

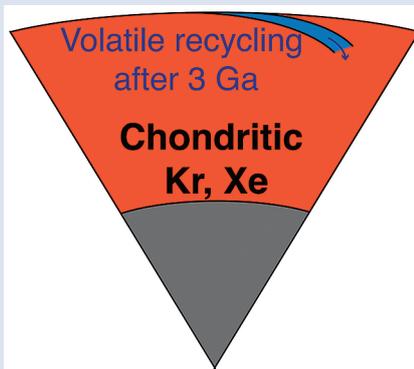
# Onset of volatile recycling into the mantle determined by xenon anomalies

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## Abstract



the mantle to be constrained at around 3 Gyr ago, implying that volatile recycling before 3 Ga would have been negligible.

Noble gases serve as unique tracers of the origin and evolution of Earth's volatile reservoirs owing to their inert nature and contribution from extinct and extant radioactivities. However, noble gases are low in abundance relative to many other elements, particularly in the Earth's mantle. Additionally, mantle-derived samples show large post-eruptive atmospheric contamination, rendering the determination of the primary mantle composition challenging. The sources of mantle krypton and xenon remain debated due to their partially resolvable excess, if any, relative to the atmosphere. Atmospheric noble gases also appear to be recycled into the mantle *via* subduction, progressively overprinting the initial mantle signature. Here we develop a new protocol to accumulate non-contaminated mantle-derived xenon, in particular the low abundant  $^{124-126-128}\text{Xe}$ . The results show the highest excesses in  $^{124-126-128}\text{Xe}$  ever measured in the mantle relative to the atmosphere and point toward a chondritic origin for mantle xenon. The fissionogenic isotopes  $^{131-132-134-136}\text{Xe}$  allow the onset of efficient xenon recycling in

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## Letter

The inert noble gases (He, Ne, Ar, Kr, Xe) serve as an invaluable tool for constraining the volatile origin and evolution of terrestrial planetary reservoirs. Among them, Xe with its nine isotopes is an ideal tracer of both volatile origin and mantle evolution because all of its isotopes represent distinct geochemical signatures (Kunz *et al.*, 1998; Moreira *et al.*, 1998; Caffee *et al.*, 1999; Holland and Ballentine, 2006; Pujol *et al.*, 2011; Mukhopadhyay, 2012; Tucker *et al.*, 2012; Parai and Mukhopadhyay, 2015, 2018; Avicé *et al.*, 2017; Marty *et al.*, 2017). Indeed,  $^{124-126-128-130}\text{Xe}$  are non-radiogenic, stable isotopes whereas  $^{129}\text{Xe}$  is radiogenic (decay product of the now extinct  $^{129}\text{I}$  radioactivity) and  $^{131-132-134-136}\text{Xe}$  are fissionogenic, both deriving from the fission of the now extinct  $^{244}\text{Pu}$  nuclide (half life 80 Myr) and the still alive  $^{238}\text{U}$  nuclide.

Many studies have focused on the radiogenic and fissionogenic Xe compositions of the Earth's mantle from analyses of mid-ocean ridge basalts (MORBs) (Kunz *et al.*, 1998; Moreira *et al.*, 1998; Parai *et al.*, 2012; Tucker *et al.*, 2012; Parai and Mukhopadhyay, 2015), plume-influenced back-arc basin basalts (Petö *et al.*, 2013), oceanic island basalts (OIBs) (Poreda and Farley, 1992; Trieloff *et al.*, 2000, 2002; Mukhopadhyay, 2012),  $\text{CO}_2$  well gases (Caffee *et al.*, 1999; Holland and Ballentine, 2006; Holland *et al.*, 2009) and thermal springs (Caracausi *et al.*, 2016; Moreira *et al.*, 2018) because these isotopes are relatively abundant. However,  $^{124-126-128}\text{Xe}$  isotopes are very rare and thus extremely difficult to measure. Initial studies measured

the abundances of  $^{124-126-128}\text{Xe}$  in mantle-derived samples but proved these to be unresolvable from that of the atmosphere (Kunz *et al.*, 1998). The only successful attempts to resolve  $^{124-126-128}\text{Xe}$  excess have been during the analyses of  $\text{CO}_2$  well gases and thermal springs (Caffee *et al.*, 1999; Holland and Ballentine, 2006; Caracausi *et al.*, 2016). However, recycling of atmospheric xenon *via* subduction into the convecting mantle effectively overprints and erases the primitive mantle signature, as more than 80 % of Xe in the mantle is assumed to be derived through the subduction of oceanic lithosphere (Caffee *et al.*, 1999; Holland and Ballentine, 2006; Mukhopadhyay, 2012; Parai and Mukhopadhyay, 2015). Consequently it has long been assumed that anomalies of  $^{124-126-128}\text{Xe}$  were undetectable in basaltic glasses (Trieloff *et al.*, 2000).

A second issue surrounding the determination of  $^{124-126-128}\text{Xe}$  excess is that basaltic glasses are highly susceptible to post-eruptive contamination by air (Ballentine and Barfod, 2000). Typically air can enter glass samples and be hosted within small cracks and open vesicles (Ballentine and Barfod, 2000), so that when samples are crushed, this air component mixes with mantle gases from intact bubbles, rendering determination of Xe anomalies even more difficult if not impossible.

Here a new protocol is developed to accumulate air-free xenon from intact glass vesicles of MORBs and determine whether  $^{124-126-128}\text{Xe}$  anomalies can be detected in the convecting mantle. To this end, the gas-rich popping rock 2πD43 sample is analysed, which has been extensively studied

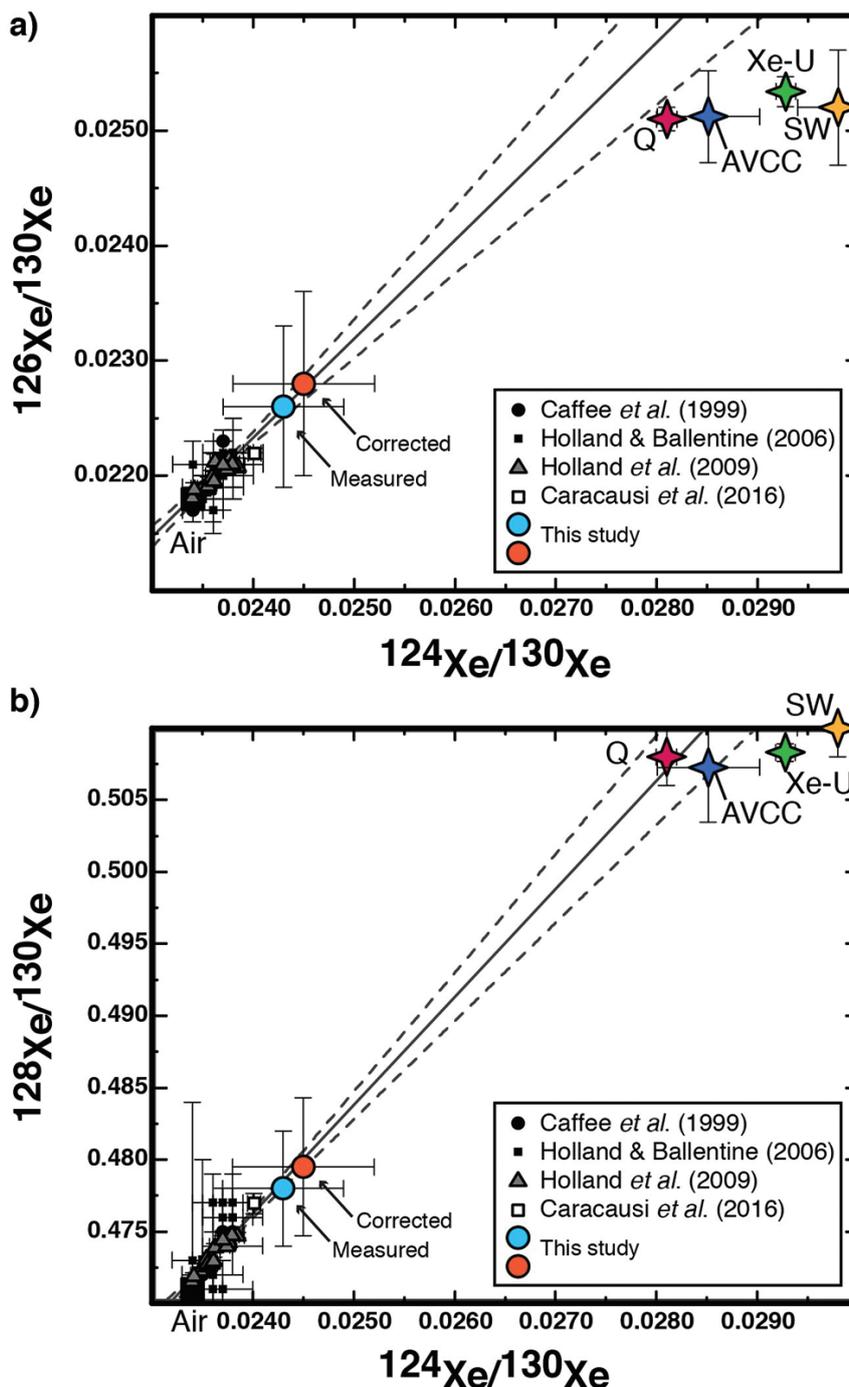
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(Burnard *et al.*, 1997; Kunz *et al.*, 1998; Moreira *et al.*, 1998). The new protocol consists of sequential crushing steps, with the neon composition of each step being used as a monitor of post-eruptive atmospheric contamination, as Ne displays distinct atmospheric and mantle compositions ( $^{20}\text{Ne}/^{22}\text{Ne}$  ratios of 9.8 and 12.5 respectively). If the  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio is higher than 11.8, then the heavy noble gases from each crush step are accumulated on activated charcoal (Fig. S-1 and Supplementary Information).

