z \) axes were divided by the mean error of the data set for normalization purpose. This was done to avoid overestimation of residuals resulting from different scale ranges (Supplementary Table 1). For each point a randomly generated cloud of 5,000 points was then created in order to properly describe the error surface fitting ‘sft’ of Matlab was applied to the 80,000 points. ‘sft’ is a total least squares regression method through the entire cloud of points, the robust option permitting removal of outliers on an iterative basis based on least absolute residuals. Plots of residuals are shown in Supplementary Fig. 2. The fitting method led to a \( ^{40}\text{Ar}_{\text{K}}/\text{K} \) value of 6.63 × 10\(^{-5} \) (± 8 × 10\(^{-6} \), 2\( \sigma \), s.e.m.) for B that formally corresponds to an age of 3.3 (± 0.1) Ga (2\( \sigma \), s.e.m.). A more precise initial \( ^{40}\text{Ar}_{\text{excess}}/\text{K} \) trapped in Barberton quartz, is 45±8 (2\( \sigma \), s.e.m.) higher than the present day atmospheric value of 298.6. This higher value is almost certainly due to some \( ^{40}\text{Ar} \) excess remaining even after correction for \( ^{40}\text{Ar}_{\text{excess}} \) linked to the chlorine content (Supplementary Fig. 3) and for radiogenic \( ^{40}\text{Ar} \) from \( \text{in situ} \) decay of \( ^{40}\text{K} \) during 3.3 Ga. The code used in this section is available through requests to G.A. (gavice@caltech.edu).

A second method originally proposed by Pujol et al.\(^{20}\) has been applied to sample BMGA3-13 for which \( ^{40}\text{Ar}_{\text{excess}} \) is less evidently linked to the Cl content but \( ^{40}\text{Ar}_{\text{K}}/\text{K} \) measured during experiments are lower (see Fig. 1, Supplementary Fig. 3 and results in Supplementary Table 1). Crushing and step-heating results show a similar correlation in the \( ^{40}\text{Ar}_{\text{Cl}}-\text{Cl} \) diagram (Fig. 1). A Cl-\( ^{40}\text{Ar}_{\text{excess}} \) ratio of 6,500 ± 949 was thus obtained from analysis of crushing results. Second, this ratio was used to subtract \( ^{40}\text{Ar}_{\text{excess}} \) using the chlorine content released during each heating step multiplied by \( ^{40}\text{Ar}_{\text{K}}/\text{K} \). A set of initial \( ^{40}\text{Ar}_{\text{K}}/\text{K} \) ratios and times of fluid entrapments for \( \text{in situ} \) decay of \(^{40}\text{K} \) were then manually tested. A best solution was found for an initial atmospheric \( ^{40}\text{Ar}_{\text{K}}/\text{K} \) ratio of 202 ± 58 (2\( \sigma \), s.e.m.) for a fluid entrapment at 3.5 ± 1.0 Ga (2\( \sigma \), s.e.m.) with a MSWD of 1.06. This age, although less precise, is in agreement with the age of 3.3 ± 0.1 Ga (2\( \sigma \), s.e.m.) determined with the 3D correlation method applied to sample BMGA3-9. A more precise initial atmospheric ratio can be computed by taking an age of 3.3 ± 0.1 Ga (2\( \sigma \), s.e.m.). It should be noted that error correlations are
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Author contributions

G.A. and B.M. collected the samples. G.A. and R.B. performed the experiments. G.A., R.B. and R.M. analysed the data and wrote the paper.

Additional information

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