The results are shown in Figure 1 and in Tables S-1 and S-2. The  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio of the accumulated gas is  $7.41 \pm 0.03$

( $1\sigma$ ), showing limited atmospheric contamination. Indeed the upper mantle  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio is assumed to be 7.6 based on previous popping rock 2 $\pi$ D43 data (Moreira *et al.*, 1998). The measured xenon isotopic ratios are hence corrected for this limited atmospheric contamination (17%), assuming that the uncontaminated  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio is 7.6 (Table S-1) and the two data (measured and corrected) are indicated in Figure 1. The high measured  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio (7.41) allows checking that the new protocol is very efficient for determining the mantle xenon composition with almost no atmospheric contamination (Fig. S-2).

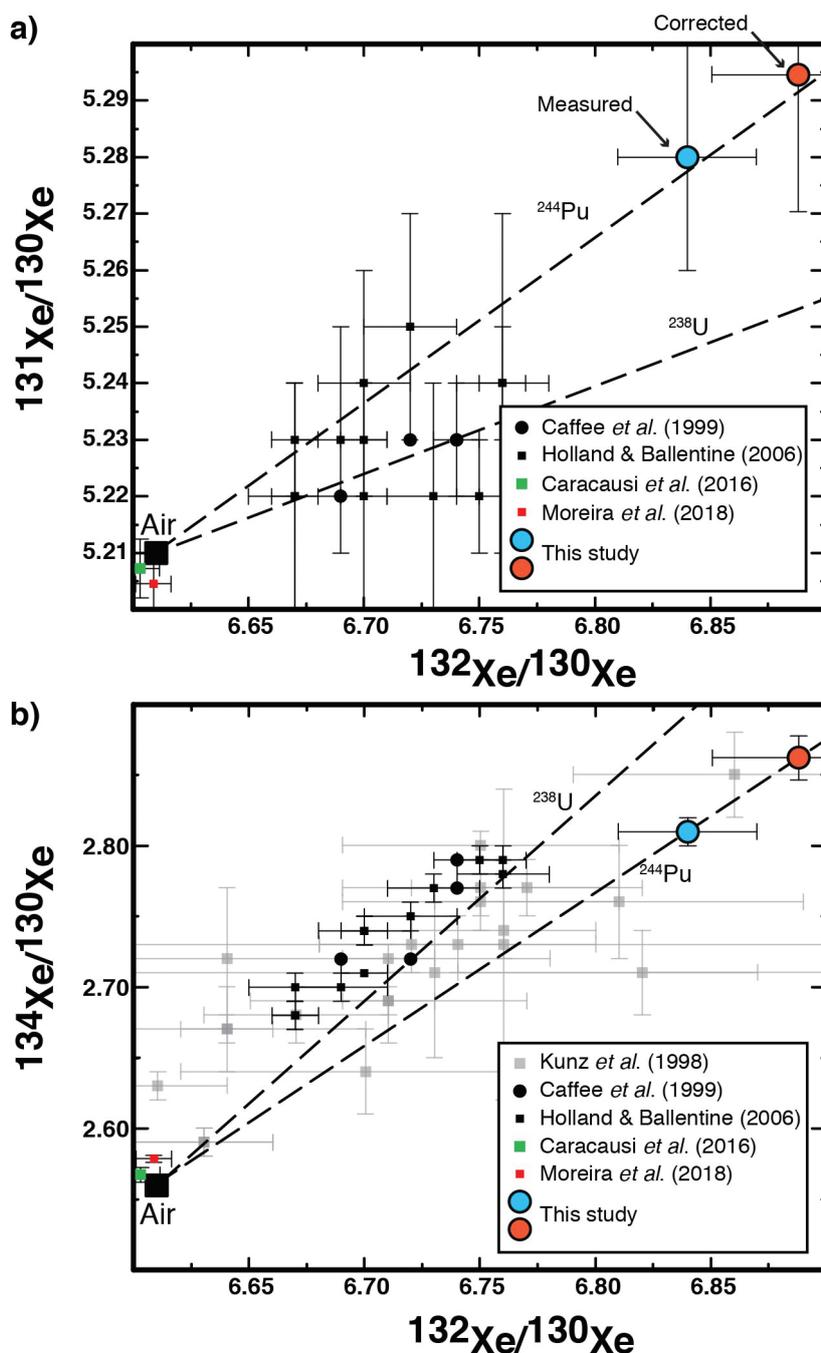


**Figure 1** Light xenon isotopic compositions for popping rock 2 $\pi$ D43. Measured data (blue dot) and corrected data for atmospheric contamination (orange dot) with a  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio of 7.6: (a)  $^{126}\text{Xe}/^{130}\text{Xe}$  and (b)  $^{128}\text{Xe}/^{130}\text{Xe}$  versus  $^{124}\text{Xe}/^{130}\text{Xe}$ . For comparison, data of CO<sub>2</sub> well gases from Caffee *et al.* (1999) (black points), Holland and Ballentine (2006) (black square) and Holland *et al.* (2009) (grey triangles), and thermal springs from Caracausi *et al.* (2016) (green square) and Moreira *et al.* (2018) (red square) are shown. The solid line is a fit of the data, except that of Holland and Ballentine (2006). The dotted lines indicate the 95% confidence interval. Phase Q (Busemann *et al.*, 2000), Solar Wind SW (Meshik *et al.*, 2014), Xe-U and AVCC (Pepin, 2003). These new data suggest a chondritic origin (Phase Q or AVCC) for upper mantle Xe.



An excess in  $^{124-126-128}\text{Xe}$  is clearly observed for sample popping rock 2πD43. This excess is greater than the previously measured excess observed in CO<sub>2</sub> well gases (Fig. 1), and is the first significant  $^{124-126-128}\text{Xe}$  excess measured in a MORB sample. A linear fit through the data suggests a chondritic xenon composition (Phase Q, the main carrier of heavy noble gases in chondrites (Busemann *et al.*, 2000) or AVCC for Average Carbonaceous Chondrites (Pepin, 2003)) for the initial mantle (Fig. 1) rather than Solar Wind. This seems also to be the case for Kr (Fig. S-3 and Table S-2). A chondritic origin of mantle Xe (Caracausi *et al.*, 2016) and Kr (Holland *et al.*, 2009) was first suggested based on analyses of CO<sub>2</sub> well gases

and thermal springs. However, the excesses in  $^{124-126-128}\text{Xe}$  measured for the Eifel spring (Caracausi *et al.*, 2016) remain questionable given that strong atmospheric contamination is needed to explain the Eifel heavy Xe pattern (Moreira *et al.*, 2018) ( $^{131-136}\text{Xe}$ ; Fig. 2). Therefore, these new data suggest a chondritic origin for upper mantle heavy noble gases. It is however not possible to distinguish between Phase Q and AVCC, contrary to the suggestion that mantle Kr and Xe were derived from material similar to AVCC (Holland *et al.*, 2009). Comets would not have contributed significantly to mantle xenon contrary to atmospheric xenon (Marty *et al.*, 2017, and discussion below).



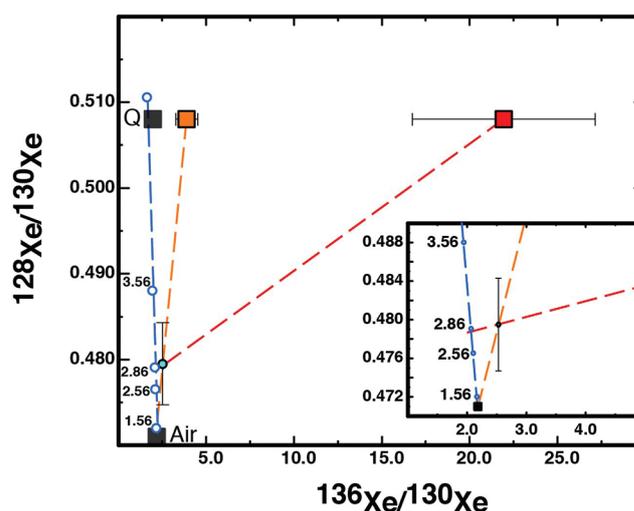
**Figure 2** Heavy xenon isotopic compositions for popping rock 2πD43. Measured data (blue dot) and corrected data for atmospheric contamination (orange dot) with a  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio of 7.6: (a)  $^{131}\text{Xe}/^{130}\text{Xe}$  and (b)  $^{134}\text{Xe}/^{130}\text{Xe}$  versus  $^{132}\text{Xe}/^{130}\text{Xe}$ . Data for sample 2πD43 from Kunz *et al.* (1998), for CO<sub>2</sub> well gases from Caffee *et al.* (1999) (black points), Holland and Ballentine (2006) (black square), and thermal springs from Caracausi *et al.* (2016) (green square) and Moreira *et al.* (2018) (red square) are shown. The trends of pure  $^{244}\text{Pu}$ - and  $^{238}\text{U}$ -derived xenon productions are also indicated. The source of sample 2πD43 seems to be more influenced by Pu-derived Xe than U-derived Xe, contrary to other MORBs (Tucker *et al.*, 2012; Parai and Mukhopadhyay, 2015).



Recycling of atmospheric Xe is required to explain the present day mantle  $^{124-126-128}\text{Xe}$  composition (Fig. 1) (Caffee *et al.*, 1999; Holland and Ballentine, 2006; Mukhopadhyay, 2012; Parai and Mukhopadhyay, 2015; Caracausi *et al.*, 2016). The fissionogenic mantle  $^{131-136}\text{Xe}$  (Fig. 2) is considered to reflect mixing of four components, namely initial Xe, recycled atmospheric Xe, Pu-derived Xe and uranium-derived Xe. The contributions of each of these four components was deconvoluted in mantle-derived samples (Caffee *et al.*, 1999; Mukhopadhyay, 2012; Tucker *et al.*, 2012; Petö *et al.*, 2013; Parai and Mukhopadhyay, 2015; Caracausi *et al.*, 2016), in an attempt to determine the ratio of Pu- to U-derived Xe in mantle sources and so better constrain their degassed states, a higher Pu- to U-derived Xe ratio reflecting a less degassed source due to the fact that  $^{244}\text{Pu}$  is now extinct. The new data shown in Figures 2 and S-4 suggest that the source of the popping rock 2 $\pi$ D43 is more heavily influenced by Pu-derived Xe than U-derived Xe, contrary to other MORBs (Tucker *et al.*, 2012; Parai and Mukhopadhyay, 2015).

Incorporation of atmospheric Xe into the mantle is further complicated by the fact that the Xe composition of the atmosphere has changed over time (Pujol *et al.*, 2011; Avice *et al.*, 2017, 2018; Bekaert *et al.*, 2018), starting with the composition of the primordial U-Xe component (Pepin, 2003) and reaching the present day composition, enriched in heavy isotopes by about 40 per mille  $\text{u}^{-1}$  compared with U-Xe, around 2 Gyr ago (Avice *et al.*, 2018). The U-Xe component was first theoretically suggested to explain the Xe isotopic pattern of the atmosphere (Pepin, 2003) and measurements of Xe in comet 67P/C-G reveal that U-Xe could be a mixture of chondritic and cometary volatiles (Marty *et al.*, 2017). Xenon loss from the atmosphere to the outer space accompanied by isotopic fractionation could explain this evolution even if the physical process leading to this loss is still debated (Avice *et al.*, 2018). Such an evolution renders a precise deconvolution of the contributions of the aforementioned four components to the mantle Xe array very difficult, because the isotopic composition of recycled atmospheric xenon strongly varied over time, whilst the mantle has continuously lost Pu- and U-derived Xe alongside initial Xe through degassing. Therefore, results from previous studies (Caffee *et al.*, 1999; Mukhopadhyay, 2012; Tucker *et al.*, 2012; Petö *et al.*, 2013; Parai and Mukhopadhyay, 2015; Caracausi *et al.*, 2016) may be biased and may not precisely estimate the ratio of Pu- to U-derived Xe in the mantle. A recent study modelled the xenon isotopic composition of the mantle taking into account degassing and regassing with an evolving xenon atmospheric composition and found that xenon recycling would have been significant after 2.5 Gyr ago (Parai and Mukhopadhyay, 2018).

Here, the limits on the mantle composition without regassing and the limit on the weighted average age of recycled air are determined, considering the evolution of the Xe atmospheric composition. First, the evolution of the Xe atmospheric isotopic ratios are derived based on a power law for the Xe fractionation factor (Bekaert *et al.*, 2018). The data corrected for shallow atmospheric contamination (Fig. 1 and Table S-1) is considered in a  $^{128}\text{Xe}/^{130}\text{Xe}$  vs. R space, where R represents the ratio of one fissionogenic Xe isotope ( $^{131,132,134,136}\text{Xe}/^{130}\text{Xe}$ ; Fig. 3). The corrected fissionogenic data are thus extrapolated to an initial chondritic (Phase Q)  $^{128}\text{Xe}/^{130}\text{Xe}$  for the mantle, as the data in this contribution point to a chondritic origin, considering mixing with the atmosphere to determine the mantle R ratio before recycling. This mixing relationship is calculated for different air compositions through time (Fig. 3), with the minimum R ratio being obtained if only present day air has been recycled and the maximum ratio represents the scenario if only ancient air has been recycled (Figs. S-5, S-6 and Supplementary Information).



**Figure 3** Determination of the maximum average age of recycled atmosphere in the mantle. The evolution of the xenon atmospheric composition is represented with the blue dashed line with the numbers indicating the time in Gyr (a power law was considered; Bekaert *et al.*, 2018). The corrected data for shallow atmospheric contamination is shown (light blue dot). The minimum ( $3.9 \pm 0.6$  ( $1\sigma$ ); orange square) and maximum ( $21.9 \pm 5.2$  ( $1\sigma$ ); red square)  $^{136}\text{Xe}/^{130}\text{Xe}$  ratios in the mantle before recycling of atmospheric xenon are calculated considering mixing with air (orange and red dashed lines) and that the initial  $^{128}\text{Xe}/^{130}\text{Xe}$  is chondritic (Phase Q; Busemann *et al.*, 2000). The red line suggests that recycling of atmospheric xenon could have been effective only since  $2.8 \pm 0.3$  ( $1\sigma$ ) Gyr ago. Otherwise, unreasonable values of  $^{136}\text{Xe}/^{130}\text{Xe}$  ratios are obtained.

The maximum air-corrected mantle  $^{131-136}\text{Xe}/^{130}\text{Xe}$  ratios (Figs. S-5, S-6) are determined for a recycling of air at  $2.8 \pm 0.3$  ( $1\sigma$ ) Gyr ago (Fig. 3). This represents a limit on the weighted average age of recycled atmosphere retained in the mantle. Ancient atmospheric gas could have been recycled but not enough to draw this average above 2.8 Ga, otherwise the slopes of the mixing lines between ancient air and the corrected data would be negative (Figs. 3, S-7).

Modelling results suggest that effective recycling of Xe, and likely of other noble gases, could not have started before 2.8 Ga. This result is consistent with the mantle evolving to a net regassing regime after 2.5 Ga (Parai and Mukhopadhyay, 2018). This time limit places important constraints on volatile evolution. Either it is consistent with studies that showed that subduction on Earth started around 3 Gyr ago (*e.g.*, Dhuime *et al.*, 2012), or subduction started earlier (*e.g.*, Harrison *et al.*, 2005) but volatile recycling was only efficient from 3 Ga. In the latter case, the delayed efficient recycling of volatiles could be related to the secular cooling of the Earth as it was suggested that noble gases and other volatiles such as water would mainly be recycled into the mantle through cold subduction zones (van Keken *et al.*, 2011; Parai and Mukhopadhyay, 2015; Smye *et al.*, 2017), while it is likely that early subduction was dominated by hot slabs (van Keken *et al.*, 2011).

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## Additional Information

**Supplementary Information** accompanies this letter at <http://www.geochemicalperspectivesletters.org/article1833>.



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## ■ Onset of volatile recycling into the mantle determined by xenon anomalies

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### ■ Supplementary Information

The Supplementary Information includes:

- Material and Method
- Tables S-1 to S-2
- Figures S-1 to S-9
- Supplementary Information References

#### ***Material and Method***

##### **Sample**

Fresh, centimetre-sized glass pieces of popping rock 2πD43 sample (Bougault *et al.*, 1988; Sarda and Graham, 1990; Javoy and Pineau, 1991; Moreira *et al.*, 1998) were selected. This basaltic glass sample from the Mid-Atlantic Ridge (around 14 °N) has a huge vesicularity, around 16 % (Sarda and Graham, 1990), and so is very rich in noble gases, making it the best sample to test a protocol for accumulating xenon.

Glass pieces were cleaned in oxalic acid (1 %) on a hot plate (60-80 °C) and then in ethanol and acetone.

Then pieces were loaded into two crushers (1.6867 g and 0.9647g respectively) for noble gas analyses and baked at 100 °C for several days in order to remove weakly bonded atmospheric gases.

##### **Step-crushing analyses**

The two crushers were connected to the Helix SFT (ThermoScientific) vacuum line in the IPGP laboratory (Fig. S-8). Gases were extracted from samples in several crushing steps. For each step, the extracted gases were first purified successively on two titanium sponges (first at 800 °C for five minutes and then at ambient temperature during 10 minutes) to remove all reactive gases. After the double purification, Ar, Kr and Xe were trapped onto the activated charcoal trap 1 (Fig. S-8) at liquid nitrogen temperature. He and Ne were then analysed with the Helix SFT as described by Moreira *et al.* (2018).

If the  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio was higher than 11.8, then Ar, Kr and Xe trapped on the trap 1 were released from the trap and re-trapped on the trap 2 (Figure S-7). Otherwise, Ar, Kr and Xe were pumped. As shown in Figure S-1, this limit allows keeping non-contaminated xenon due to the curvature of the hyperbola, a plateau is reached for low  $^{20}\text{Ne}/^{22}\text{Ne}$  values. However, this limit is too low for argon due to the inverse hyperbola curvature (Fig. S-1) and so argon should show more air contamination, which is the case (Table S-2).



In total, 22 crush steps were conducted and Ar, Kr and Xe were kept on trap 2 for 9 steps (trap 2 remained 25 days in static in total).

Then the setting with the two traps (Trap 1 and 2) was connected to the Noblesse (Nu Instruments) vacuum line for analysis of the accumulated Ar, Kr and Xe. Indeed, the xenon sensitivity on the Noblesse mass spectrometer ( $8.29 (\pm 0.35) \times 10^{-16}$  cc/cps) is more than three times better than that of the Helix SFT. The accumulated gas was analysed the 37<sup>th</sup> day after starting the accumulation protocol. An air standard was used to calibrate sensitivities on the Noblesse mass spectrometer, of which a pipette of 0.410 cm<sup>3</sup> is taken from a 1 L reservoir each time. This air standard was prepared introducing 0.410 cm<sup>3</sup> of air in this 1 L reservoir.

As explained in Moreira *et al.* (2018), data are processed with our home-made software in Matlab©, which in particular allows to interpolate each isotope to the reference isotope for the elements that are analysed in peak-jumping mode (this is the case for Kr and Xe).

The measured accumulated Ar, Kr and Xe were corrected in Tables S-1 and S-2 for the line blank (the blank was less than 1 % for Ar, Kr and Xe). The data was not corrected for a blank of 37 days. But as discussed in the main text, the high  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio of  $7.41 \pm 0.03$  ( $1\sigma$ ) shows that the blank is very limited if one considered that the mantle  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio is 7.6, based on popping rock data (Moreira *et al.*, 1998) (Fig. S-1). To take into account this small atmospheric contamination, the measured xenon isotopic ratios were corrected by extrapolation to a  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio of 7.6 (Table S-1).

The new protocol to measure non-contaminated mantle xenon and krypton appears to be very efficient, since the  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio is very high and also because the new data fall on the same mixing line as defined by mantle-derived samples, among the highest values measured so far (Fig. S-2).

### Calculation of the $^{131-136}\text{Xe}/^{130}\text{Xe}$ ratios in the mantle before xenon recycling

This calculation aims at determining a range for the fissiogenic xenon isotopic ratios ( $^{131-132-134-136}\text{Xe}/^{130}\text{Xe}$ ) in the mantle before air recycling via subduction and a limit on the weighted average age of atmosphere recycling. This is complicated by the fact that the xenon isotopic composition of the atmosphere seems to have changed over time, becoming more enriched in heavy xenon isotopes compared to the starting composition (Pujol *et al.*, 2011; Avice *et al.*, 2017, 2018; Bekaert *et al.*, 2018).

We first used the power law suggested by Bekaert *et al.* (2018) to calculate the xenon isotopic ratios of the atmosphere through time.

Then, a Monte Carlo simulation is performed, consisting of first choosing a value for each isotopic ratio ( $^{128-131-132-134-136}\text{Xe}/^{130}\text{Xe}$ ) in a  $\mu \pm 1\sigma$  space, where  $\mu$  is the corrected data and  $\sigma$  the uncertainty (Table S-1).

The minimum ratios in the mantle before xenon recycling are calculated considering a mixing line passing through the present-day atmosphere and the corrected data. The minimum fissiogenic ratios  $^{131-132-134-136}\text{Xe}/^{130}\text{Xe}$  are obtained by the intersection of this mixing line with the line of Phase Q (chondritic) for the  $^{128}\text{Xe}/^{130}\text{Xe}$  ratio assuming the initial mantle was chondritic as suggested by the new data (Fig. 3 and Fig. S-7).

For deriving the maximum possible ratios in the mantle before xenon recycling, we also considered mixing lines passing through the corrected data and each previous atmospheric composition. As can be seen in Figure 3 and Figure S-7, if a very ancient air composition is taken (at 3.5 Gyr ago for example), the slope of the mixing line is negative, meaning that the initial  $^{128}\text{Xe}/^{130}\text{Xe}$  ratio of the mantle would have been lower than the present-day value, which is not possible. So to calculate the maximum ratios, we considered the first possible mixing line with a positive slope and then the maximum ratios are obtained by the intersection of this mixing line with the line of Phase Q for the  $^{128}\text{Xe}/^{130}\text{Xe}$  ratio (Fig. 3 and Fig. S-7). Hence, this calculation allows to constrain the limit on the weighted average age of atmosphere recycling, that is the earlier time where recycling of xenon started to be efficient. We excluded mixing lines with too small slope ( $< 0.001$ ) giving unrealistically high  $^{131-132-134-136}\text{Xe}/^{130}\text{Xe}$ , but this does not influence the earlier time where effective recycling could have started. We also exclude realizations for which the fissiogenic xenon ratios ( $^{131-134-136}\text{Xe}/^{132}\text{Xe}$ ) do not fall into the triangle defined by Phase Q, pure xenon from fission of  $^{244}\text{Pu}$  and pure xenon from  $^{238}\text{U}$  (Fig. S-9). A total of  $10^5$  realizations were performed, which appear to be more than sufficient to get reproducible results. If only recycling of present-day air occurred, then the minimum  $^{131-132-134-136}\text{Xe}/^{130}\text{Xe}$  ratios would be  $5.6 \pm 0.2$ ,  $8.0 \pm 0.5$ ,  $4.0 \pm 0.5$  and  $3.9 \pm 0.6$  ( $1\sigma$ ) respectively. The maximum air-corrected mantle  $^{131-132-134-136}\text{Xe}/^{130}\text{Xe}$  ratios are determined to be  $10.8 \pm 1.5$ ,  $22.8 \pm 4.3$ ,  $19.4 \pm 4.5$  and  $21.9 \pm 5.2$  ( $1\sigma$ ), respectively (Fig. S-5 and S-6) for a recycling of air at  $2.8 \pm 0.3$  ( $1\sigma$ ) Gyr ago (Fig. 3 and Fig. S-7).

We note that the use of a power law can be debated. Indeed, if the evolution of the atmospheric xenon isotopic composition is due to xenon loss (Hébrard and Marty, 2014; Avice *et al.*, 2018; Zahnle *et al.*, 2019), similar to a Rayleigh distillation process, then an exponential law could be more appropriate. Hence, we also performed all the above calculations with the exponential law fitting U-Xe suggested by Bekaert *et al.* (2018). We found similar results, the maximum  $^{131-132-134-136}\text{Xe}/^{130}\text{Xe}$  ratios being found are  $10.7 \pm 1.5$ ,  $22.6 \pm 4.5$ ,  $19.1 \pm 4.7$  and  $21.7 \pm 5.5$  ( $1\sigma$ ) and the time for the start of volatile recycling efficiency is  $3.2 \pm 0.3$  ( $1\sigma$ ) Gyr ago.



## Supplementary Tables

**Table S-1** Xenon isotopic composition of popping rock 2πD43 analysed via the new protocol to accumulate non-contaminated, mantle xenon. For comparison, the air composition (Basford *et al.*, 1973) (used for the air standard) is indicated, as well as compositions for phase Q (Busemann *et al.*, 2000), the solar wind (Meshik *et al.*, 2014) and U-Xe (Pepin, 2000). Errors are 1 sigma uncertainties.

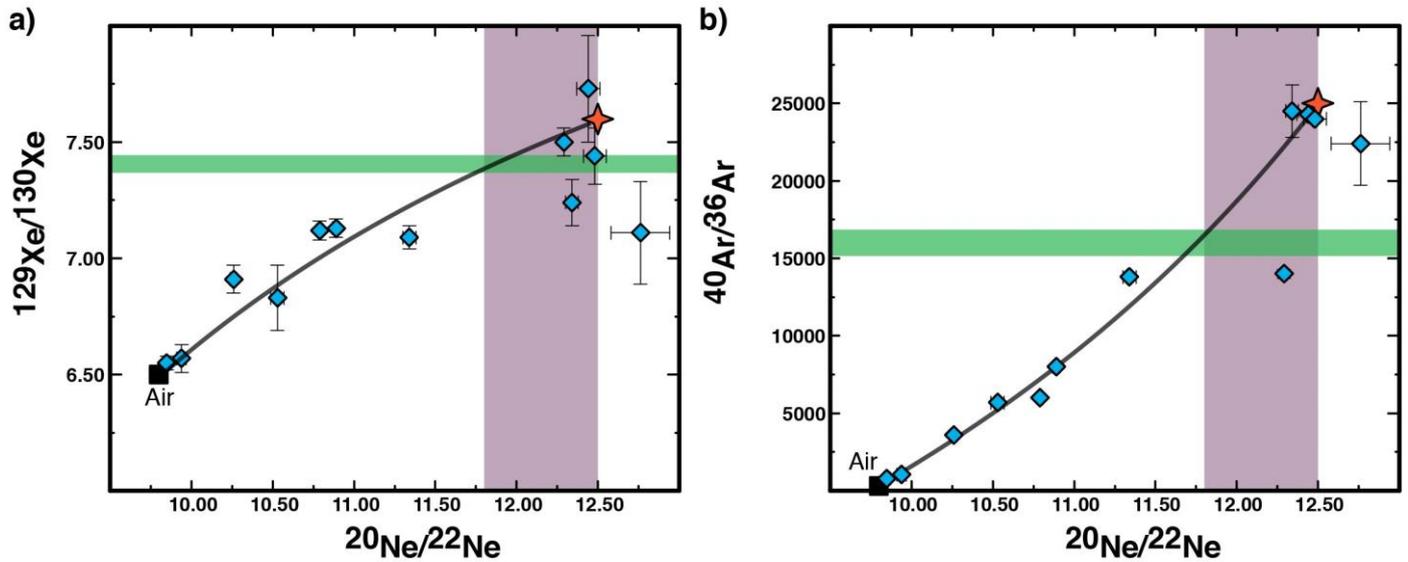
	$^{130}\text{Xe}$ x10 <sup>-12</sup> ccSTP	$^{124}\text{Xe}/^{130}\text{Xe}$	$^{126}\text{Xe}/^{130}\text{Xe}$	$^{128}\text{Xe}/^{130}\text{Xe}$	$^{129}\text{Xe}/^{130}\text{Xe}$	$^{131}\text{Xe}/^{130}\text{Xe}$	$^{132}\text{Xe}/^{130}\text{Xe}$	$^{134}\text{Xe}/^{130}\text{Xe}$	$^{136}\text{Xe}/^{130}\text{Xe}$
2πD43	1.78	0.0243	0.0226	0.478	7.41	5.28	6.84	2.81	2.47
	0.10	0.0006	0.0007	0.004	0.03	0.02	0.03	0.01	0.01
2πD43 corrected		0.0245	0.0228	0.4795	7.6	5.29	6.89	2.86	2.53
		0.0007	0.0008	0.0048	0	0.02	0.04	0.02	0.02
Air		0.0234	0.0218	0.471	6.50	5.21	6.61	2.56	2.18
Phase Q		0.0281	0.0251	0.508	6.44	5.06	6.18	2.33	1.95
Solar wind		0.0298	0.0252	0.510	6.31	5.00	6.06	2.24	1.82
U-Xe		0.02928	0.02534	0.5083	6.286	4.996	6.047	2.126	1.657

**Table S-2** Argon and krypton isotopic compositions of popping rock 2πD43 analysed via the new protocol to accumulate non-contaminated, mantle gases. For comparison, the air composition (Nier, 1950; Basford *et al.*, 1973; Sano *et al.*, 2013) (used for the air standard) is indicated, as well as compositions for phase Q (Busemann *et al.*, 2000) and the solar wind (Meshik *et al.*, 2014). Errors are 1 sigma uncertainties.

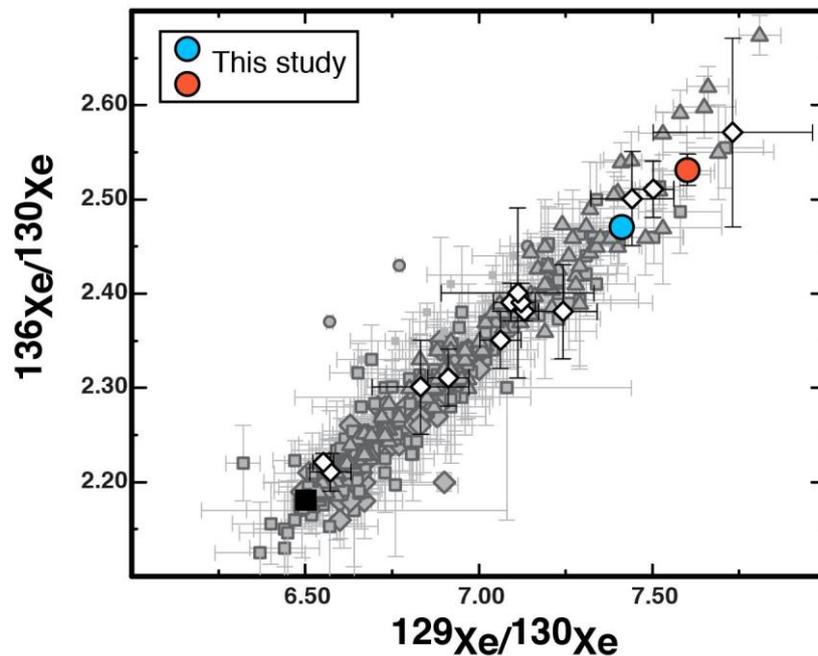
	$^{36}\text{Ar}$ x10 <sup>-9</sup> ccSTP	s	$^{38}\text{Ar}/^{36}\text{Ar}$	s	$^{40}\text{Ar}/^{36}\text{Ar}$	s	$^{84}\text{Kr}$ x10 <sup>-10</sup> ccSTP	s	$^{86}\text{Kr}/^{84}\text{Kr}$	s
2πD43	4.52	0.07	0.1919	0.0006	15169	139	1.59	0.07	0.3059	0.0007
2πD43 (aliquot 2 for Ar only)			0.1895	0.0004	16856	103				
Air			0.1880		295.5				0.3052	
Phase Q			0.1873						0.3095	
Solar wind			0.1814						0.3012	



Supplementary Figures

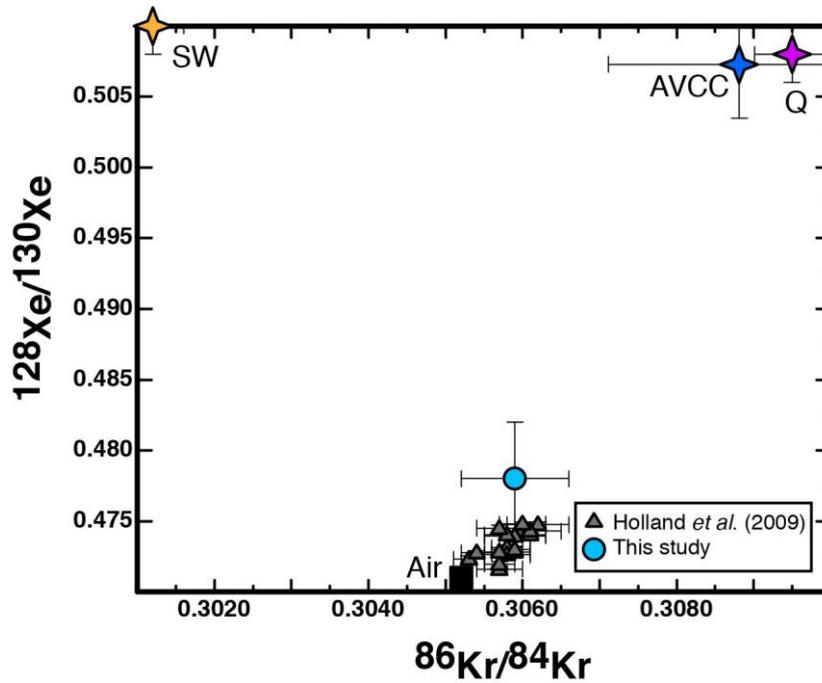


**Figure S-1** Correlation of (a)  $^{129}\text{Xe}/^{130}\text{Xe}$  isotopic ratio and (b)  $^{40}\text{Ar}/^{36}\text{Ar}$  isotopic ratio with the  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio for the popping rock 2πD43 (Moreira *et al.*, 1998). The orange star is the upper mantle composition (Moreira *et al.*, 1998). The pink areas show the  $^{20}\text{Ne}/^{22}\text{Ne}$  range (11.8-12.5) for which Ar, Kr and Xe from crush steps were trapped. If the  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio of one crush step was lower than 11.8, Ar, Kr and Xe were pumped (see text). This  $^{20}\text{Ne}/^{22}\text{Ne}$  range allows keeping only non-contaminated xenon but not for argon given the inverse hyperbola curvature. The green bars correspond to the measured  $^{129}\text{Xe}/^{130}\text{Xe}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios for the accumulated gas from the popping rock 2πD43 (Tables S-1 and S-2).

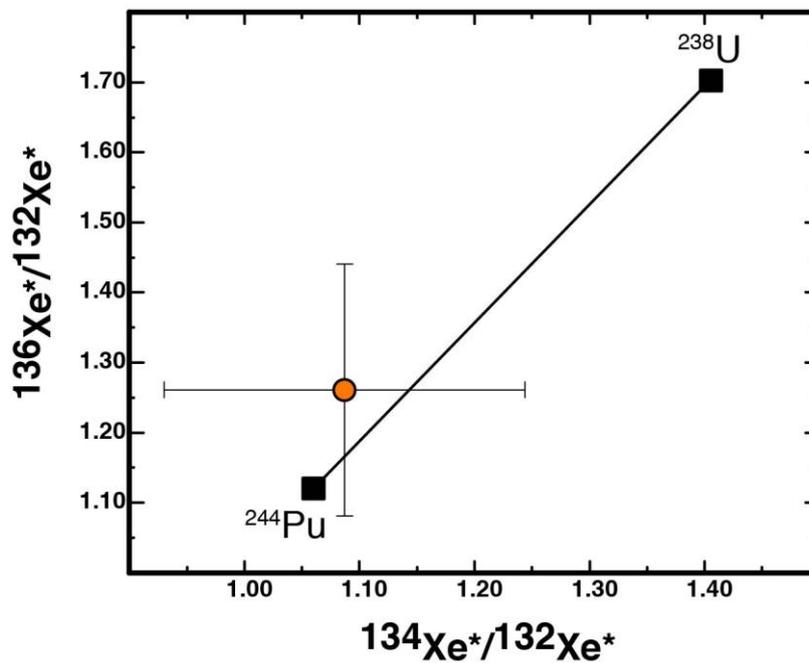


**Figure S-2** Compilation of xenon data for MORBs, OIBs, CO<sub>2</sub> well gases and thermal springs. Data from the literature for MORBs (Kunz *et al.*, 1998; Parai *et al.*, 2012; Tucker *et al.*, 2012; Parai and Mukhopadhyay, 2015), OIBs (Poreda and Farley, 1992; Trieloff *et al.*, 2000; Mukhopadhyay, 2012), CO<sub>2</sub> well gases and thermal springs (Caffee *et al.*, 1999; Holland and Ballentine, 2006; Holland *et al.*, 2009; Caracausi *et al.*, 2016; Moreira *et al.*, 2018) are in grey. Previous data for the popping rock 2πD43 are in open diamonds (Moreira *et al.*, 1998). The measured data with the new protocol is indicated with the blue circle and the corrected data with the orange circle. The new data fall on the same mixing line as previous data. Air (black square).



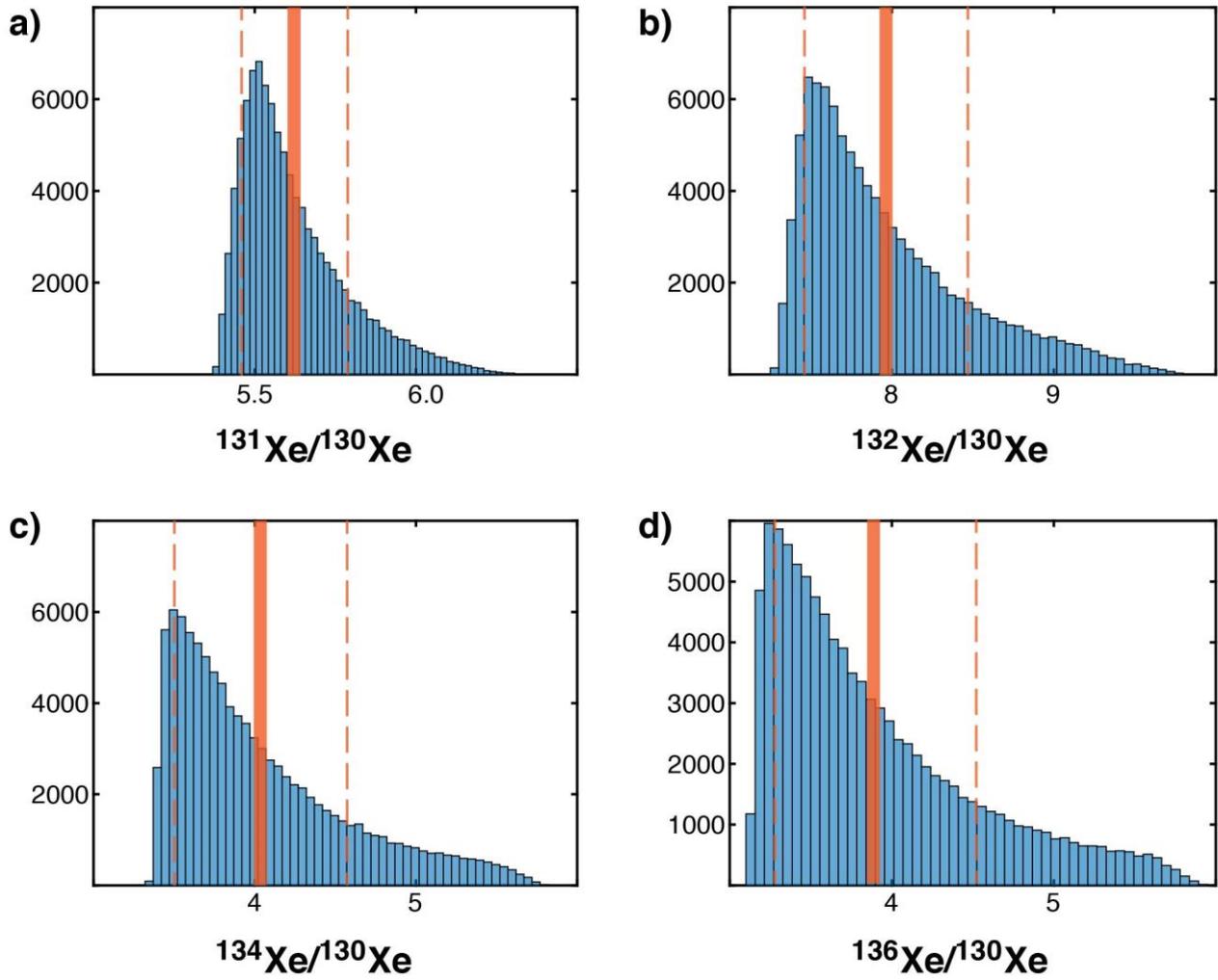


**Figure S-3**  $^{86}\text{Kr}/^{84}\text{Kr}$  versus  $^{128}\text{Xe}/^{130}\text{Xe}$  for popping rock 2πD43 (blue dot) analysed in this study. Data of Holland *et al.* (2009) (corrected for crustal uranium fission, grey triangles) are also shown with the composition of phase Q (Busemann *et al.*, 2000), the solar wind (Meshik *et al.*, 2014) and AVCC for Average Carbonaceous chondrites (Pepin, 2003).

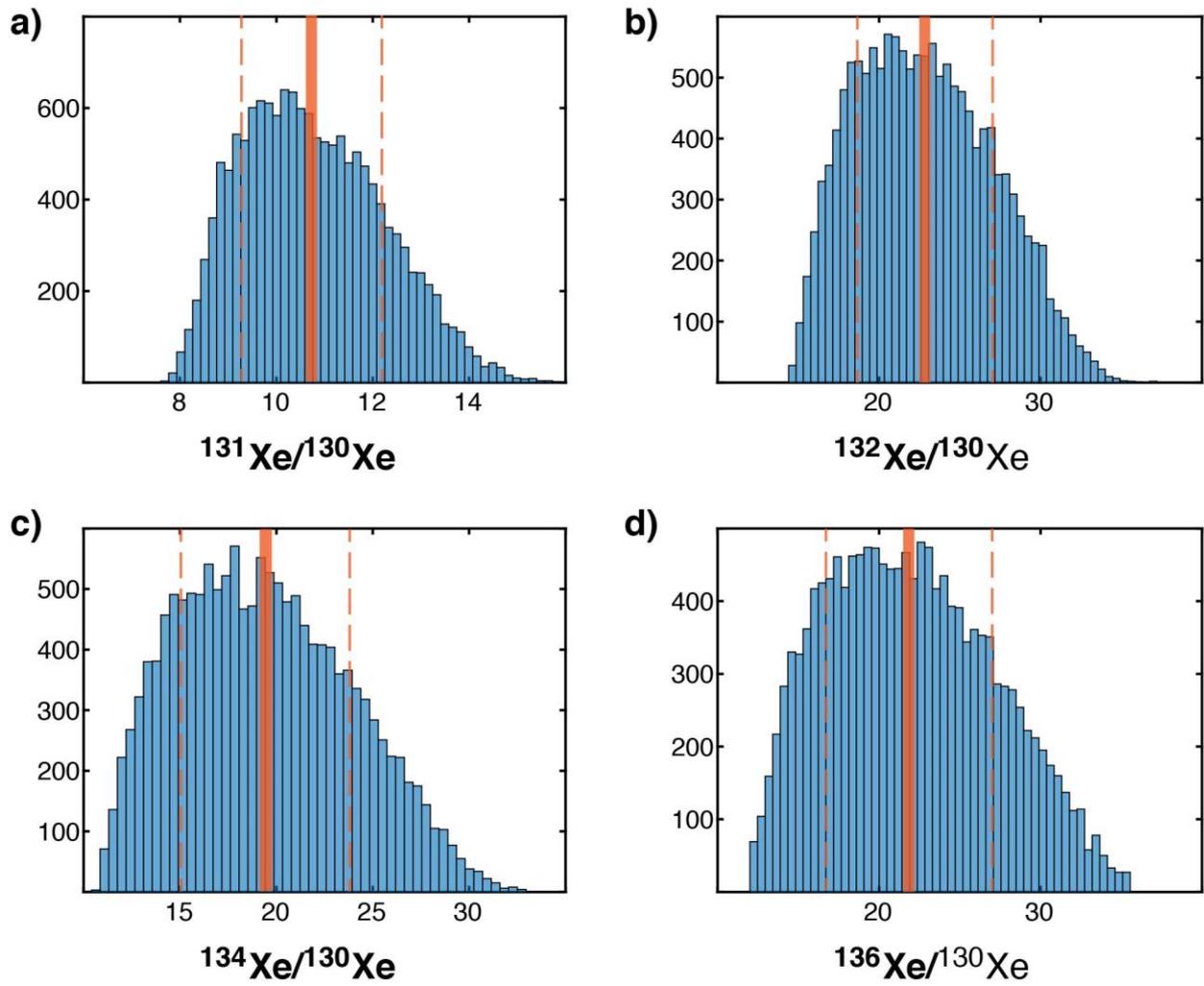


**Figure S-4** Excess of fissiogenic xenon in sample 2πD43 to present-day air. The orange dot is obtained from the popping rock data corrected for atmospheric contamination (see method in Moreira, 2013). The fissiogenic xenon in the 2πD43 source shows more Pu-derived xenon contribution than uranium-derived xenon, contrary to other MORBs data (Tucker *et al.*, 2012; Parai and Mukhopadhyay, 2015).

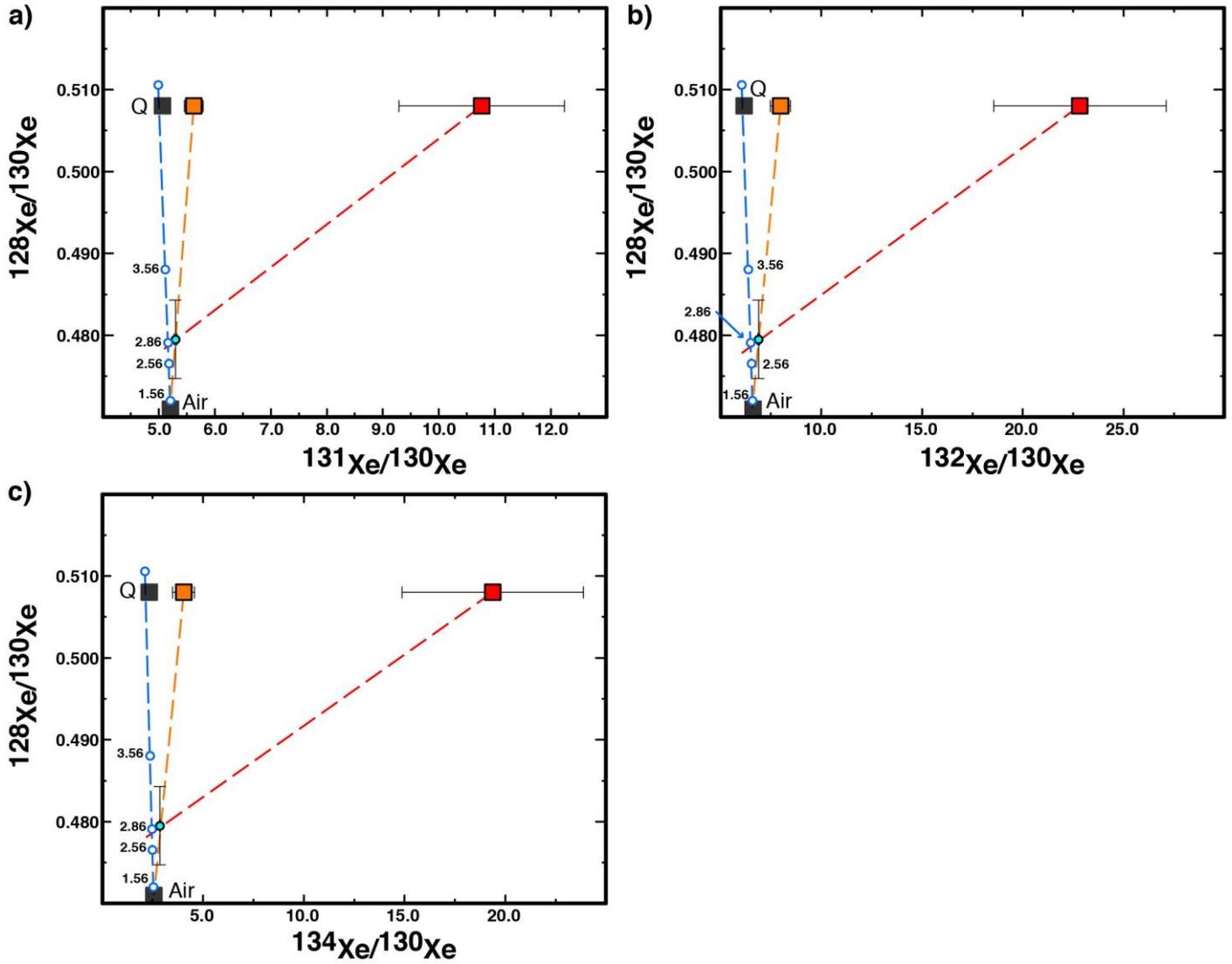




**Figure S-5** Histograms of the Monte Carlo simulations to determine the minimum  $^{131-132-134-136}\text{Xe}/^{130}\text{Xe}$  ratios in the mantle before atmospheric xenon recycling. The orange bars show the mean values and the orange dotted lines the 1 sigma uncertainties.

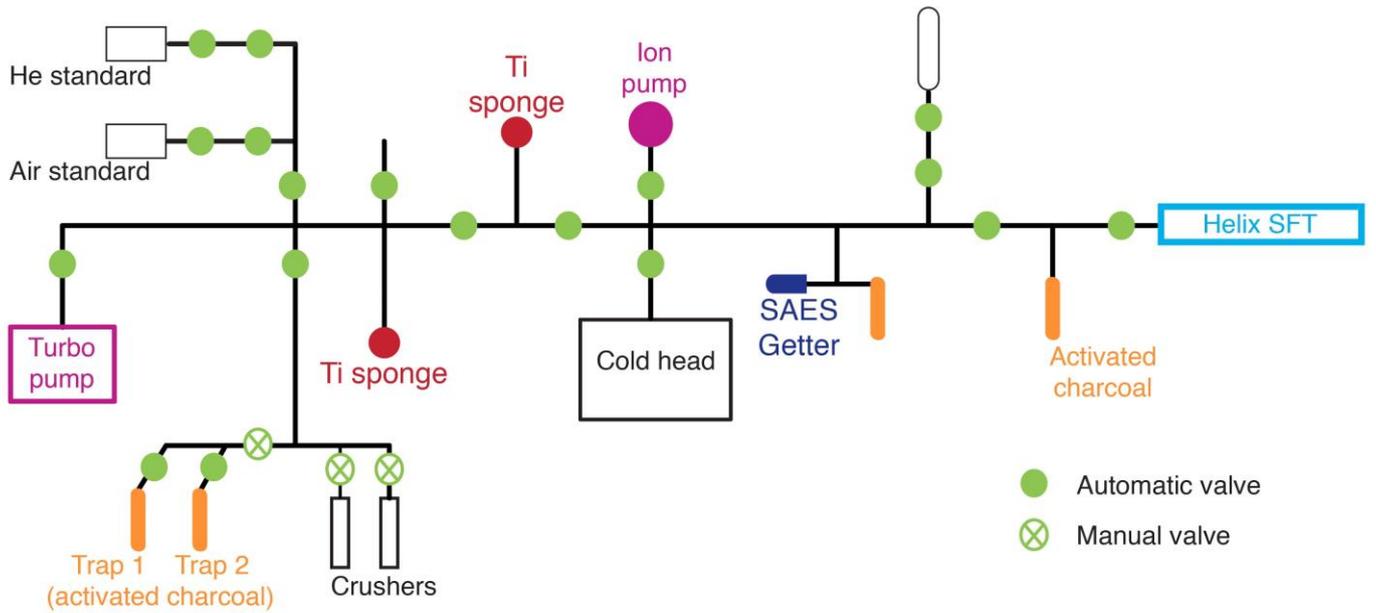


**Figure S-6** Histograms of the Monte Carlo simulations to determine the maximum  $^{131-132-134-136}\text{Xe}/^{130}\text{Xe}$  ratios in the mantle before atmospheric xenon recycling. The orange bars show the mean values and the orange dotted lines the 1 sigma uncertainties.

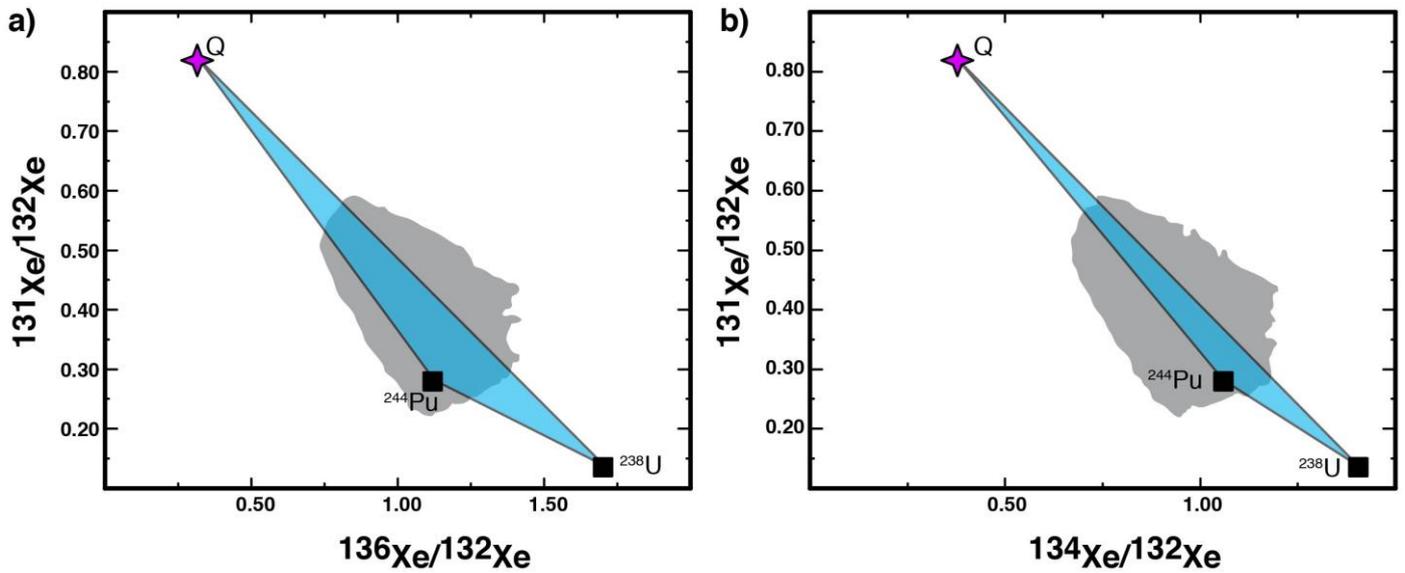


**Figure S-7** Determination of the mantle xenon isotopic ratios before recycling. The evolution of the xenon atmospheric composition is represented with the blue dots and blue dotted lines with the numbers indicating the time in Gyr (a power law was considered (Bekaert *et al.*, 2018)): (a) for the  $^{131}\text{Xe}/^{130}\text{Xe}$  ratio, (b) for the  $^{132}\text{Xe}/^{130}\text{Xe}$  ratio and (c) for the  $^{134}\text{Xe}/^{130}\text{Xe}$  ratio. The corrected data for shallow atmospheric contamination is shown (light blue dot). The minimum (orange square) and maximum (red square)  $^{131-132-134}\text{Xe}/^{130}\text{Xe}$  ratios in the mantle before recycling of atmospheric xenon are calculated considering mixing with air (orange and red dotted lines) and that the initial  $^{128}\text{Xe}/^{130}\text{Xe}$  is chondritic (Phase Q). The red lines suggest that recycling of atmospheric xenon could have been effective only since  $2.8 \pm 0.3$  ( $1\sigma$ ) Gyr ago (see text). Otherwise, unreasonable values of  $^{131-132-134-136}\text{Xe}/^{130}\text{Xe}$  ratios are obtained. Phase Q (Busemann *et al.*, 2000).





**Figure S-8** Schematic view of the vacuum line connected to the Helix SFT mass spectrometer (ThermoScientific).



**Figure S-9** Heavy xenon fissionogenic isotopes plot. The calculated maximum  $^{131-132-134-136}\text{Xe}/^{130}\text{Xe}$  ratios of all the realizations fall in the grey areas. Only calculated maximum  $^{131-132-134-136}\text{Xe}/^{130}\text{Xe}$  ratios that fall into the blue triangles, defined by Phase Q (Busemann *et al.*, 2000), pure xenon from fission of  $^{244}\text{Pu}$  and pure xenon from fission of  $^{238}\text{U}$ , are considered.

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